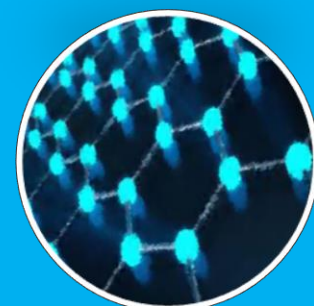


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RECENT ADVANCES IN FABRICATION TECHNOLOGY OF NANOMATERIAL'S **RAFTN - 2022**



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Recent Advances in Fabrication Technology of Nanomaterial's

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PREFACE

We are delighted to publish our book entitled "Recent Advances in Fabrication Technology of Nanomaterial's Volume: - I". This book is the compilation of esteemed articles of acknowledged experts in the various fields of Physics, Chemistry, Nanotechnology and Medical Science providing a sufficient depth of the subject to satisfy the need of a level which will be comprehensive and interesting. It is an assemblage of variety of information about rapid advances and developments in fabrication technology of nanomaterials. With its application oriented and interdisciplinary approach, we hope that the students, teachers, researchers, scientists and industrialists makers in India and abroad will find this book much more useful. The articles in the book have been contributed by eminent scientists, academicians. Our special thanks and appreciation goes to experts and research scholars whose contributions have enriched this book. We thank our publisher Prarup Publishing, India for taking pains in bringing out the book. Finally, we will always remain a debtor to all our well-wishers for their blessings, without which this book would not have come into existence.

- Editors

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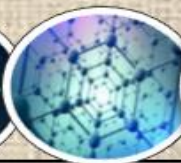
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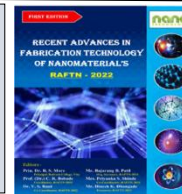
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**Recent Advances in Fabrication Technology of
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Magneto electric effect in Dy-doped Ni-Co substitution ferrite and PZT Ferroelectric

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KEYWORDS

ME Effect,
 ME composites, Dielectric
 properties, Saturation
 polarization.

ABSTRACT

The ME composites with compositions $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ with $y = 0.10$ to 0.30 in steps of 0.05 were prepared by a standard double sintering ceramic method. The presence of cubic spinel ferrite phase and tetragonal perovskite ferroelectric phase in the ME composites was confirmed by X-ray diffraction technique. The dielectric properties such as dielectric constant, loss tangent were studied in the frequency range 20 Hz to 1 MHz at room temperature. These parameters show decreasing trend at lower frequencies and remain constant at higher frequencies, showing the usual dielectric dispersion due to space charge polarization.

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1. Introduction

Magnetoelectricity is a product property and it occurs due to the presence of inherent properties such as magnetostriction and piezoelectricity of the constituent phases in the composites. Ferrite and ferroelectric are two different phases of ME composites which show different coupling properties such as magnetoelectric effect, magneto-optic effect etc. For better ME effect in composites, the constituent phases should remain distinct without any chemical reaction. The magnetostriction coefficient of ferrite phase, piezoelectric coefficient of ferroelectric phase and resistivity of both phases should be high enough, to avoid leakage of charges [1], proper poling method should be adopted to obtain higher ME coefficient [2]. The proper selection of ferromagnetic and ferroelectric phases is important parameter to get the maximum value of magnetoelectric voltage coefficient. Composite bulk samples of nickel ferrite or cobalt ferrite with lead zirconate titanate (PZT) were of great interest [3]. One of the common characteristics of nickel ferrite nanoparticles is the superparamagnetic behaviour and reduction of the saturation magnetization (M_s) in comparison with the bulk materials [4]. Soft ferrite NiFe_2O_4 having low anisotropy and high initial permeability is a capable candidate for magnetomechanical coupling. Also, by introducing some additional amount of cobalt oxide one can increase the net magnetic moment which favors the ME effect [5]. Substitution of cobalt ions in nickel piezomagnetic material gives large increase in the resistivity. Stabilization of Co^{2+} ions in octahedral sites gives rise to a degenerate or near-degenerate orbital angular momentum [6]. This results in strong spin-lattice interaction which induces a stress in the piezoelectric lattice to yield high ME output in the composites. Substitution of rare earth element causes lattice distortion and change in symmetry of the crystal which in turn induces strain in the material [7]. PZT is one of the ideal piezoelectric material having high piezoelectric constant following polarization, high dielectric permittivity and superior coupling factor [8].

Important parameter in the synthesis of ME composites is the interface coupling between the piezoelectric and magnetostrictive phases [9,10]. Researchers have proved that bulk ME composites are more beneficial to obtain high ME coefficient [11,12]. Although, magnetoelectric layered composites play important role in coupling between ferrite and ferroelectric phases [13], it is still valuable to synthesize ferrite and ferroelectric nanostructures to obtain large ME coefficient in bulk composites. In

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present work, nickel ferrite with cobalt and dysprosium substitution as a ferrite phase and lead zirconate titanate as a ferroelectric phase were selected to get better magnetic and electric properties. For better realization of conduction mechanism in ME composites the electrical properties such as dielectric constant, ac conductivity and dc resistivity are important whereas for realization of magnetic properties magnetoelectric effect is important. In this paper, we report the structural, dielectric, polarization and magnetoelectric properties of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ composites synthesized by double sintering ceramic method.

2. Experimental

The ME composites with the general formula $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$, $y = 0.10, 0.15, 0.20, 0.25$ and 0.30 were prepared by the solid state reaction method. For this series of ME composites Dy content is kept fixed i.e. $x = 0.050$. The ferrite phase $\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$ was prepared by solution combustion method and ferroelectric phase was prepared by ceramic method. The general scheme for the preparation of ME composites is given in Fig. 1. The ME composites were prepared by mixing 10, 15, 20, 25 and 30 mol % of ferrite phase with 90, 85, 80, 75 and 70 mol % of ferroelectric phase, respectively. The mixture was ground for 3 hours for uniform mixing. The mixed powder mixture was pressed into pellets having diameter of 1.5 mm and 1-2 mm thickness using a hydraulic press by applying a pressure of 7 tons/sq. inch for 10 minutes. The pellet samples were final sintered at 1050°C for 12 hours and cooled naturally to yield the final product.

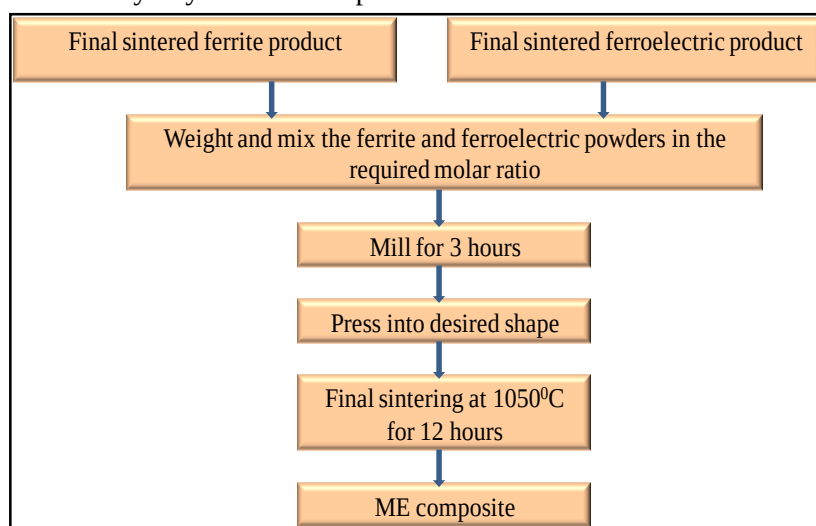


Fig. 1 Flow chart for the preparation of ME composites

The powders were characterized by a Bruker D2-Phaser X-ray diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) to confirm phase formation. The surface morphology was observed using a JEOL JSM-6360 scanning electron microscope. The frequency dependence of dielectric permittivity (ϵ'), dissipation factor ($\tan\delta$) and ac conductivity in the range 20Hz to 1MHz were studied using a precision LCR meter bridge (HP 4284 A).

3. Result and discussion

3.1. X-Ray diffraction

The X-ray diffraction patterns of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites with $y = 0.10, 0.15, 0.20, 0.25$ and 0.30 are shown in Fig. 2. The XRD patterns confirm polycrystalline nature of composites. Diffraction patterns show the presence of both ferrite and ferroelectric phases without any impurity phase. Cubic spinel structure of ferrite phase and tetragonal perovskite structure of ferroelectric phase was also confirmed [14].

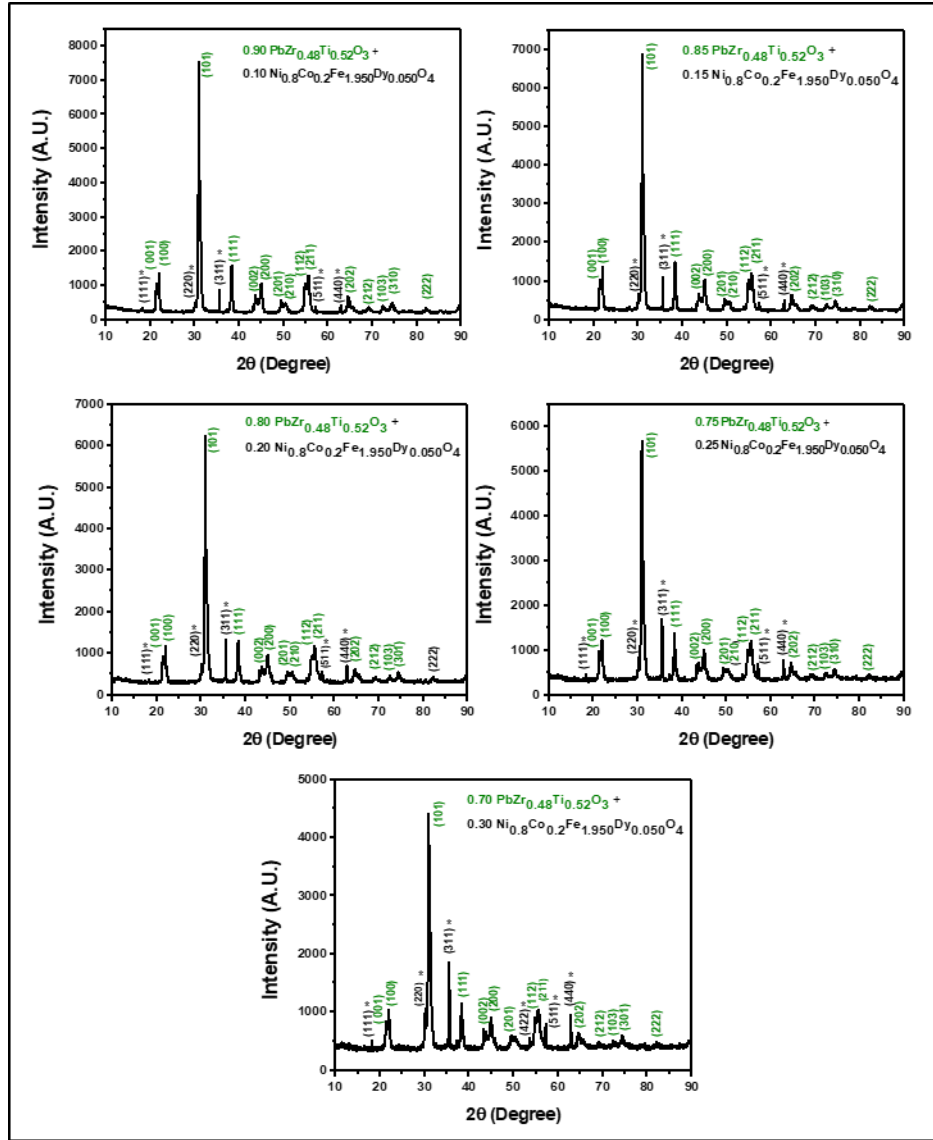


Fig. 2 XRD patterns of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y) [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites

The results obtained from the X-ray diffraction study are in good agreement with the JCPDS card Nos. 01-074-2081 and 00-050-0346. The tetragonal structure of the ferroelectric phase remains same in all the composites which prove the absence of impurity phase i.e. pyrochlore phase. Two phases remain distinct in the composites. Thus, there is no any chemical reaction between them and no structural changes in the composites.

Table 1. Lattice parameters for $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y) [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites

Composite	Ferrite a (Å)	Ferroelectric		c/a
		a (Å)	c (Å)	
0.10[$\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$] + 0.90 [$\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$]	8.394	4.042	4.154	1.027
0.15[$\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$] + 0.85 [$\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$]	8.361	4.021	4.128	1.026
0.20[$\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$] + 0.80 [$\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$]	8.356	4.029	4.134	1.025
0.25[$\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$] + 0.75 [$\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$]	8.324	3.993	4.114	1.030
0.30[$\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$] + 0.70 [$\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$]	8.357	4.016	4.128	1.027

The intensity of (101) peak in ferroelectric phase decreases while the intensity of (311) peak in ferrite phase increases with increasing ferrite content in the composites. The intensity and number of peaks in the composites depend on the percentage of corresponding phases [15]. The lattice parameters for both

phases in all composites listed in Table 1 matches fairly well with those of the constituent phases. The lattice parameters for ferrite phase vary between $8.35 \text{ \AA}$ and $8.39 \text{ \AA}$, while for ferroelectric phase, the c/a ratio lies between 1.026 to 1.030 which are in good agreement with reported values [16].

3.2. Scanning electron microscopy

The SEM micrographs of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y) [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites with $y = 0.10, 0.15, 0.20, 0.25$ and 0.30 are shown in Fig. 3.

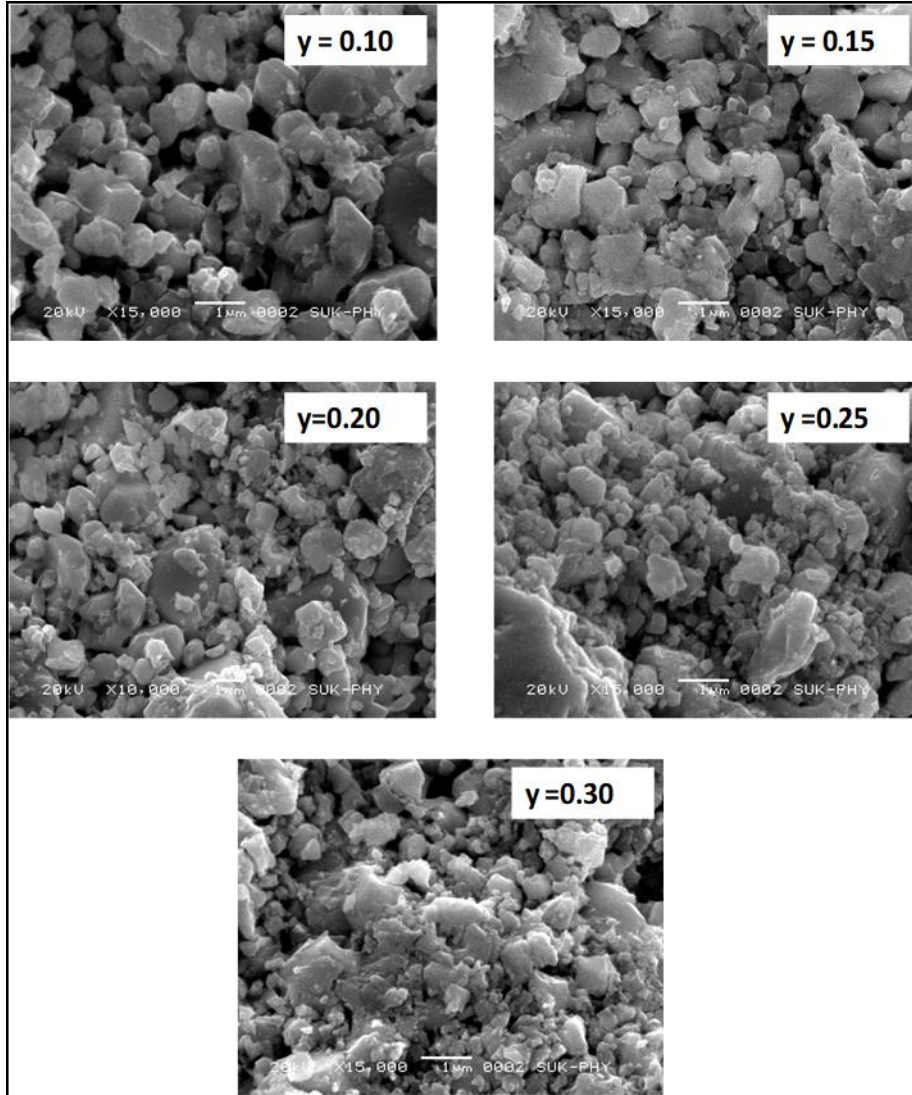


Fig. 3 SEM images of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y) [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites

Table 2. Grain sizes for $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y) [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites

Composition	Grain size (μm)
$0.10[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + 0.90 [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$	1.214
$0.15[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + 0.85 [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$	1.153
$0.20[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + 0.80 [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$	1.038
$0.25[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + 0.75 [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$	0.877
$0.30[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + 0.70 [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$	0.724

From the micrographs it is seen that there is random distribution of ferrite and ferroelectric phases throughout the matrix. Randomly distributed large sized well grown grains of ferroelectric phase and small sized grains of ferrite phase co-exist in composites. This is due to the fact that the average grain size of

the ferrite phase is smaller than the ferroelectric phase. Average grain size of composites in variation with y are given in Table 2. In the present work, all the composites were prepared in a ferroelectric rich region, hence average grain size varies with ferrite content.

3.3. Dielectric properties

3.3.1. Variation of dielectric constant with frequency

Fig. 4 shows the variation of dielectric constant with frequency at room temperature for $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites with $y = 0.10, 0.15, 0.20, 0.25$ and 0.30 . It is observed that the dielectric constant decreases rapidly with increasing frequency in the range of 100 Hz to 10 KHz and remains constant in the high frequency range of 10 KHz to 1 MHz showing normal dielectric behaviour. The high value of dielectric constant observed at lower frequencies is explained on the basis of space charge polarization due to heterogeneous dielectric structure [17]. Under the influence of applied electric field, space charges provided by the ferrite phase accumulate at the ferrite-ferroelectric grains interface. Also, the dielectric material exhibit induced electric moment under the influence of applied electric field. As frequency increases, ionic and orientation polarizabilities decreases and finally disappear due to the inertia of the molecules and ions [18]. At higher frequencies, the dielectric constant remains independent of frequency due to the inability of electric dipoles to follow the fast variation of the alternating applied electric field and accordingly the friction between them will increase.

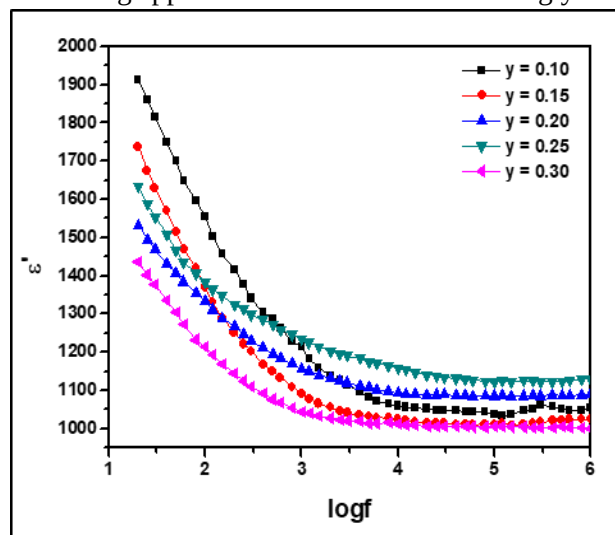


Fig. 4 Variation of dielectric constant with frequency of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites,

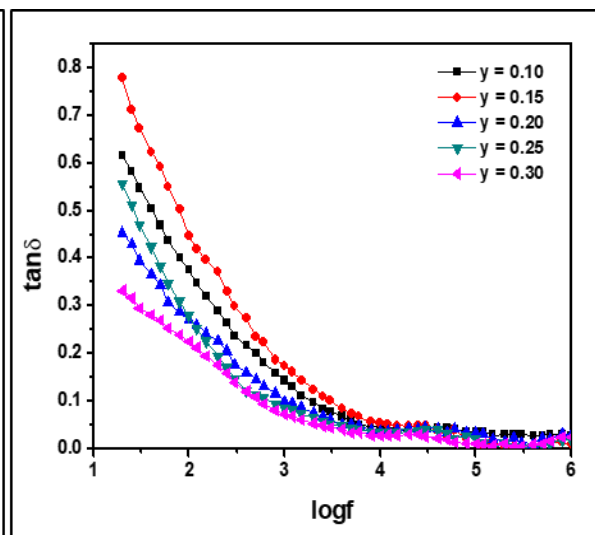


Fig. 5 Variation of dielectric loss with frequency of $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y)[\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites

In present study, the presence of $\text{Ni}^{2+}/\text{Ni}^{3+}$, $\text{Co}^{2+}/\text{Co}^{3+}$ ions in ferrite phase and $\text{Pb}^{2+}/\text{Pb}^{3+}$ ions in ferroelectric phase gives rise to p type carriers. The displacement of p type carriers in the direction of applied electric field contributes to the net polarization in addition to that of n-type carriers. However, the electron exchange between the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Zr}^{4+}/\text{Zr}^{3+}$ or $\text{Ti}^{4+}/\text{Ti}^{3+}$ ions is larger than the p type contribution. The mobility of n-type carriers is larger than the p-type carriers. So the contribution of p-type carriers to the polarization decreases more rapidly with increase in frequency which results in rapid decrease in dielectric constant [19]. Also, the high value of dielectric constant is not intrinsic but due to the fact that ferroelectric PZT grains are surrounded by non-ferroelectric ferrite grains [20]. From Fig. 4 it is observed that the relative dielectric constant for the composites initially decreases with increase in ferrite content. It is due to the decrease in polarization contributed by ferroelectric phase and increase in the conductive ferrite phase of the ME composites [21]. Beyond 20-80 composition, dielectric constant vary in random fashion. It is obvious because ferrite and ferroelectric grains are randomly mixed together. Also,

it is well known that there are 10 possible connectivity in diphasic composites. Hence, it is more difficult to calculate the effective value of dielectric constant for the composites.

3.3.2. Variation of $\tan\delta$ with frequency

Variation of $\tan\delta$ with frequency for $y[\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4] + (1-y) [\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3]$ ME composites with $y = 0.10, 0.15, 0.20, 0.25$ and 0.30 is shown in Fig. 5. For all samples, the dielectric loss decreases with increase in frequency. The dielectric loss possesses similar behavior in accordance with the dielectric constant (ϵ'). The larger dielectric loss at low frequencies is attributed to the fact that the time of relaxation process is same as the period of applied external field. When the relaxation time is more as compared to the period and frequency of the applied field respectively, losses are small [22]. Also it is reported that, the dielectric loss of the ME composite increases with increase in ferrite content. This is due to the increasing conductive ferrite phase in ME composites which provides the leakage path for the stored charge carriers [21]. Also, it can be attributed to the collective response of p and n type of charge carriers to the polarization [19]. Therefore, the position of $\tan\delta$ peak depends on the majority charge carriers in the particulate composites [23]. The minimum value of dielectric loss for particular composition gives higher value of ME coefficient.

4. Conclusions

The ME composites consisting of $\text{Ni}_{0.8}\text{Co}_{0.2}\text{Dy}_{0.050}\text{Fe}_{1.950}\text{O}_4$ and $\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$ have been prepared by ceramic method and were characterized by XRD studies. The presence of both piezomagnetic and piezoelectric phases without any impurity phase show the formation of ME composites. The high value of dielectric constant at lower frequencies is explained on the basis of space charge polarization. The decrease in dielectric constant with ferrite content is due to the decrease in polarization effect contributed by ferroelectric phase in ME composites.

Acknowledgements

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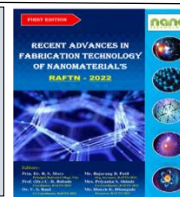
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**Recent Advances in Fabrication Technology of
 Nanomaterials**

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La³⁺ substituted Ni-Cu-Zn Nanoferrites: Room-temperature high-performance ammonia gas sensor

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KEYWORDS

La-NCZ sensors
 Nanoferrites
 Room temperature sensitivity
 Selectivity
 Reproducibility.

ABSTRACT

The In current investigation, we revealed a room-temperature ammonia gas sensor based on La³⁺ substituted Ni-Cu-Zn (La-NCZ) semiconducting ferrite thick films. The La-NCZ thick film sensors of were prepared by depositing co-precipitationally synthesized Ni_{0.7}Cu_{0.1}Zn_{0.2}RExFe_{2-x}O₄ (where x = 0, 0.015, 0.025 and 0.035) nanoferrites powder on an ultrasonically cleaned glass substrates using screen printing method. The sensing parameters of the La-NCZ ferrite thick film sensors were examined by exposing sensing elements under 100 ppm concentrations of several gases like ammonia, chlorine, acetone, ethanol, LPG etc. at room temperature. It was understood that the tested semiconducting nanoferrites sensor series revealed not only outstanding response towards ammonia gas, but also it shows faster response and recovery time with good repeatability. The system under investigation shows distinctive advantages of La-NCZ ferrites for manufacturing of ammonia sensor.

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1. Introduction

A hazardous gas is any gas when breathed, that is responsible for an undesirable effect on humans and other creature's health. Breathing a higher quantity of toxic gas displaces oxygen in the body and causes unconsciousness. The ammonia (NH₃) is a colourless gas with a distinct strong odor. Ammonia contributes significantly to the nutritional demands of terrestrial species by acting as a precursor to food and fertilizer. Ammonia is also used to produce numerous pharmaceuticals, although ammonia is both toxic and corrosive when used in large quantities. Anhydrous ammonia is commercially accessible [1-2].

Now a days, the researchers from material science, physics, chemistry and metallurgy are try to fabricate the gas sensors from metal oxides, polymer, sulfides, selenides, composites, chalcogenides, ferrites etc. researchers try to develop the sensor which are less expensive, high performable and easy to utilized in factories, industries as well as in public places. The capability of materials to change the electrical resistance in presence of lower concentrated gas establishes the sensing property to monitor the various present or leaked gases in surrounding. [3-5]. Seiyama et al. [6] in 1962 first time proposed Metal oxide semiconductor gas sensors, thereafter various researchers have been working on it. The materials like Fe₂O₃, WO₃, SnO₂ and ZnO have semiconducting nature are widely considered due to their ability of detecting reducing gases [7]. From last few decades, researchers are impressed with semiconducting metal oxide nanoparticles as a potential candidate for gas sensing application because of its improved physico-chemical properties [10]. Amongst all the semiconducting metal oxides, the ferrites (MFe₂O₄) were considered as a potential gas sensing material due to their higher porosity, high surface area and high electrical resistivity. Several ferrites sensors like NiFe₂O₄, CuFe₂O₄, ZnFe₂O₄ and CoFe₂O₄ have been

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utilized for the detection of hydrogen (H_2), hydrogen sulfide (H_2S), ammonia (NH_3), chlorine (Cl_2), acetone ($(CH_3)_2CO$), liquefied petroleum gas (LPG), and ethanol (C_2H_5OH) gases [11-18].

Recently Sonwane et al. [19] synthesized the $NiFe_2O_4/PANI$ composite nanofibers by electrospinning and polymerization technique and reported that the nanofibers shows faster response in 15 to 54 seconds whereas the recovery time is in between 21 to 65 seconds time for 250 ppb to 100 ppm concentration of ammonia gas at room temperature. Madake et al. and others [20-23] was deposited the Cu-Ni-Zn ferrites thin films by spray pyrolysis technique and carried out its structural, elemental, morphological and gas sensing properties. They reported that the Cu-Ni-Zn ferrite thin films shows better responds for SO_2 gas at $120^\circ C$. The choice of rare earth metal ions as a substituent or dopant in ferrites because of its important properties like it improve the oxygen vacancies as well as surface area and emerging a better electronic structure for faster charge transfer in material [24-25].

The current study, we investigate the gas sensing properties of $Ni_{0.7}Cu_{0.1}Zn_{0.2}La_xFe_{2-x}O_4$ (where $x = 0, 0.015, 0.025$ and 0.035) nanoferrites (La-NCZ) system towards Cl_2 , LPG, C_2H_5OH and NH_3 exposer at room temperature.

2. Expérimental

The synthesis of La^{3+} substituted Ni-Cu-Zn (La-NCZ) nanoferrites having chemical composition $Ni_{0.7}Cu_{0.1}Zn_{0.2}La_xFe_{2-x}O_4$ (where $x = 0, 0.015, 0.025$ and 0.035) using oxalate co-precipitation method was reported in our previous publication [26]. The Impact of La^{3+} substitution on DC electrical resistivity, Initial permeability, dielectric constant and energy bandgap of La-NCZ system was also reported elsewhere [27].

2.1. Fabrication and gas sensing measurement of sensor element

The gas sensing performance of La-NCZ ferrite system is tested on a thick films sensor made up of depositing the nanocrystalline ferrite powder on ultrasonically cleaned glass substrate by screen printing method. The glass substrate having 10 mm x 10 mm in dimensions are particularly used to fabricate the sensor elements. The deposited thick films are sintered in muffle furnace at $200^\circ C$ for two hours for the removal of added binder solution from films. The silver adherent paste (ordered from Alfa Acer Pvt. Ltd) is applied on both the ends of thick film and preheated at $70^\circ C$ for 30 minutes. The fabricated sensor elements of the La-NCZ system were used to record the gas sensing performance. The measurements of gas sensing parameters are done by inserting a different concentrations of Ammonia (NH_3), Acetone ($(CH_3)_2CO$), Ethanol (C_2H_6O), Liquefied petroleum gas (LPG) and Chlorine (Cl_2) gases. Keithley 6524 Electrometer interfaced with computer software (Kickstart 2.0) was used to record variation in resistance with 0.5 sec time intervals is shown in Fig. 1.

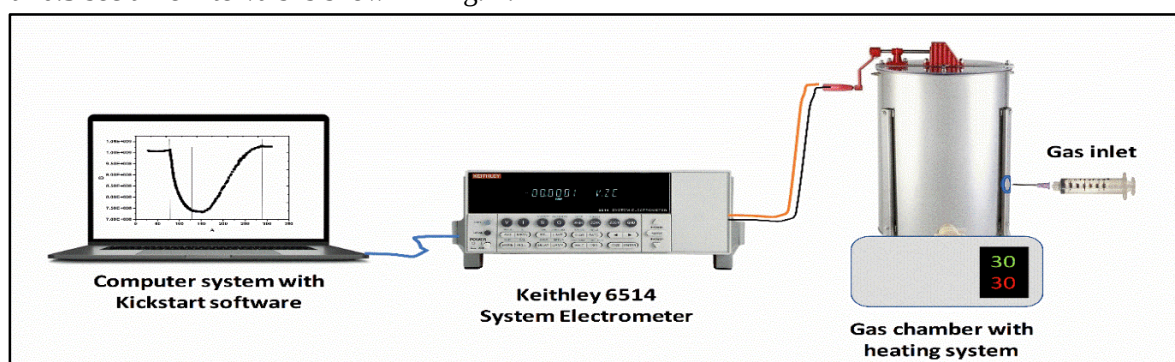


Fig. 1 Schematic diagram of gas sensing set up, sensor element holder and thick film based sensor element

The response of sensor element was measured using the relation

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100 \% \quad \text{----- (1.1)}$$

Where, R_a is the resistance in air and R_g is the resistance in test gas

3. Result and discussions

Based on the successful structural, electrical, dielectric, magnetic and optical characterizations [26, 27] the sensing performance of single transitional metal (La^{3+}) substituted Ni-Cu-Zn nanoferrites were investigated under an exposure of various gases. Ferrites are the useful sensing materials because of their diverse composition and high structural stability. In order to understand the selectivity of $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0, 0.015, 0.025$ and 0.035) system, it were tested under the gases like ammonia, chlorine, ethanol, acetone, LPG etc. towards 100 ppm constant concentration at room temperature is shown in Fig. 2. (a). From this figure, it is observed that the material under testing shows an extraordinary gas sensing performance towards ammonia and chlorine as compared with acetone, ethanol and LPG. This may be attributed to presence of more lone pair of electrons in NH_3 and Cl_2 whereas comparatively lower response towards $(\text{CH}_3)_2\text{CO}$, $\text{C}_2\text{H}_6\text{O}$ and LPG is because of an absence of unshared electrons pair [28,29]. The maximum variation in resistance of La-NCZ system with ammonia and chlorine exposure compared to other volatile gases signifies better selectivity towards ammonia and chlorine. Thus, NH_3 and Cl_2 are preferred over other gases (ethanol, LPG and acetone) for the measurement of rest sensing parameters.

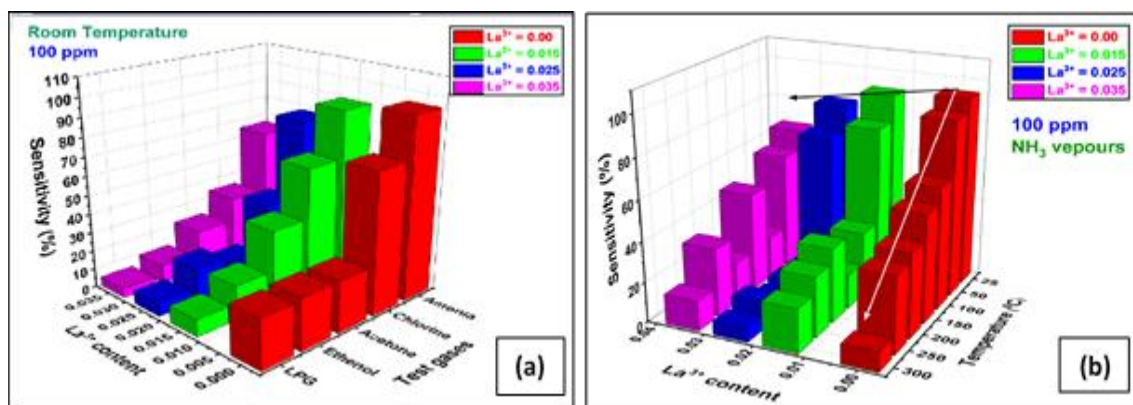
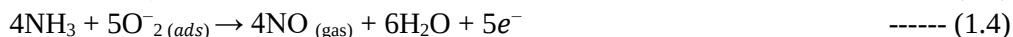


Fig. 2(a) Room temperature selectivity, (b) Sensitivity of $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0, 0.015, 0.025$ and 0.035) system under 100 ppm test gases

Fig. 2 (b) shows that, the variation in sensitivity of La-NCZ system with increasing temperature under 100 ppm constant concentration of ammonia gas. Significantly, the composition $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ shows a higher sensitivity for 100 ppm concentration of ammonia and chlorine gas at room temperature and this may be due to excellent oxygen absorption property of investigated material [30]. From this figure, it is observed that the response of the NCZ sensor under investigation shows approximately constant response towards 100 ppm NH_3 gas at room temperature which confirms the reproducibility or repeatability of the sensor. Table 1 presents the comparable study of gas sensing parameters of rare earth substituted Ni-Cu-Zn ferrite sensors. From this table it is observed that, ferrite sensors are capable for the detection of various gases like ammonia (NH_3), chlorine (Cl_2), acetone ($(\text{CH}_3)_2\text{CO}$), liquefied petroleum gas (LPG), and ethanol ($\text{C}_2\text{H}_5\text{OH}$), hydrogen (H_2), hydrogen sulfide (H_2S), sulphuric dioxide (SO_2) even present in lower concentration [31].

The gas sensing mechanism for metal oxides was understood on the basis of variation in the depletion layer, which changes the oxygen absorption properties of the sensor material. The adsorption of O_2 molecules forms an electron-depletion layer on a sensor's surface when it is exposed to air. The ionization of O_2 ions into O_2^- , O^{2-} or O^- ions by adding an electrons from conduction bands. The ammonia sensing mechanism is given as



In current investigation, Ni-Cu-Zn nanoferrites exhibit highest sensitivity towards ammonia gas. When ammonia gas molecules are entered in chamber, it tends to transfer the trapped electrons towards the

conduction band, leading to a decrease in the depletion layer with increased electron concentration implying absorption and desorption reaction on nanoferrites surface. It also depends upon the structural arrangement of the investigated material [28].

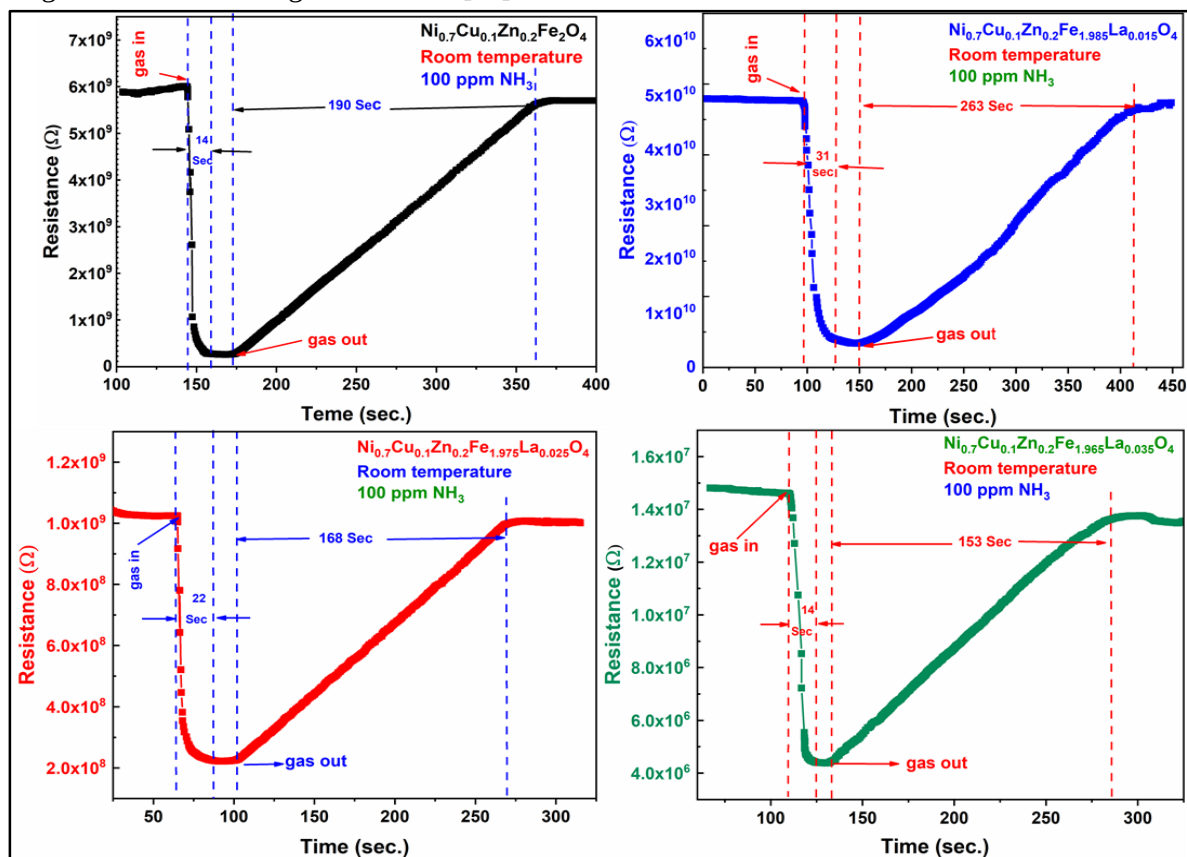


Fig. 3 Response and recovery time for $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0, 0.015, 0.025$ and 0.035) system towards 100 ppm ammonia gas at room temperature

Table 1. The gas sensing parameters comparison rare earth substituted ferrite sensors

Sr. No.	Material Composition	Test gases	Operating temp. ($^{\circ}\text{C}$)	Response time (Sec)	Recovery time (Sec)	Sensitivity (%)	Ref.
1	$\text{Ni}_{0.25}\text{Cu}_{0.5}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$	Ethanol Acetone	Room temperature	10 (min) 30 (min)	28 (min) 20 (min)	68 77	[13]
2	$\text{NiCuZnFe}_2\text{O}_4$	SO_2	120	24	145	76	[14]
3	5% Y^{3+} MgFe_2O_4	LPG	218	150-215	200-300	85	[25]
4	Co- $\text{Sm}_{0.1}\text{Fe}_{1.9}\text{O}_4$	LPG	225	580	178		[26]
5	$\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{Fe}_{2-x}\text{La}_x\text{O}_4$	Ammonia	Room temperature	(Table 2)	(Table 2)	(Table 2)	This work

The room temperature gas sensing performance of La^{3+} substituted Ni-Cu-Zn nanoferrites system having chemical composition $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0, 0.015, 0.025$ and 0.035) system with its response and recovery time under 100 ppm conc. of ammonia gas is shown in Fig. 3. It shows the variation of sensitivity and resistance of material under testing towards ammonia gas. The figure notifies

that, when ammonia gas is allowed to enter a gas chamber the resistance of sensor material decreases and thereafter shows consistent behaviour till the removal of gas from the chamber. The sensor under investigation signifies a quick response rate within 10-20 s. After removing gas from chamber, the resistance increases almost up to its initial value within 100-200 sec. The minimum response and recovery time of a material under investigation suggest La-NCZ nanoferrites are the better sensors for ammonia gas. The response and recovery time of $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0, 0.015, 0.025$ and 0.035) system towards 100 ppm ammonia gas at room temperature is presented in Table 2.

Table 2. The sensing parameters of $\text{Ni}_{0.7}\text{Cu}_{0.1}\text{Zn}_{0.2}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0, 0.015, 0.025$ and 0.035) system towards 100 ppm ammonia gas at room temperature

RE ³⁺ ions	Content (x)	Test gases				Sensitivity
		Ammonia (NH ₃)		Chlorine (Cl ₂)		S (%)
		Response time (Sec)	Recovery time (Sec)	Response time (Sec)	Recovery time (Sec)	NH ₃
La ³⁺	0.00	14	190	28	138	95.3
	0.015	34	263	27	92	89.7
	0.025	22	168	24	105	78.2
	0.035	14	153	05	71	68

Deepapriya et al. [29] synthesized the La³⁺ substituted Ni-Zn-Cu-Co ferrites using ecofriendly chemical co-precipitation method and reported that amongst all the invented sensors the La-Ni-Zn-Cu-Co-Fe₂O₄ nano-composite sensor demonstrated outstanding sensitivity towards 50 ppm of NH₃ gas at room temperature (86.2%).

4. Conclusions

The La³⁺-substituted Nickel-Copper-Zinc nanoferrite thick film gas sensors elements were successfully fabricated from co-precipitationally synthesized nanoferrite powder. The fabricated sensor elements show highest sensitivity performance through sensitivity, stability, response time and recovery time under ammonia gas as compared to the other target gases. Thus the La-NCZ sensor can be utilized in developing the room temperature NH₃ sensors.

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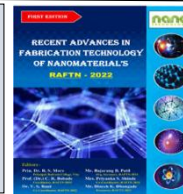
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Recent Advances in Fabrication Technology of Nanomaterials

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DNA Nanobiosensor: Rapid On-Spot Direct Observation of *Mycobacterium* Tuberculosis in Pulmonary Sputum Sample

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KEYWORDS

MTB
GNP-Gold nanoparticle,
DNA Nano-Biosensor.

ABSTRACT

Indian Government has declared that nation will be get free from tuberculosis by the year 2025. This can happen only by implementing innovative technologies for the diagnosis along with prevention and treatment. One of the excellent technologies today is the nanomaterial-based medical devices. In the present investigation, we have developed the nanomaterial-based detection of *Mycobacterium tuberculosis* at an early stage with the predominant sensitivity as compared with the existing devices. Herein, we report a straightforward, on-spot colorimetric detection by using DNA gold nano probe for early detection of TB. Shape of gold nanoparticle is sphere ³and size is 13.4 nm were synthesized by citrate reduction method. Gold nanoparticle characterisation were done by UV-vs absorption spectrophotometry, X- ray diffraction, dynamic light scattering (DLS) measurements and transmission electron microscopy (TEM). In this DNA gold nanoparticle -based detection system, GP-1, and GP-2 for *IS6110* were designed to specifically hybridize with target DNAs of MTBC. This research work shows that, we have developed a DNA gold nano biosensor for on-spot colorimetric detection of MTBC as a low-cost alternative to current amplification-based detection platforms for tertiary health care centre.

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1. Introduction

Tuberculosis (TB) is top ten most infectious diseases at international level. However, globally TB shows a major cause of ill-health and mortality. Still TB is one of the leading human bacterial pathogens. In 2021, 1.5 million deaths and 9.9 million human beings had been declared due to TB infection [1]. The effect on TB incidence of gaps in TB case detection caused by the SARS-CoV-2 virus pandemic was limited in 2020, especially when compared to the effect on TB deaths. There are two major reasons for the longer-term effect on TB incidence and deaths. Nanotechnology plays an important role for effective molecular diagnostics. Various nanoparticle-based methodologies have been implemented to diagnose TB infection with sensitivity. Recently, researchers have turned their attention to the development of nanotechnology-based portable devices that are low-cost, durable, and reproducible [2]. As such, nanoparticle-based methods are forecast to progress step by step through the years to satisfy the needs required in the area. Gold nanoparticle (AuNPs) were synthesized with thiol modified DNA (Au-Nano-probe) were used for the early detection of pathogens, including *Mycobacterium tuberculosis* [3]. The most genome - based diagnostic methods for pathogen screening have been improved for single disease detection, which takes more time, is more expensive, and requires trained laboratory technicians and microbiologists.[4]. Today, AuNPs plays important role in the diagnostic laboratory with highly sensitive, quick, and simple assays, which are cost-effective. AuNPs are used to construct point-of-care devices and novel testing plans. Among these, molecular characterization based on RT-PCR amplification and DNA

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hybridization methods that detect specific molecular signatures in a couple of hours, as compared to traditional methods that can take several days to produce a final result, has received special attention [5]. The AuNPs have been the subjected to the potent research for use in biomedicine over the past few periods. AuNPs, also denoted as colloidal gold, which possess some optical and physical properties that shows them as a prime spot for new promising tools for diagnostic applications. Despite being appropriate for centrally located, well-equipped diagnostic laboratories, these procedures fall short when moved to more remote locations and when a rapid screening is required to support scientific procedures. As a result, rapid, low-cost, and user-friendly molecular point-of-care devices are required, which would have a significant impact on the capacity for early-stage diagnosis and treatment of pathogen-associated infections. Fast and accurate results, i.e., early-stage detection, are of highest importance for the supervision of patients in terms of fast spreading infection and proper execution of control and treatment measures. Today, researchers are focusing their efforts on the development of nano robotic systems that are inexpensive, robust, and reproducible [6].

Here, we established thiol-linked ssDNA modified Au Nanoprobe for on-spot colorimetric finding of *Mycobacterium tuberculosis*. As such, gold nanoparticle-based approaches are predictable to evolve incrementally over time, permitting to meet the needs faced in the field. In specific, systems based on AuNPs functionalized with thiol-modified DNA (Au nano probes) have been broadly used for the early detection of pathogens, including *Mycobacterium tuberculosis* [7]. The third pillar of the "End TB Strategy" is increased research and innovation. This includes research and development of affordable and accessible rapid point-of-care tests for TB disease; shorter, safer, and more effective treatments for TB infection, innovative strategies to address broader determinants of TB. Aggregation of Au-Nanoprobe induced by increased ionic strength in the presence or absence of a specific target sequence causes colour change: the presence of a complementary target sequence stops aggregation, and the solution stays at the red (LSPR) band 525nm); In the absence of a specific target sequence, the addition of salt causes the nanoparticles to aggregate and turn purple (red wavelength of the LSPR peak, 600– 650 nm). Importance for the management of patients in terms of fast spreading infection and proper implementation of control and treatment measures [8]. In conclusion, we have established a DNA gold nano biosensor for on-spot detection of MTB. The developed assay predicts a great potential in early-stage detection of TB as a point-of-care device used in tertiary health care center, clinical laboratory and hospital

2. Materials and methods

All chemicals were obtained from Sigma Aldrich and were of analytical grade. HPLC purified labelled oligonucleotides were purchased from IDT and used without further purification. The thiol oligoprobe GP-1 and GP-2 were used to synthesize with gold nanoparticle. Biological samples Clinical isolates obtained from pulmonary respiratory positive samples for acid-fast bacilli from patients of the D. Y. Patil Medical College hospital and research Institute Kolhapur. (*M. tuberculosis* IS6110). Ethical considerations: Ethics approval to conduct this study was granted by the Institutional Ethical Committee of D. Y. Patil University, Kolhapur, 416006, Maharashtra, India (2016/44/PA, Ph.D.). Collection and processing of biological samples: Clinical isolates obtained from respiratory samples positive for acid-fast bacilli from patients of the D Y. Patil Medical College hospital and research institute Kolhapur. In a sterile plastic disposable container, pulmonary sputum samples were taken from D. Y. Patil Medical College Hospital and Research Institute, Kolhapur. Samples were pre-treated with NALC (0.5 % N-acetyl L-cysteine) and 2% sodium hydroxide for digestion and decontamination. Samples were combined with NALC NaOH solution in a vortex mixture, centrifuged at 3000 rcf for 20 min at 4°C. The supernatant decanted and transferred the sediment in 2 ml of phosphate buffer pH 6.8.

2.1 Sample pre- treatment with 0.5% N-acetyl-L-Cystine (NALC)

All Samples used for this study are confirmed by conventional microscopic observation by using Acid-fast staining using ZN (Ziehl-Neelsen) stain. The pulmonary sputum samples obtained from clinical

and radiological evidence of tuberculosis and these samples were selected for MTBDNA extraction. All specimens were treated with 0.5 % N-acetyl-L-Cysteine (NALC) 2% NaOH method for digestion and decontaminated and concentrated by centrifuging at 3000 rpm for 15 minutes. The aqueous phase is removed carefully and the sediment is placed in 2 ml of phosphate buffer pH 6.8. The sediment was used for ZN staining and DNA extraction [9].

2.2 Microscopic acid-fast staining

The ZN stain was covered on the AF (acid fast) smear and heated for 5 minutes. The slide was decolorized with 3% acid alcohol. The smear was counterstained with 0.5% w / v methylene blue for 2 min and finally rinsed with tap water and oil immersion was observed under high power objective lance for red colour AF bacilli. The acid-fast microscopy of *Mycobacterium tuberculosis* is depicted in Figure no.1

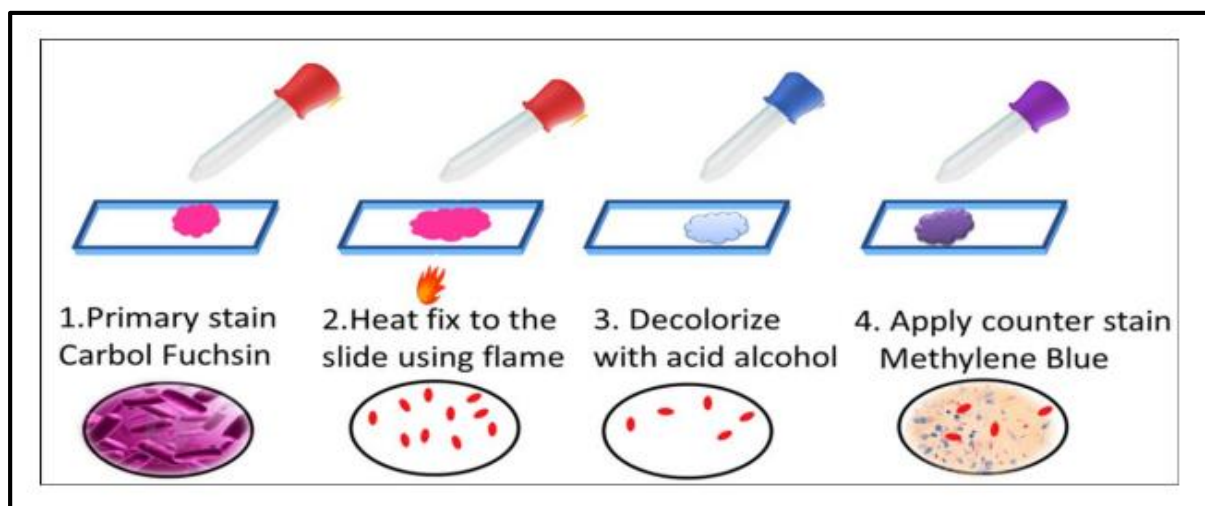


Figure 1: Schematic representation of acid-fast staining microscopy of *M. tuberculosis*

2.3 MTB Purification and DNA extraction

The commercial kit used for the extraction of MTB DNA samples [10]. MTB DNA was extracted by commercially available QI Amp DNA kit (QIAGEN) with one initial additional step. The pre-treated samples were kept at 80°C for 10 minutes for inactivation of Mycobacteria [11]. The material was then further processed in accordance with the manufacturer's specifications. Finally, the extracted DNA sample is kept in elution buffer. The purified DNA was then kept in -20 °C.

2.4 Real time PCR conditions

Isolated MTBDNA from clinical sputum samples is processed for in vitro diagnostic use using real-time PCR (Bio-Rad CFX 1000 USA). The total reaction volume of the master mix is 25 l. It includes 12 l (R1) super mix, magnesium solution, 2.5 l (R2) MTB complex, and internal control IC-1 (R3) RG 0.5 l and 10 l extracted DNA samples. As a negative control, PCR grade water was used [12,13]. The cycling conditions were as follows: 1 cycle initial activation at 95 °C for 10 minutes, 45 cycles, denaturation at 95 °C for 15 seconds, annealing at 60 °C for 20 seconds, and an extension step at 72 °C for 15 seconds shown in table no.1.

2.5. PCR amplification

The conserved regions of using *IS6110* and/or 16S rDNA were amplified in a PCR reaction using sets of primer designed to obtain fragments: 110 bp *rpoB* amplifications were executed on BIO-RAD CFX-1000 thermo-cycler (USA) in 50 µL final volume with 1× D. Taq Buffer, 0.1 mM of each DNTPs, 2 µM of each primer and 0.1 U/µL of D. Taq DNA polymerase and ~1 µg/mL of template DNA with the following thermal cycling conditions: initial 5 min denaturation at 95°C, followed by 30 amplification cycles of denaturation at 95°C for 30 s, annealing at 55°C for 30 s, elongation at 72°C for 45 s, and a final elongation at 72°C for 5 min. Synthesis of Au nanoparticles: Gold Nanoparticle colloids were prepared by

the citrate reduction method, 39.37mg of $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ was dissolved in 100ml of double distilled deionized water by heating and stirring [14,15]. Then 10ml of 38.8 mM sodium citrate solution was added as the solution was boiling. The colour of the solution change ruby red, approximately ~13.4nm diameter gold nanoparticle prepared by using clean glassware, rinsed.

Table 1: Thermal RT PCR amplification program

RT-PCR steps	Ct / Threshold	Thermal temps	Reaction time
Initial denaturation	1	95 °C	10 mins
Denaturation	1	95 °C	15 mins
Annealing	45	60 °C	20 seconds
Elongation	45	72 °C	15 seconds

3. Results and discussion

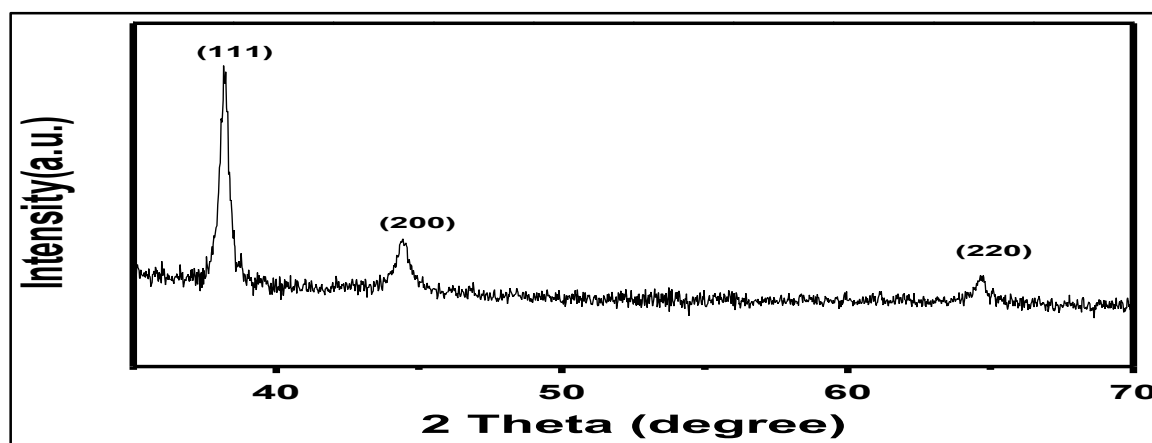


Fig 2. X-ray diffraction pattern

Based on the molecular signs of MTBC pathogens, we established RT-PCR amplification and ensuing hybridizing with a specific gold nanoprobe. We targeted two loci: *rpoB* for MTBC and 16s rRNA genomic sequences. The presented method relies on the differential aggregation profile of Au-Nanoprobe following an increase to ionic strength of the medium by salt. Hybridization to the complementary target stabilizes the Au-Nanoprobe from the induced aggregation and the solution remains red; whereas no hybridization to extensive aggregation and concomitant red-shift of the plasmon band and the solution turns purple. The principle of a functionalized Au-Nanoprobe relies on the simultaneous functionalization of Au Nps with specific oligonucleotides for both target sequences GP-1 and GP-2. This Au-Nanoprobe was able to detect each target sequence individually in solution and when the target was in a multiplex PCR mixture [16]. The crystalline structure of the prepared gold nanoparticles was investigated using XRD analysis shown in Fig. 2. These peaks were characteristics of the crystalline structure of GNPs. A number of Bragg's reflections characteristic planes (111), (200), (220), (221), (222), clearly show that gold nanoparticles formed by reduction of Au (iii) ions.

3.1. Fabrication of Au nano- probe for on-spot colorimetric detection of TB

Gold nanoparticles, with an average diameter of ~13.4 nm were synthesized and functionalized as described Mirkin's strategy. Au-nanoparticles capped with 3'- and 5'-thiol terminated oligonucleotides were prepared. Briefly, thiol-modified oligonucleotides were incubated with the gold nanoparticle with high salt concentration, in ordered to decrease non-specific bonds between the thiol-modified oligonucleotides and the AuNPs [17]. After 16 h, the solution was centrifuged, the resulting pellet re-suspended in 10 mM phosphate buffer (pH. 8), 0.1 M NaCl, and stored in the dark at 4°C till further used.

3.2Au-nano probe colorimetric assay: The colorimetric assays were performed in a final volume of 30 μl containing Au-nano probes at a final concentration of 2.5 nM in 10 mM phosphate buffer (pH 8). The mixture was heated up at 95°C for 5 min and then cooled down to 25°C for 5 min. The assay consists of a

spectrophotometric UV-visible comparison non-reactive template, 10 mM phosphate buffer (pH 8), NaCl (0.1M) was added to each reaction, and after 30 min at room temperature for colour development, the combinations and the blank examined by UV-visible spectroscopy in a micro plate reader (FLUO STAR OMEGA). The concept of DNA gold nanoprobe colorimetric assay with UV depicted in figure no.3

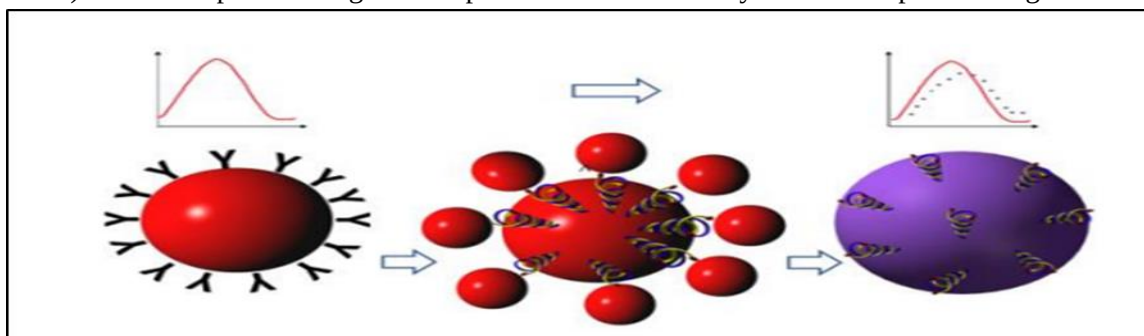


Fig. 3 MTB DNA gold nanoprobe assay: bare gold nanoparticle (red colour), MTB target (purple colour)

3.2. On-spot result development and reading

Detection of presence of target DNA was achieved by adding 1 μ l in 30 μ l of Au probe. The mixture suspension was denatured at 95 °C for 10 minutes before cooling to 55 °C for 2 hours of DNA hybridization. Positive reactions result from a red shift in the SPR of Au nanoparticles, resulting in a change in colour from red to purple and agglutination of the Au probe [18]. Mylab life solution Pvt. Ltd. 2017-18/D/95 comparative tools were used to design Au Nanoprobe sequences that aligned with the targeted genes. [19-21]. A multi-functional Au Nanoprobe was designed to detect MTB pathogens using specific sequences in Au Nps: Oligonucleotides GP-1 and GP-2: a sequence that complements MTBC group members, as shown in Fig 2. To reduce non-specific bonds between the thiol-modified oligonucleotides and the Au Nps, thiol-modified oligonucleotides were incubated with increasing salt concentrations. After 16 h, the solution was centrifuged, and the pellet was added to 10 mM phosphate buffer (pH 8), 0.1 M NaCl, and kept in the dark at 4 °C until further use. The gold nano biosensor distinguishes MTB bacilli from other bacteria found in clinical samples. The assay model employs group and species-specific oligo targets that detect the 16S rDNA TB gene, which is an extremely conserved sequence between Mycobacteria genus that differentiates species within the same genus. Amplified DNA was quantified and serially diluted to detect 10 femtomoles of an oligonucleotide, and the detection limit of the assay is 1.95 10^{-2} ng/ml.

3.3. RT-PCR amplification:

The conserved regions of MTBC rpoB gene 16 s ribosomal RNA sequencing (16 S rRNA) was amplified in a single and multiplex PCR reaction using two sets of primer pairs designed to obtain fragments: On the BIO-RAD C1000 thermo cycler, 110 bp rpoB amplifications were performed (USA). The template DNA with the following thermal cycling conditions: initial 5 min denaturation at 95°C, followed by 30 amplification cycles of denaturation at 95°C for 30 s, annealing at 58°C for 30 s, elongation at 72°C for 45 s, and a final elongation at 72°C for 5 min [22]. Both Unknown Sample A and Sample B are detected in this assay.

4. Conclusions:

Rapid and early On-spot detection of MTB DNA point of care device identify the pathogen. Here, for the first time, simple direct observation of gold nanoprobe based single reaction of TB detection is established. Our main aim for fabrication of medical device which is used tertiary health care center where no need for microbiologist or medical technologist. A simple, rapid, low-cost affordable point of care medical device with different types of pathogens will stand one of the alternative methods for early detection of TB.

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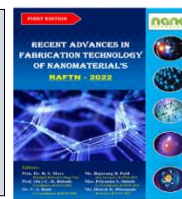
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Structural, Optical, Electrical Properties of Molybdenum Oxide (MoO_3) Thin Films

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KEYWORDS

Spray pyrolysis technique; Molybdenum trioxide; Thin films; SEM

ABSTRACT

MoO_3 thin films have been deposited onto glass substrates by using a simple and inexpensive spray pyrolysis technique. The MoO_3 powder was dissolved in ammonia solution at room temperature to form ammonium molybdate and doubly distilled water was added to obtain an appropriate concentration of spraying solution. The aqueous ammonia solution of MoO_3 powder has been used to obtain good quality deposits at fixed temperatures of 350°C . The spraying solution concentration was varied as 5, 10 and 15 mM. The structural, electrical and optical properties were studied and values of room temperature electrical resistivity, its activation energy, and band gap energy were estimated. The X-ray diffraction studies show that the films are polycrystalline having α -Orthorhombic crystal structure with reflections along (0 2 0) reflections with $k=1, 2$ and 3. Electrical resistivity increases with increase in solution concentration. The SEM studies reveal the compact morphology to mesh type structure.

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1. Introduction

MoO_3 is one of the transparent partially ionic transition metal oxides, which can be prepared in thin film form by using a wide number of techniques with a view to use them in photochromic cell, electrochromic cell, image recording, and holography MoO_3 have great technical interest, due to their optical and electronic properties [1]. MoO_3 finds application as a cathode material in the development of high-energy-density solid-state micro-batteries [2]. It is considered as a promising chromogenic /electrochromic material, as it exhibits electrochromic, photochromic, and gasochromic effects by virtue of which the material is of much interest for the development of electrochromic display devices, optical switching coatings, display devices, and smart window technology [3-7] Indeed these transition metal oxides can be switched between two different optical states promoted by photochromic, thermochromic or electrochromic effect. The polycrystalline films of MoO_3 with oxygen deficiency contain excess metal atoms, which act as doping centres. These centres control the electrical and optical properties of films. In the present work, the effect of solution concentration on the structural, electrical, optical properties of molybdenum oxide has been reported [8]. The films prepared for solution concentration was carried out as: 5mM, 10mM, 15mM, and films are denoted by M_1 , M_2 , M_3 respectively. The sprayed droplets undergo evaporation, condensation, and thermal decomposition, thereby resulting in the formation of molybdenum oxide thin films at 350°C [9].

2. Experimental Details

Molybdenum oxide thin films are deposited onto the glass substrates by spray pyrolysis technique. MoO_3 powder (GR grade, Loba Chemie) was dissolved in ammonia solution at room temperature to form ammonium molybdate and doubly distilled water was added to obtain an appropriate concentration of spraying solution [2]. The precursor concentration was varied from 5-15 mM. Films deposited on glass substrates were used for structural, electrical and optical properties.

The structural identification was carried out using Philips X-ray diffractometer (PW-3710) with Cu K α radiation ($\lambda = 1.5405\text{\AA}$). JEOL-JSM 6360 scanning electron microscope (SEM) was used for morphological studies. Various thicknesses were measured by using AMBIOS make XP-1 surface profiler and are found to be 320, 460, 540 nm. The optical characterization was carried out using UV-VIS Systronics spectrophotometer over 350 nm to 850 nm range at room temperature.

3. Results and Discussion

3.1. X-Ray Diffraction Studies

The structural changes and identification of phases were studied with the help of XRD technique. The diffracting angle 2θ was varied from 10 to 500. Fig. 1 shows XRD patterns for M1, M2, and M3 samples. The observed XRD patterns were compared with standard JCPDS card (file numbers: 35–508). Films are polycrystalline with well-defined diffraction peaks along (0 2 0) reflections with $k = 1, 2$ and 3. The good agreement of d values with standard ones indicates that films are phase pure with MoO $_3$ α -orthorhombic structure. The XRD patterns of samples manifest that (040) plane appears with relatively higher intensity. Besides this major peak, planes corresponding to (020), (110), (040), (060) are observed [7,10]. The calculated grain size was 45, 47 and 45 nm for sample M $_1$, M $_2$ and M $_3$ respectively. It is seen from the figure that crystallinity ameliorates with the increase in solution concentration owing to increment in crystal size.

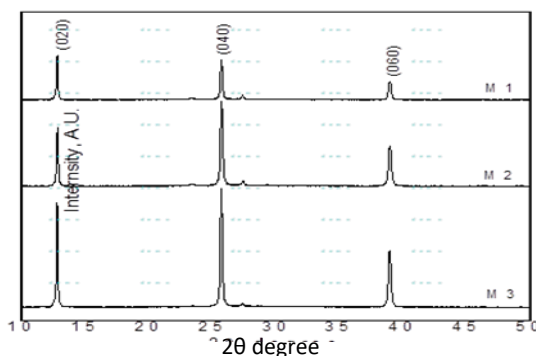


Fig.1 X-ray diffraction patterns of MoO $_3$ thin films deposited at different concentrations; 5 mM, 10 mM, and 15 mM.

3.2. Scanning Electron Microscopy (SEM)

The morphology of the film was studied using a Scanning Electron Microscope (JEOL-JSM-6360). The scanning electron microscope (SEM) has been used for the surface morphological analysis of MoO $_3$ thin films. Fig.2 shows the SEM image for the MoO $_3$ thin film prepared for M $_1$, M $_2$ and M $_3$ samples on the glass substrate. It clearly shows thread like micro mesh-type surface morphology for M $_3$ sample. This type of morphology was distributed uniformly throughout the film surface. The film appears multi-layered thread like, with thread mean diameters of about (1 μm) [11].

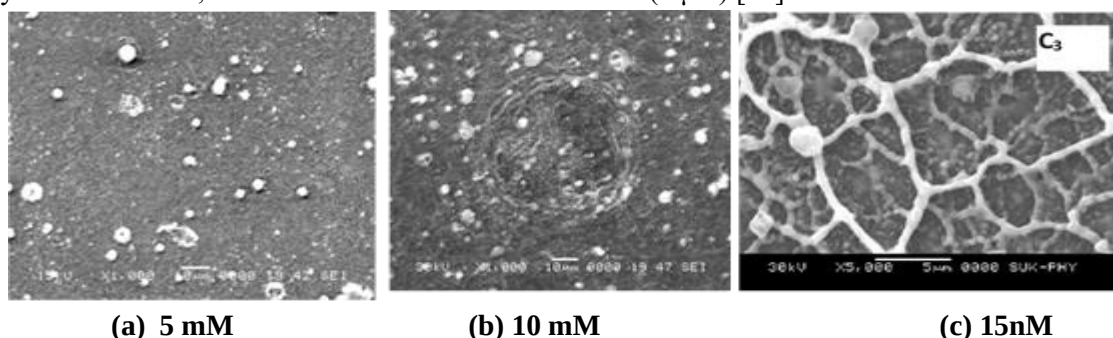


Fig. 2 SEM micrographs of MoO $_3$ films obtained for different solution spraying concentrations; (a) 5 mM (M $_1$), (b) 10 mM (M $_2$) and (c) 15 mM (M $_3$).

3.3. Thickness Measurement

The thickness of as-deposited films was found to be between 320 to 540nm as solution concentration increases from 5 to 15mM. The values of film thickness are given in Table 1. The rise in solution concentration causes the increase in evaporation rate of the initial product, leading to increasing in mass transport towards the substrates, which results into increase in film thickness [12].

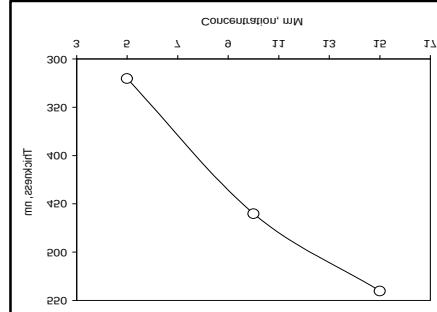


Fig. 3: Variation of film thickness with solution concentration

3.4. Electrical Resistivity

DC electrical resistivity was measured and found to be of the order of $10^5 \Omega\text{cm}$ at room temperature. The values of room temperature electrical resistivity listed in Table 1. The variation of d.c. electrical resistivity with temperature in the range 27 to 227°C was studied and shown in Fig. 4. The resistivity increases with increase in solution concentration. The room temperature resistivity increases from 0.15×10^5 to $5.5 \times 10^5 \Omega\text{-cm}$ [13]. Activation energy also increases with solution concentration increases. It varies from 0.063 to 0.074 eV for sample M_1 to M_3 .

3.5. Optical Studies

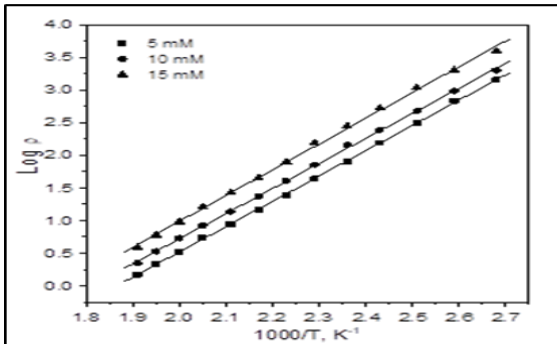


Fig. 4: The plot of $\log \rho$ versus $1000/T$ for MoO_3 thin films deposited at different concentrations; 5 mM, 10 mM and 15 mM

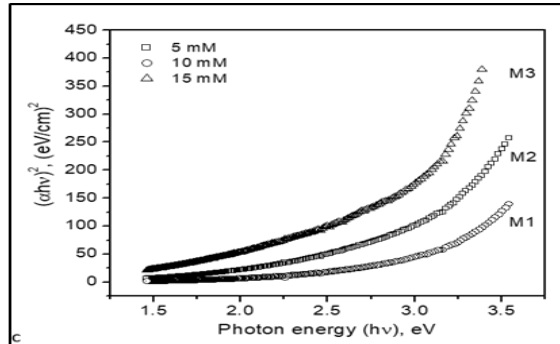


Fig. 5: The plot of $\alpha h\nu^2$ versus $h\nu$ for MoO_3 thin films deposited at different concentrations;

Table 1. Effect of solution concentration; M_1 , M_2 , and M_3 on properties of MoO_3 thin films prepared by spray pyrolysis

Sample Code	Solution Conc. (mM)	Thickness, 't' (nm)	Crystallite Size (nm)	Band gap, Eg (eV)	Activation energy (eV)	RT Resistivity $\rho_{RT} (\Omega\text{cm})$
M_1	5	320	45	3.11	0.063	0.1568×10^5
M_2	10	460	47	3.05	0.067	1.2246×10^5
M_3	15	540	45	3.04	0.074	5.4950×10^5

The optical absorption spectra for all the as-deposited samples were recorded in the wavelength range of 350-850 nm at room temperature. The variation of $(\alpha h\nu)^2$ versus $(h\nu)$ for all the samples is shown in fig 5. The nature of the plots indicates the existence of direct optical transition. The extrapolation of the

straight line to zero absorption coefficient ($\alpha=0$) led Table 1. The bandgap energy for all the samples lays in the range 3.11-3.04 eV to the estimation of band gap energy (E_g) values [14].

4. Conclusions

In the present work, it was planned to deposit molybdenum oxide thin films from ammonium molybdate by using a simple and inexpensive SPT at various solution concentrations in view of their application for in electrochromic (EC) devices. The structural, electrical, optical and electrochemical properties of the films deposited at three different solution concentrations from 5 mM to 15 mM are carried out. The effects of solution concentration on a thickness and band gap energy of film material were studied. The self-assembled thread-like morphology of thin film was confirmed by SEM.

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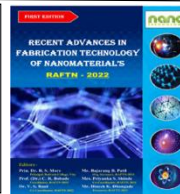
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Review on $\text{La}_2\text{Mo}_2\text{O}_9$ Electrolyte material for Solid Oxide Fuel Cell

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KEYWORDS

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LAMOX,
Electrolyte,
Dielectric properties

ABSTRACT

In an era when renewable energy resources are in high demand, the fuel cell represents a highly efficient, clean, and sustainable energy conversion source. According to the types of electrolyte and fuels used, fuel cells can be classified into six categories. Solid oxide fuel cells (SOFCs) technology is gaining popularity among researchers as a promising power generation system with high energy efficiency, increased fuel flexibility, and low environmental impact when compared to conventional power generation systems. SOFCs are devices that convert chemical energy directly into electrical energy with minimal emissions. SOFCs have low pollution characteristics, high efficiency (60%), and a wide range of fuel options with minimal environmental impact. A single cell component of SOFCs is made up of an anode, a cathode, and an electrolyte that are stacked layer by layer to produce more power. The dense ceramic electrolyte transports O_2 ions and fills the material space between the electrodes. In this review, the article presents; overview of the $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX) electrolyte material.

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1. Introduction

For a wide power range, SOFCs can make direct conversion of chemical to electrical energy. Nonetheless, high operating temperature near about 1000 °C essential for the conduction of oxide ions via electrolytes limits their practical application [1]. The novel electrolyte from LAMOX family having high oxide ion conduction ability would lower operating temperature of the cell [2]. The electrolyte ($\text{La}_2\text{Mo}_2\text{O}_9$) LAMOX shows phase transition near about 580 °C from monoclinic to cubic phase, phase transition increase the ionic conductivity of order twice as of monoclinic phase [3]. However, one disadvantage of using LAMOX as electrolyte is inability to withstand in reducing atmosphere [4-6]. Several authors, reported an increase in ionic conductivity when crystallite size was reduced to nano range [7-10].

2. Different electrolyte materials for SOFC

2.1. Yttria Stabilized zirconia (YSZ)

The undoped zirconia (ZrO_2) shows monoclinic structure up to 1446 K [11]. However, by using doping of Y_2O_3 , CaO , or MgO makes high temperature phases stabilized at room temperature. For the stabilization of zirconia cubic phase widely Yttria used as dopant [12]. Zirconia-based electrolytes have been studied for several years in the field of SOFC, with divalent and trivalent dopants. At 1000 °C, ionic conductivity of zirconia based electrolyte is 0.1 S/cm. Thermal stresses in SOFC components increase as the temperature rises. However, it has very good chemical and mechanical stability [13]. Thermal barrier coating for gas turbines, where low thermal conductivity is required for insulation, is another application for YSZ ceramic [14]. Because of its higher ionic conductivity, ScSZ is a substitute to YSZ for SOFC applications at intermediate temperatures. ScSZ configurations containing 8-12 mole % Scandia have maximum ionic conductivity of any Zr based electrolyte [15].

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2.2. Ceria based electrolyte

The Gd and Sm doped ceria electrolytes are promising candidates for 550 °C-650 °C temperature range, cause of their high conductivity. A common disadvantage is they are n-type semiconductors in reducing atmosphere, resulting in a decrease in cell output [16-20].

2.3. Bismuth oxide based electrolyte

Amongst all electrolytes, bismuth oxide ion conductors have the highest conductivity >1 S/cm. The only disadvantage is that it is only stable between 730 °C-800 °C, and its melting point is 804 °C. This phase has a fluorite-like structure [21, 22].

2.4. Perovskite related electrolyte

Another type of electrolyte system is perovskite $\text{Ba}_2\text{In}_2\text{O}_5$. This phase is known as oxygen-deficient perovskite. The oxide ion vacancies are ordered at room temperature, resulting in an alternate layer of tetrahedral and octahedral indium oxide. Above 900 °C, this phase become tetragonal perovskite due to an ordered transition, resulting in a significant increase in ionic conductivity near about 0.1 S/cm at 900 °C [23].

2.5. Apatites

Rare earth apatites material having common formula $\text{A}_{10}(\text{XO}_4)_6\text{O}_{2+y}$, where A is the rare or alkaline earth metal & X is P, Si or Ge. At intermediate temperature range and low oxygen partial pressure apatites show high oxide ion conductivity [24, 25]. They have been targeted as potential solid electrolyte alternatives reported by Nakayama et. al. [26] on the silicate based system.

2.6. Pyrochlores

Pyrochlores are potentially appealing solid electrolytes with the general formula $\text{Ln}_2\text{M}_2\text{O}_7$, where Ln is Sn or Lu and M is Ti, Hf, or Zr. They are part of the $\text{Ln}_2\text{O}_3\text{MO}_2$ system, which is expected to have intrinsic ionic conductivity. The first studied pyrochlores were $\text{Ln}_2\text{Zr}_2\text{O}_7$ types, also known as zirconate pyrochlores, where Ln is Nd, Sm, and Gd with the structure of fluorite having defects. Less is known about the LnHfO_7 (Ln= Nd, Sm, and Gd) hafnates $\text{R}_2\text{Ti}_2\text{O}_7$ (R= Y, Gd, and Lu) and rare earth pyrochlore structures. [27].

2.7. LAMOX based electrolyte

Lacorre and his group reported the first LAMOX ($\text{La}_2\text{Mo}_2\text{O}_9$) based oxide ion conductor in the year 2000. At 800 °C, oxide ion conductivity of LAMOX is greater than YSZ [3]. Lacorre and his colleagues previously investigated the effect of ball milling on Lanthanum molybdate-based compound. At temperatures above 580 °C, the LAMOX compound shows phase transition from monoclinic to cubic. When compared to the monoclinic phase, cubic phase conductivity increases by an order of two and reaches 0.06 S/cm at 800 °C. Because of molybdenum phase transition and reducibility, various substitutions have been tried to stabilize the cubic phase at lower temperatures.

2.7.1. Importance of LAMOX based electrolytes

The discovery of a LAMOX-based electrolyte in the year 2000 drew a lot of attention in the SOFC field. They are classified as fast oxide ion conductors. At low temperatures, these have higher oxide ion conductivity than YSZ [3]. At temperatures above 580 °C, LAMOX undergoes phase transition from monoclinic to cubic. At the reducing atmosphere ceria based electrolyte become n-type semiconductors is the main disadvantage, resulting in a decrease in cell voltage. Another disadvantage is that they contain silica as a common impurity, which reduces ionic conductivity. The most extensively studied YSZ electrolytes shows decent mechanical and chemical stability over extensive range of both oxygen partial pressure and temperature. The only disadvantage is that the desired conductivity is achieved at a higher temperature of about 1000 °C, where conductivity is 0.1 S/cm, which ultimately leads to a high operating temperature and manufacturing cost by using noble metals interconnect and cathode as current collectors. After considering all of the factors, it is possible to conclude that the LAMOX-based system is more effective than the other electrolyte system.

2.7.2. Conduction path in LAMOX

From the preceding discussion, it is clear that the oxide ion is in charge of conduction in a LAMOX-based system. Goutenoire 2000 et al. [28], solved the crystal structure of β -LAMOX and discovered three distinct sites occupied by the O atom, namely 4a, 12b, and 12c. The O(1) & O(2) sites are both 50 % free, while O(3) sites are less than 50 % occupied. Some of the O(2)-O(3) & O(3)-O(3) bond length of 2.5 Å. In these cases, any one sites is unoccupied by an oxygen, and an oxygen from the other site is near to a vacancy. The smallest distance between O(2)-O(3) & O(3)-O(3) indicates the oxide ions conduction path [29].

3. Literature survey

The high oxide-ion conducting material has been of fascinating extensive interest because of prospective applications in SOFCs, oxygen pumps, oxygen sensors and catalysts etc. [30-33]. Mainly the oxide-ion conductors are classified into four groups i.e., deficient perovskites, fluorite, pyrochlores and Aurivillius [34-37]. The widely studied and commonly used oxide-ion conducting material amongst all oxide ion conducting material is yttria-stabilized zirconia (YSZ). However, for such customary oxide-ion conducting material, high working temperatures were necessary to achieve satisfactory oxygen-ion conduction for competent operation of the SOFC. In 2000, Lacorre et al. developed a novel fast oxide ionic conductor material $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX) [38], which exhibited high oxide-ionic conductivity compared to other oxide ion conductor and nearly equal to the YSZ [39, 40]. The LAMOX material was first synthesized by France scientist Fournier et al. in 1970 [41], more recent reports were published on the structural characterization and the high ionic conductivity of lanthanum molybdenum oxide (LAMOX) [38, 42]. The lone pair substitution (LSP) was used to explain the remarkable high oxide-ion conductivity of $\text{La}_2\text{Mo}_2\text{O}_9$, in this lone pair substitution concept considered the without lone pair electrons in cation generates the intrinsic vacancies in anionic sublattice [43]. The structural phase transition of newly discovered solid electrolyte $\text{La}_2\text{Mo}_2\text{O}_9$ observed from α -monoclinic to the much-improved conductor β -cubic near about 833 K. This transition in LAMOX is like to be reported in all other fast ionic conductors such as $\text{Bi}_2\text{V}_4\text{O}_{11}$ & Bi_2O_3 is frequently related to a readjustment in the oxygen sublattice [44, 45]. The transport and structural properties of fast oxide ion conducting LAMOX family depend on the lanthanum molybdenum oxide ($\text{La}_2\text{Mo}_2\text{O}_9$) were firstly reported by Goutenoire et al. [46].

The fluorine doped lanthanum molybdates ($\text{La}_2\text{Mo}_2\text{O}_{9-0.5x}\text{F}_x$) successfully synthesized and characterized were reported by Arulraj et al. [47]. The first order phase transition showed by fluorine-doped lanthanum molybdates. As increasing the fluorine content, decrease in transition temperature is observed. In range $0.18 < x < 0.30$ composition had much lower ionic conductivity as compared to the range $0 < x < 0.12$ composition below the transition temperature. In comparison to the parent compound of the LAMOX family $\text{La}_2\text{Mo}_2\text{O}_9$, the fluorine doped lanthanum molybdate has high activation energy. The ionic conductivity of fluorine doped lanthanum molybdate in comparison with the parent compound of LAMOX family $\text{La}_2\text{Mo}_2\text{O}_9$ is higher above the transition temperatures. By using SIMS analysis and isotope exchange depth profile the series of augmented material in LAMOX family with the parent compound $\text{La}_2\text{Mo}_2\text{O}_9$ was studied by Georges et al. [48]. The coefficients of oxide-ion diffusion are lower in any fluorite use as an electrolyte as compared to the parent and optimized compound in the LAMOX family.

Further, it was observed that in H_2 $^{18}\text{O}/^{16}\text{O}$ atmosphere a significant enhancement in the substitution of isotopic oxygen as compared to the dry air atmosphere. The impact of tungsten and chromium on the structural arrangement of $\text{La}_2\text{Mo}_2\text{O}_9$ was studied by Corbel et al. [49]. The cell volume changes as the function of W first slightly rises (W: Mo<1) & then suddenly decreases (W: Mo>1). This particular development has been associated with the surrounding of the O1 site which changes nonlinearly and in case of the variation occurs in the O2 or O3 site which makes the decrease in the tungsten ions coordination number. The occurrence of transport mechanism due to the amendment distribution of conducting oxide-ions. The rare earth element like (Nd, Gd, Y) makes their impact on the structure was studied by Georges et al. [50]. The suppression in phase occurs when the doping of Gd and Y increases beyond a certain level

and β -cubic structures are stabilized at room temperature were observed. The sintering and electrical conductivity of the LAMOX family with some substitution of rare earth elements were premeditated by the Georges et al. [51]. For reducing the size of the particle or grain for the material of optimized, two physical methods were used Attrition and ball milling. From above of these two methods, due to the pollution issue comes for zirconia in the attrition method, therefore only the ball milling method could be reserved and the stabilization of $\text{La}_2\text{Mo}_2\text{O}_9$ against the reduction problem solved by the tungsten substitution, this tungsten substitution not makes any effect on the oxide ion conduction of the $\text{La}_2\text{Mo}_2\text{O}_9$. The synthesis of $\text{La}_2\text{Mo}_2\text{O}_9$ on the Al_2O_3 alumina ceramic substrate by RF sputtering was firstly reported by Laffez et al. [52]. The main two parameters that were important in the synthesis of the pure $\text{La}_2\text{Mo}_2\text{O}_9$ films are the temperature of alumina substrate and oxygen partial pressure. The stoichiometric variation in the film occurs by varying both the parameter and Mo-rich and Mo-deficient films were achieved. Thick and dense film of $\text{La}_2\text{Mo}_2\text{O}_9$ is achieved by an upsurge in ratio of La: Mo.

The physicochemical compatibility of different materials like CGO, LSM and LSC electrode with the $\text{La}_2\text{Mo}_2\text{O}_9$ was investigated by Corbel et al. [53, 54]. The rate of the chemical reaction is different for different materials at different temperatures, the chemical reaction occurred between the $\text{La}_2\text{Mo}_2\text{O}_9$ electrolyte and LSCF electrode within 600 °C -700 °C, whereas, in case of the electrode LSM, the chemical reaction just started with the electrolyte $\text{La}_2\text{Mo}_2\text{O}_9$ in the range of temperature of 700 °C -800 °C. These electrode and electrolyte chemical reactions arise due to the strontium depleted from the perovskite oxide, this depleted strontium reacts with molybdenum in electrolyte $\text{La}_2\text{Mo}_2\text{O}_9$, ultimately forming extra products such as SrMoO_4 and/or $\text{La}_2\text{Mo}_2\text{O}_9$. The result of this chemical reaction exhibited that strontium is present in the electrode materials, to prevent the substitution with $\text{La}_2\text{Mo}_2\text{O}_9$ -related materials it should be avoided. With the CGO electrode, the $\text{La}_2\text{Mo}_2\text{O}_9$ -related materials have good chemical compatibility was reported by Georges et al. [55]. The rise in reducibility under dilute hydrogen takes place when lanthanum is substituted by the rare earth element. The opposite fact observed is lowered reducibility when tungsten is substituted in $\text{La}_2\text{Mo}_2\text{O}_9$. In the $\text{La}_{1.92}\text{Ca}_{0.08}\text{Mo}_2\text{O}_{8.96}$ material, the evidence of meta-stability and recombination was examined by Selmi et al. [56] and in the case of $\text{La}_{1.92}\text{Ca}_{0.08}\text{Mo}_2\text{O}_{8.96}$ powder, the very complex phase transition was found. The series of $\text{La}_2\text{Mo}_{2-y}\text{W}_y\text{O}_9$ ($y < 1.4$) oxide ion conduction properties were studied by Georges et al. [57]. Two conduction systems were evidenced for each composition: for Arrhenius type, the conventional system is low temperature and VTF (Vogel-Tammann-Fulcher) type, with extremely free oxide ions, conventional system is a high temperature. The features VTF system the nonlinear variation with an extremum at $y=0.1$, those of the Arrhenius type system developed with the tungsten substitution with regular manner. The successful synthesis of lanthanum molybdate oxide was done by using the physical method of ball milling described by Lacorre et al. [58]. Main disadvantage of such system was the phase of crystallinity phases. However, the crystallinity improved considerably if annealing treatment is given in an appropriate atmosphere. The use of citrate nitrate combustion in the synthesis of the Nd-doped $\text{La}_2\text{Mo}_2\text{O}_9$ fast oxide-ion conductors reported by Basu et al. [59].

There is no major effect of Nb doping on the order-disorder transition showed by pure $\text{La}_2\text{Mo}_2\text{O}_9$ fast oxide ion conductor. The Nb doping has considerably lowered both the enthalpy change related to the transition temperature and transition temperature. As the Nb concentration show inverse relation with oxide-ion conduction and at 700°C, the oxide ion conductivity was found 0.069 and 0.062 S/cm for the value of x were 0.06 and 0.1 respectively for the composition $\text{La}_2\text{Mo}_{2-x}\text{Nb}_x\text{O}_{9-\delta}$. The lowest doping oxide ion conductivity for the composition $\text{La}_2\text{Mo}_{1.4}\text{Nb}_{0.06}\text{O}_{9-\delta}$, at 800°C about 0.113 S/cm, this oxide ion conductivity was nearly twice that of the pure lanthanum oxide material. Another composition of lanthanum molybdenum oxide $\text{La}_{2-x}\text{Ba}_x\text{Mo}_2\text{O}_9$ was successfully synthesized by using the citrate-nitrate auto-ignition method reported by Basu et al. [60].

The resistive transition of pure $\text{La}_2\text{Mo}_2\text{O}_9$ materials suppressed by Ba doping is near about 3%, which makes room temperature stability of β -cubic phase and at 800°C the maximum value of oxide ion

conductivity about 0.084 S/cm exhibited by the material $\text{La}_{1.94}\text{Ba}_{0.06}\text{Mo}_2\text{O}_9$. The synthesis and characterization $\text{La}_{1-x}\text{M}_x\text{Mo}_2\text{O}_9$; $\text{M}=\text{Ca}^{2+}$ Sr^{2+} or Ba^{2+} the SrO doped $\text{La}_2\text{Mo}_2\text{O}_9$ showed maximum oxide ionic conductivity described by Subasri et al. [61]. Synthesis of $\text{La}_2\text{Mo}_2\text{O}_9$ by using fix 0.3 citrates to nitrate ratio in citrate nitrate auto-ignition process reported by Subasri et al. [62]. Immediate pure phase formation of $\text{La}_2\text{Mo}_2\text{O}_9$ possible by using this method and sintering treatment at 800 °C and 950 °C showed high oxide ion conductivity 0.052 S/cm and 0.080 S/cm respectively reported by Subasri et al. [63]. The ionic conductivity was investigated by Subasri et al. for the $\text{La}_2\text{Mo}_2\text{O}_9$ is 7.94×10^{-5} S/cm at 1173K. The $\text{La}_2\text{Mo}_2\text{O}_9$ were synthesized by using the spark-plasma sintering method reported by Yang et al. [64]. They found the oxide ion conductivity $\text{La}_2\text{Mo}_2\text{O}_9$ was higher than other sintered methods.

4. Conclusions

Various kinds of electrolyte systems employed in solid oxide fuel cell systems have been studied. The most extensively researched electrolyte is YSZ and GDC, which at present time are still used commercially. The operation of YSZ at 1000 °C makes it a very robust system for high temperature application and the highest conductivity showed is 0.1 S/cm^{-1} at 1000 °C. The GDC-based electrolyte also shows the potential-based application system. Other systems like perovskite electrolyte systems have also been studied by various researchers. Apart from advantages, some of the limitations like the use of noble metal current collectors at high temperature of operation increase the overall cost of the YSZ fuel cell system for GDC-based SOFC's the appearance of electrical conductivity under reducing conditions resulting in reduced cell output voltage. Similarly, the volatilization In_2O_3 in the perovskite electrolyte system restricts its commercial application in SOFC. Bismuth oxide electrolytes despite having excellent ionic conductivity of 1 S/cm are stable over 730-800 °C and melt at 804 °C, which also restricts its application in SOFC. Among all electrolyte systems recently discovered $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOXY) based electrolyte can be considered as a potential electrolyte compared to YSZ and GDC ceramics which are commercially used in industry. In literature of fast oxide ion conductor $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOXY) study the doping at various sites of LAMOXY.

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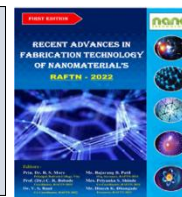
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Recent Advances in Fabrication Technology of Nanomaterials

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The study of yttrium sulphide-based storage electrode in storage cell

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KEYWORDS

Storage cell, storage electrode, photoelectrode, Counter electrode agar-agar gel.

ABSTRACT

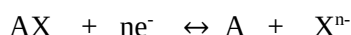
The study of yttrium sulphide as storage electrode was carried out by designing a special three electrode storage cell system. It consists of three electrodes, namely, storage electrode, photoelectrode and counter electrode. Electrodeposited yttrium sulphide film and CdSe film on to a stainless steel substrate has been used as a storage electrode and photoelectrode respectively. The graphite rod was used as a counterelectrode. These three electrodes were immersed in two rectangular transparent plastic boxes containing suitable electrolytes. Boxes were bridged together by agar-agar gel. The cell was illuminated by a high intensity lamp. The electrical characteristics in the mode of charging and discharging were studied

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1. Introduction

In this modern world, the social prosperity and economic development depend on the sustainable energy conversion and storage, for a sustainable society, energy is unquestionably one of the grand challenges [1, 2]. There is urgent need of clean, affordable and reliable energy that can substitute fossil fuels and limits the carbon emission issue. Therefore, the interest of researchers focused towards the development of technology to make availability of clean and renewable energy, especially the intermittent energy, energy conversion and storage [3, 4]. Now a day, there is vast demand for electrochemical energy conversion and storage devices, especially portable devices, consumer electronics, and electric vehicles [5–7]. Derek P Gregory has been reported use of rare earth hydrides for storing hydrogen in both stationary and mobile applications [8]. Therefore, it should require rapid development of new materials with high performance in energy conversion and storage devices. In our opinion, scientists underestimated this field and started working with material having low cost and easy availability. The best materials, for examples, so far reported with relatively with high efficiency and stability for long time are CdSe, WSe₂, CuIn Se₂ [9-12].

Photo electrochemical cell can be converted into rechargeable electrochemical storage cell, when storage electrode, capable of undergoing a reversible chemical change is used in it [13]. A reversible chemical reaction occurs at the storage electrode of the type,



Where A is storage electrode, X is solute present in the electrolyte. Construction of such a cell requires stable low resistance separator which minimizes direct chemical reaction of the electro active redox species, and the selected redox couples suitable to semiconductor photoelectrode. The PEC cells employing third electrode as a storage electrode have been reported in the literature [14-19].

2. Experimental

2.1. Preparation of electrode films and electrolytes

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Yttrium sulphide films have been electrodeposited from the non-aqueous formaldehyde bath $[0.05\text{M Y}(\text{NO}_3)_3 - 0.05\text{M CH}_3\text{CSNH}_2 - 0.05\text{M CH}_3\text{COONa}]$ onto a stainless steel substrate at room temperature. The CdSe films are electrodeposited from the aqueous bath $[0.1\text{M CdCl}_2 - 0.05\text{M SeO}_2]$ onto stainless steel substrates. The PEC properties of the film were tested with the electrolyte $0.1\text{ M} (\text{Na}_2\text{S} - \text{S} - \text{NaOH})$ as an electrolyte 2.1. and graphite as a counterelectrode. In order to increase the photo effect, the films were annealed at 200°C .

The electrolytes are prepared by using analytical grade chemicals in doubly distilled water. The stable electrolyte for the photoanode (CdSe) is polysulphide [20]. It was prepared by taking A.R. Grade Sodium hydroxide and sulphur from. B.D.H., India, and A. R. Grade sodium sulphide, from the Fluka. Appropriate amount of NaOH and Na_2S were dissolved in double distilled water at room temperature. In this solution, sulphur powder was added and mixture warmed up to 55°C with constant stirring. The mixture was maintained at this temperature till all sulphur powder dissolves. The solution was cooled to room temperature, filtered and preserved in the glass stopper air tight bottle. The colour of the solution was yellowish pink. The yttrium sulphide films are stable in the ferri-ferrocyanide electrolyte. This electrolyte was prepared by taking appropriate amount of potassium ferricyanide and potassium ferrocyanide of analytical grade, dissolved in double distilled water and preserved in the glass stopper air tight bottle.

2.2. Design of the Three Electrodes Storage Cell

The design of three electrode battery was reported by many researchers in various journals [21-25]. Here, cell consists of three electrodes, namely, CdSe as a photo electrode, graphite as counter electrode and yttrium sulphide as storage electrode. Two rectangular transparent plastic boxes were fixed with M-seal by conducting bridge of 3 cm in length formed with Agar-Agar gel. The size of each rectangular box is $4.0 \times 1.5 \times 7.5\text{cm}^3$. One compartment of cell consists of CdSe as a photoanode (5 cm^2 area) and graphite rod (6.2 cm^2 area) as the counterelectrode. The volumes of the electrolytes were 35 cc in each compartment of the cell. The electrolyte $0.1\text{ M} (\text{Na}_2\text{S}-\text{NaOH})$ was used in first compartment. The other compartment consists of $0.1\text{ M} [\text{K}_3\text{Fe}(\text{CN})_6] - \text{K}_4\text{Fe}(\text{CN})_6$ electrolyte with yttrium sulphide storage electrode which is kept in dark.

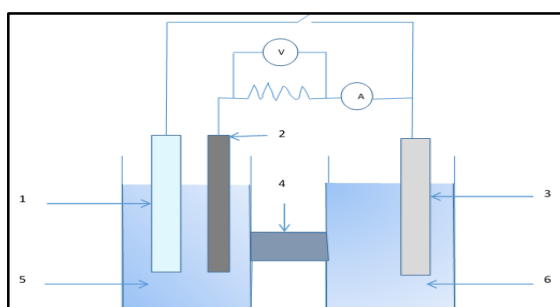
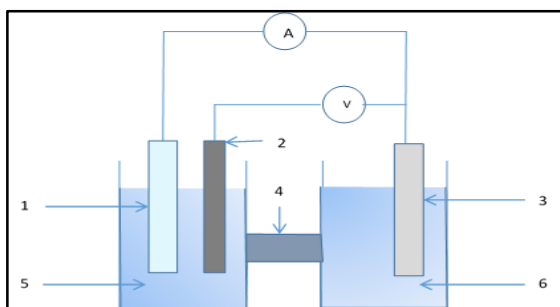


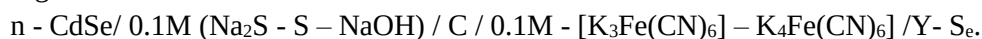
Fig.1: Schematic diagram of the redox storage cell during charging, **Fig.2:** Schematic diagram of the redox storage cell during discharging

The cell was illuminated by using 500 Watt tungsten filament lamp. The light intensity was $200\text{mW}/\text{cm}^2$. The electrical characteristics in the mode of charging were studied with the circuit diagram shown in fig.1 and fig.2 respectively. In fig. 1)- CdSe photoanode, 2)-Counter electrode, 3) Y-S storage electrode, 4) Agar-Agar gel, 5) $0.1\text{ M} (\text{Na}_2\text{S} - \text{S} - \text{NaOH})$ and 6) $[\text{K}_3\text{Fe}(\text{CN})_6] - \text{K}_4\text{Fe}(\text{CN})_6$. The current and voltages were recorded using the digital current and volt meters respectively.

3. Result and Discussion

3.1. The Configuration of the Cell and Charge Transfer Mechanism

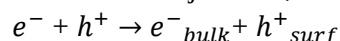
The configuration of the cell was as follows:



During charging the photoreaction occurring at the two electrodes can be described as follows:



Due to localized electric field at junction,



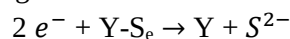
(i.e. near the interface of the semiconductor electrolyte)



i.e. oxidation of electrolyte would occur, which is present near interface.



(Transfer to through back of semiconductor to the storage electrode)



Where, Y-S_e is the storage electrode.

During discharging,



Charging and Discharging Studies of the CdSe/ 0.1M (Na₂S - S - NaOH) / C / 0.1M - [K₃Fe(CN)₆] - K₄Fe(CN)₆] / Y- S

During the period of charging, photocurrent raised from 0.15 to 225 mA/cm², while cell voltage rose from 30 to 200 mV as shown in fig.3 within the period of 120 minutes. Discharging of the cell using 6 KΩ load across the storage electrode and counterelectrode results in an initial current of 14.1 μA/cm² and after the period of two hours current drops to 12.0 μA/cm². The cell voltage also decreased from 600 to 300 mV as shown in fig.4. It can be seen that the potential and current decreases rapidly within first twenty minutes and slowly thereafter.

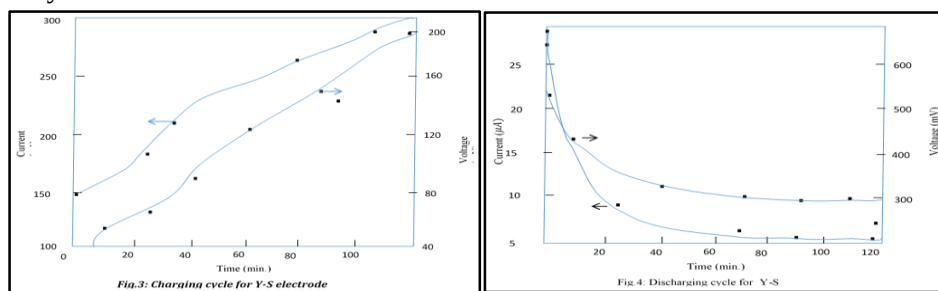


Fig.4. Cell Potential

4. Conclusion

From above studies of charging and discharging characteristics, it is concluded that yttrium sulphide film may be used as a storage electrode.

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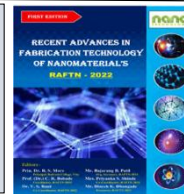
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**Recent Advances in Fabrication Technology of
 Nanomaterials**

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A Role of Supercapacitor as an Energy Storage Device

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KEYWORDS

Supercapacitor,
 Energy storage device,
 Principle,
 Supercapacitors applications.

ABSTRACT

Supercapacitor is one of electrochemical energy storage device, widely used in different applications like transportation, consumer electronics, uninterrupted power supply (UPS) system etc. It stores hundred times more energy per unit volume than electrolytic capacitors and has ability to make fast charging-discharging over number of cycles as compare to traditional batteries. So, researchers are attracted towards capacitor technology, which is expanding very fast as demand grows for a new generation of supercapacitors. As per this view, it is necessary to aware about the actual role of supercapacitor by knowing its different types, construction and working principle, and choice of different materials for electrodes and electrolytes for better performance of supercapacitors. Such a detailed information is discussed under this article. instinctive advantages of La-NCZ ferrites for manufacturing of ammonia sensor.

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1. Introduction

Today, fossil fuels are the major source of man-made electric energy, but, the depletion of fossil fuel and their tremendous pollution become a major issue ahead for long time utilization. Also, demand of energy is continuously increases due to rapid increase the world population and industrialization. In order to meet today's power demand, it is necessary to make alternative ecofriendly energy source like supercapacitor which is safe to operate, cost effective and has ability to solve the future energy crisis and reduce the pollution [1]. The commonly used energy storage devices are supercapacitor, batteries and conventional capacitor, these are differentiated in Figure1A. Figure1B show Ragone plot for commonly used energy storage devices [2]. In that, supercapacitors are one of the effective energy storage systems, which convert mechanical energy into electric energy and generally considered the bridge between the batteries and capacitors [3]. Its electrochemical energy conversion is high and reusable large number of cycles Batteries can hold large amount of power but they take more time to charge up. On the other hand, capacitor charge instantaneously but store small amount of power [4] Owing to this, the supercapacitors have high power density, long life cycles, cost effective due to compact size [5]

This paper includes the detailed background about supercapacitor, different types, working principle, choice of different materials for electrodes and electrolyte for better performance of supercapacitors and its applications [6].

2. Background about Supercapacitor:

Supercapacitors or electrochemical capacitors are called as ultra-capacitor, which able to attain greater energy densities and maintain the characteristic high-power density of conventional capacitors.

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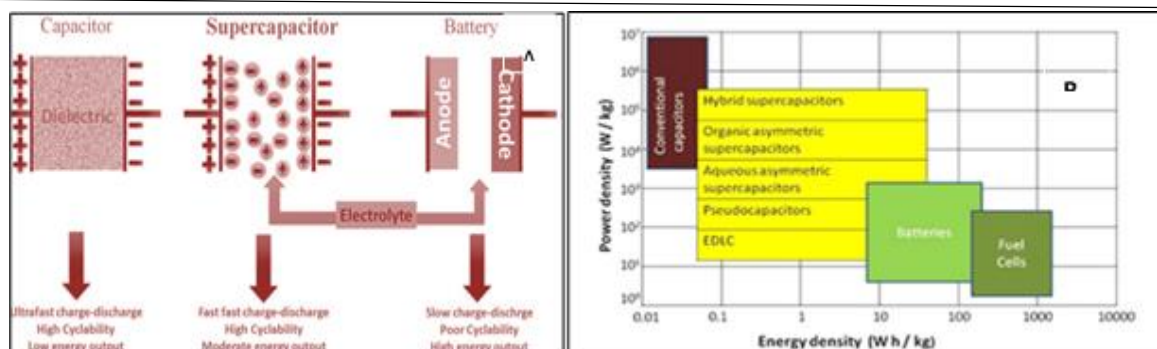


Fig. 1 (A) Characteristics outline for capacitor, battery and Supercapacitor. (B) Ragone plot for different energy storage and conversion devices

A supercapacitor cells consist of three main components like electrodes, electrolyte, and separator. The electrolyte solution is ionic conductive medium. The two electrodes are separated by membrane act as a separator that allows the mobility of charged ions. The separator also prevents direct contact of the two electrodes while allowing freely moving electrolyte ions. Among these, electrodes are the most important. Its properties like porosity, high surface area and chemical stability significantly control the performance of supercapacitor. The porous materials facilitate charge storage and transport of ions while high surface area is useful to store energy on the surface. The schematic representation of supercapacitor is shown in Figure 2A.

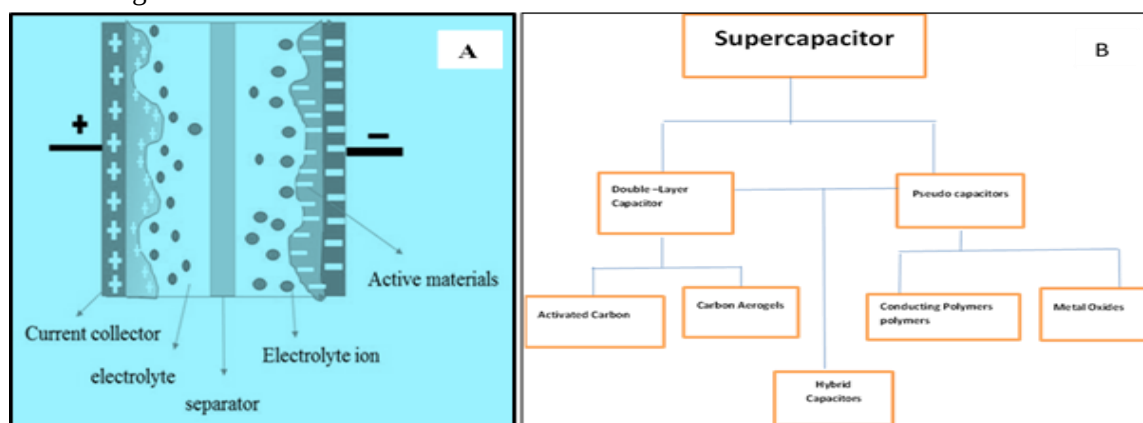


Fig. 2 (A) Schematic diagram of a supercapacitor, (B) Classification of Supercapacitors

3. Working Principle of Supercapacitors:

A supercapacitor operates by storing electrical energy between two electrostatic double layers created by the formation of thin charge layers on the electrolyte-electrode interface. In case of supercapacitor, electrical charge storage mechanism is same as conventional capacitor, but charge interface conductor and electrolyte form a double layered, one of the layers is the charged electrode and other one is created due to the electrolytic ions. The charge storage is no faradic in nature because no electron transfer across the electrode-electrolyte interface storage charge [8]. The capacitance value of a supercapacitor is relative to the surface area of the electrodes. An applied electric field across these electrodes provides the main driving force for the ions [9].

4. Types of Supercapacitors:

Supercapacitors are classified into main two classes, depending on charge storage mechanism. Different types are illustrated in Figure 2B.

1. Dielectric double-layer capacitor (EDLC), and
2. Pseudocapacitor.

However, a combination of these two produces hybrid supercapacitor.

4.1. Electrostatics Double Layers Capacitor (EDLC):

In the evolution of capacitor to supercapacitor, the third generation is referred to as electrochemical double layer capacitor (EDLC). In this generation, activated carbon is used as electrode material and aqueous, organic electrolyte is used. In EDLC, the energy is stored at the interface between electrode and electrolyte. It has high power density than the batteries. [10]

The mechanism of EDLCs shown in Figure 3A, arises from charge accumulation in the electric double-layer formed at the electrode/electrolyte interface; but, the specific capacitance of an EDLC is several orders of magnitude higher than a traditional capacitor.

The concept of electrochemical double-layer was developed by Gouy in 1910 using thermal factor.

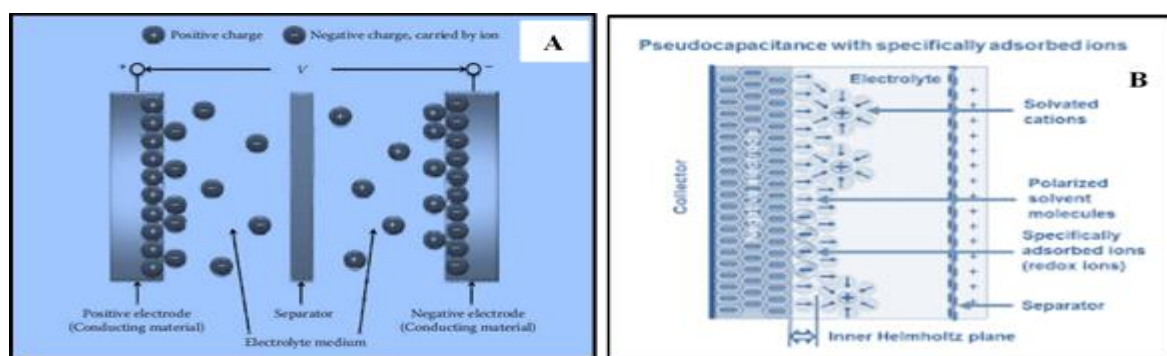


Fig. 3 (A) Electrical double layer capacitor, (B) Pseudocapacitor.

The thermal motion makes ions to keep nearer to the electrode surface. According to Gouy-Champman model, the electric double-layer space is divided into two layers, one layer occurred at the inner layer, called as Helmholtz layer or compact layer, due to the absorption of counter ions on the charged surface. Behind this other layer is seen, called as diffusive layer. In the diffusive layer, the counter ions were not specifically adsorbed alternatively it was adsorbed as a result of long-range electrostatic attraction between solvated ions and the charged electrode surface. Meanwhile, it doesn't depend on the chemical properties of ions (Gouy 1910; Chapman 1913) [11].

4.2. Pseudocapacitor:

Pseudocapacitors are also called as Faradaic supercapacitors. Since pseudocapacitor is based on fast and reversible redox reactions, known as Faradaic charge transfer reactions, on the surface of electrode that create charge and transfer of these charge takes place via double layers, it is similar to the battery charging and discharging action. This reaction leads to deficiency in cycle stability and low power density, but much higher energy density than EDLCs. Charge storage mechanism [12] in pseudocapacitor is shown in Figure 3B.

4.3. Hybrid supercapacitor:

The hybrid supercapacitor is the combination of EDLC and pseudocapacitor, has more enhanced characteristics than the combining components. One-half of the hybrid supercapacitor acts as EDLC while another half behaves as pseudocapacitor. Comparatively hybrid supercapacitors possess higher energy densities as well as power densities than the normal EDLC and pseudocapacitor [13].

5. Choice of materials for the components of supercapacitors:

5.1. Electrode materials:

Electrode materials play important roles in supercapacitors. They decide power density, energy density, cycling life, rate capability, and stability. In particular, the surface area of the electrodes that can be accessed by ions/charges is a critical factor deciding the performances of supercapacitors. Following materials are mostly choose for electrodes-

5.1.1. Carbon-based materials:

Carbon is well known for its high surface area and hence is a suitable material for supercapacitor. Additionally, it provides high conductivity, low cost, non-toxicity, wide operating range, functionality of the surface and electrochemical stability. However, tuning the morphology of the material and increasing the surface area and pore size distribution are important factors for the electrochemical studies. Carbon based material are used mainly in electrochemical double layer capacitors. Now-a-days the electrode materials are based on cheap precursor like biowaste material co-doped with heteroatoms controlling the pseudo capacitance and electric double layer capacitance [14].

5.1.2. Metal oxide electrode materials:

The metal oxide provides high energy density and stability for supercapacitors on comparing with carbon-based material. There are many numbers of metal oxide materials reported in literature for supercapacitor applications [15]. B.E Conway reported Ruthenium oxide (RuO_2) and other oxides electrode materials give high pseudocapacitance, but they are costly materials and performance is poor at high current densities. Theoretically the oxide base material has been reported for very high specific capacitance of 3650 F/g. These materials exhibit faradaic reactions. The properties of the oxide-based material should be electronically conductive, existence of various oxidation states and facile inter conversion resulting in high performance. Beside these properties, extensive research is being conducted with oxide materials extensively to give excellent performance [16].

5.1.3. Conducting polymer electrode material:

Conducting polymer is advantage in electrode material, due to low cost, high conductivity, high potential window, adjustable redox motion via chemical variation and good storage capability. There are various other polymers available for high its better performance [17]. On analyzing the CV pattern of polymer as an electrode material, it does not show rectangular shape provided with one peak. During the oxidation process, ions are transferred to the electrode material, and during reduction, the ions are back into electrolyte. These redox reactions are completely reversible. The ion insertion into polymer matrix is called doping. Because during oxidation process, they are called positively charged polymer and attributed to P doping, during reduction they are called as negatively charged polymer and attributed to n doping. The capacitance values of these electrode materials are higher than carbon-based material. Literature study shows polymers like polyaniline (PANI), poly lactic acid (PLA) and many other materials viz., biobased degradable polymer are used to reduce environmental issues and for high performance. The drawbacks of these conducting polymers are that they get degraded during stability test. Hence many research groups work on these types of materials to gain mechanical strength, availability, low cost and natural occurrence.

5.2. Current Collector materials:

Usually, collectors are made up of aluminum, because of its low cost. Al is cheaper than titanium and platinum.

5.3. Separator materials:

The separator material should be transparent but should be an insulator to avoid direct contact of the porous electrodes to prevent from short circuit. The utilization of activated carbons material upgrades the surface area and estimation of explicit capacitance and electrolyte with low internal resistance increments the power density

5.4. Electrolyte materials:

They are classified into three categories as-

- Aqueous electrolyte,
- Organic electrolyte and
- Ionic liquid.

Some examples of aqueous electrolytes are H_2SO_4 , KOH, NH_4Cl , Na_2SO_4 , and so on. They provide low resistance and higher ion conductivity. These types of electrolytes are reported for high capacitance

than organic electrolytes probably, due to higher concentration and small ionic radius [18]. Organic electrolyte is preferred for commercial applications due to wide range of potential window and it is a big advantage over aqueous electrolyte. The most commonly used organic electrolytes are acetonitrile and propylene carbonate (PC). These electrolytes are toxic and nontoxic. Some organic salts like tetraethyl ammonium tetrafluoroborate are also used. Ionic electrolyte is also called as molten salt. This electrolyte is promising candidate among other electrolytes due to lower vapors pressure and higher thermal stability. The potential window is relatively large. Example of ionic liquids used is imidazolium and so on. The challenges in the ionic liquid can be altered by the some added substances, but the alteration causes other related problems in the performance and results in environmental issues.

6. Applications of supercapacitors:

The significant advantage of supercapacitors is that they can be used in electric vehicles as electric storage device especially in hybrid vehicles which can be charged quickly and discharging power to a large extent is possible. Compared to battery in terms of energy density this cannot be excellent, but extensive research work is being carried out to improve its performance. Other additional devices are also used with supercapacitors for burst power [19].

6.1. Transportation:

The most promising market for super capacitor is in the transportation industry. They can be used in automobiles by coupling them with other energy sources, particularly batteries. They can also improve fuel efficiency by storing energy when an automobile is braking and then releasing the energy when it accelerates. Automobiles powered by coupling fuel cells with super capacitor are ideal choices for stop-and-go traffic.

6.2. Consumer electronics:

Supercapacitor are widely used in consumer electronics as back-up energy sources for system memories, microcomputers, system boards and clocks, toys, and mobile phones. They are ideal for devices requiring quick charges. Super capacitors are cost-effective options because they have extremely long lifetimes and do not need replacement during the lifetimes of the device.

6.3. Uninterrupted power supply (UPS) system:

Supercapacitor can be used for temporary back-up power in UPS system. They can provide instant of mission-critical applications. Supercapacitor quickly bridge the power application for stationary UPS system that are augmented with fuel cells. In addition, supercapacitor is best suited to provide power for start –up and during peak load buffering [20].

6.4. Other applications:

Supercapacitor also shows promise for critical load operations such as hospital, banking centers, airport control towers, and cell phone towers the critical time between a power outage and the start of a generator can be bridged effectively by supercapacitor because they provide power within milliseconds to a few seconds after an outage.

7. Conclusions

The brief introduction of supercapacitors has shown great potential in future for many industrial, transportation and electronic fields. The huge potential market will also infinite opportunities for the development of supercapacitors. However, there are still clarity of new energy vehicles and smart wearable devices. it is an important development of goals will be, long life time, increasing voltage and operating temperature and also increasing energy and power density. While proper choice of electrode and electrolyte materials, it will restrict the excellent performance and cost of supercapacitor will remain the focus of future research. It is hoped that this survey may further stimulate the development for future applications also.

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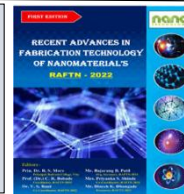
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Literature Survey of Nickel Doped ZnO Thin Films

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KEYWORDS

Doping
 Thin films
 ZnO thin films
 Literature Survey

ABSTRACT

Particularly, transition-metal-doped ZnO based DMSs have been extensively investigated since theoretical studies predicted their Curie temperature (T_c) to be above room temperature. Moreover, ZnO has broad band gap, and possesses a large excitation binding energy of 60 meV and UV lasing properties at room temperature. Combining the excellent optical properties with room-temperature ferromagnetism, many magnetic-optical devices could be made from ZnO-based DMSs. Ni doped ZnO semiconductors have not been conclusively determined because there are several reports which revealing absence of room temperature ferromagnetism, while some results have been achieved the room temperature ferromagnetism. Because of these fluctuating results of Ni doped ZnO thin films we are trying to study the behaviour of Ni doped ZnO thin films by chemical bath deposition method.

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1. Introduction

To obtain the detailed information of Ni doped ZnO thin films we have studied extensive literature survey based on Ni doped ZnO thin films by various methods. Ren L.L. et al. have reported the magnetic properties of diluted magnetic semiconductors (DMSs), Ni-doped ZnO materials, prepared by sol-gel method with the measurement of magnetization as functions of magnetic field. They observed that the temperature has great effects on the magnetic properties of Ni/ZnO at high original mole ratio of Ni/Zn while it has slight effects on the magnetic properties of Ni/ZnO at low original mole ratio of Ni/Zn whatever low or high sintered temperature [16].

S.H. Chiu and J.C.A. Huang investigated the structural, electric and magnetic characteristics of ZnO and Ni: ZnO nanorods fabricated via a chemical bath deposition. In their report the vertically aligned ZnO and Ni:ZnO nanorods arrays were grown on sapphire substrate along with the interesting observation for SEM results reveal a variation of aspect ratio between ZnO and Ni:ZnO nanorods. Furthermore, the ZnO nanorod/p-type Si hetero junction displayed rectifying current-voltage characteristic of a as formed p-n junction diode and light emission under forward bias [17]. R.K. Singhal et al have studied the effect of hydrogen and vacuum annealing on electronic and magnetic properties of 5% Ni-doped ZnO pellets using various characterizations. The SQUID measurements exhibit a paramagnetic state for the as-synthesized Zn_{0.95}Ni_{0.05}O. The post annealing in H₂ and in vacuum, drives it to a ferromagnetic state at 300 K. Resistance of annealed samples is three orders of magnitude lower than their as-synthesized counterparts. The XPS results confirm bivalency of Ni ions and creation of O vacancies upon annealing, owned to Ni (3d)-O (2p) hybridization. The ferromagnetism and the consequent electronic changes are retraceable on re-heating the annealed samples in air [18].

2. Literature survey of Ni doped ZnO thin films

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Xingu Mao et al have been prepared Ni-doped ZnO samples with ferromagnetism at room temperature by solid state reaction. They found that the ferromagnetism originates from the nanosized Ni clusters formed from the decomposition of NiO during calcinations. The magnetic properties can be explained by the microstructure of sparsely distributed, randomly oriented and magnetically saturated Ni clusters. Their experiments show that the addition of Cu ions will block the decomposition of NiO because Cu^{2+} is more likely reduced to Cu^+ . Hall effect confirms the absence of exchange coupling between local spins and charge carriers [19]. Xing Zhao et al were used XPS depth profiles to investigate the effects of rapid thermal annealing under varying conditions on the structural, magnetic and optical properties of Ni-doped ZnO thin films. Oxidization of metallic Ni from its metallic state to two-valence oxidation state occurred in the film annealed in air at 600 °C, while reduction of Ni^{2+} from its two-valence oxidation state to metallic state occurred in the film annealed in Ar at 600 and 800 °C. In addition, to that they observed significant diffusion of Ni from the bottom to the top surface of the film during annealing in Ar at 800 °C. Both as-deposited and annealed thin films displayed a room temperature ferromagnetism (RTFM) which was from metallic Ni, Ni^{2+} or both with two distinct mechanisms. The ultraviolet emission of the Ni-doped ZnO thin film was restored during annealing in Ar at 800 °C, which was also attributed to the diffusion of Ni [20].

B. Pandey et al report synthesis of a transparent magnetic semiconductor by incorporating Ni in zinc oxide (ZnO) matrix. ZnO and nickel-doped zinc oxide (ZnO: Ni) thin films (~ 60 nm) are prepared by fast atom beam (FAB) sputtering. They observed both undoped and doped films show the presence of ZnO phase only. Magnetization measurement using a SQUID magnetometer shows that the Ni-doped films are ferromagnetic, having coercivity (H_c) values 192, 310 and 100 Oe and saturation magnetization (M_s) values of 6.22, 5.32 and 4.73emu/g at 5,15 and 300K, respectively [21]. P. K. Sharma et al. synthesized the ZnO: Ni^{2+} nanoparticles of mean size 2–12 nm at room temperature by the simple co-precipitation method. The crystallite structure, morphology and size were determined by different characterization techniques. They observed that wurtzite structure of ZnO gradually degrades with the increasing Ni doping concentration and an additional NiO-associated diffraction peak was observed above 15% of Ni^{2+} doping. The change in magnetic behavior of the nanoparticles of ZnO with varying Ni^{2+} doping concentration was investigated using a vibrating sample magnetometer (VSM). Initially, these nanoparticle showed strong ferromagnetic behavior, however, at higher doping percentage of Ni^{2+} , the ferromagnetic behavior was suppressed and paramagnetic nature was observed. The enhanced antiferromagnetic interaction between neighboring Ni–Ni ions suppressed the ferromagnetism at higher doping concentrations of Ni^{2+} [22].

E. Liu et al were grown Ni doped ZnO thin films on quartz substrates via magnetron sputtering deposition process with the Ni concentrations of 5, 10 and 20 at.% in the films. They studied effects of Ni doping level and post annealing on the structural and magnetic properties of Ni doped ZnO thin films by different characterization techniques. They observed that higher magnetic moment was acquired from the annealed Ni doped ZnO thin film doped with 5 at. % Ni, which was attributed to a better preferred orientation from a primary phase Ni^{2+} : ZnO in the film. A relatively more pronounced ZnO (002) peak observed from the Ni doped ZnO thin film doped with 5 at.% Ni indicated a good crystallinity of the film, which was attributed to a lower level of Ni content in the film as well as the Ni^{2+} ions substituted for the Zn^{2+} ions to form Ni^{2+} :ZnO. Along with that a slight shift in ZnO(002) peak position for the 5 and 10 at.% Ni doped ZnO films could be due to the distortion of the ZnO lattice caused by the Ni^{2+} ion substituent's for the Zn^{2+} ions [23].

S. Abed et al studied zinc oxide doped Nickel thin films (ZnO: Ni) deposited on glass substrates using a chemical spray ultrasonic technique. They investigated the effect of Ni concentration on the structural, electrical, optical, and non-linear optical (NLO) properties of the ZnO: Ni thin films. They observed polycrystalline structure with a preferential growth along the ZnO (002) plane, the optical transmittance was found to be higher than 80% and the band gap (E_g) varied from 3.19 to 3.27 eV [24].

Yan Wang were successfully prepared Ni-doped ZnO nanoparticles (NPs) by bioassisted synthesis technique in the template of silk-fibroin (SF) peptide at room temperature. They observed that dopant Ni ions were incorporated into the wurtzite structure of ZnO crystal and photoluminescence results of Ni-doped ZnO particles indicated a strong emission band at 410 nm. The field dependence of magnetization measured at room temperature exhibited the good ferromagnetic properties [25].

H. Colder et al were prepared Ni doped ZnO dense ceramics from Ni doped ZnO nanoparticles. They investigate the thermoelectric properties of all samples from room temperature to 1000 K. All doped samples showed a n-type semiconducting conductivity. For Ni contents higher than $x = 0.03$, the increase of the secondary phase content induced a decrease in σ and $|S|$. They found highest power factor ($0.6 \text{ mW m}^{-1} \text{ K}^{-2}$) and ZT (0.09) for $\text{Zn}_{0.97}\text{Ni}_{0.03}\text{O}$ at 1000 K [26]. C. Xia et al. have grown Ni-doped ZnO rod arrays on zinc foils by a hydrothermal method. They observed that Ni^{2+} ions were incorporated into the ZnO lattices and Photoluminescence peak of the rod arrays shifts to a little longer wavelength and its intensity decreases with the increase in Ni content by characterization of the rod array with X-ray diffraction and X-ray photoelectron spectroscopy. Along with that green light emission as a result of oxygen vacancies was observed when excessive Ni ions were doped in ZnO. The rod arrays have exhibited room-temperature ferromagnetic behavior with the remanence of 0.454, 0.605 and 0.526 emu/cm^3 for the Ni concentration of 2.38, 4.35 and 5.54 at %, respectively. They proposed exchange interaction between local spin-polarized electrons and conductive electrons as a cause of the room-temperature ferromagnetism [27].

B. Pandey et al were reported the preparation of pure zinc oxide (ZnO) and nickel-doped zinc oxide thin films ($\sim 100 \text{ nm}$) by fast atom beam (FAB) sputtering technique and their characterization in the perspective of transparent conducting oxide (TCO). The different characterization techniques were done. The X-ray photo electron spectroscopy (XPS) results show that zinc and nickel are in 2^+ states. They explained High electrical conductivity of undoped film on the basis of presence of oxygen vacancies deduced from O1s spectra of the films and decrease of electrical conductivity due to nickel doping was explained on the basis of compensation of oxygen vacancies [28].

S. Yılmaz et al were successfully synthesized undoped and Ni-doped ZnO micro-rod arrays on glass substrates. They analyze the samples with X-ray diffraction and scanning electron microscopy which showed that these micro-rod arrays had a polycrystalline wurtzite structure with a highly c-axis preferred orientation. Photoluminescence studies at both 300 and 10° K show that the incorporation of nickel leads to a relative increase in the visible blue light band intensity. Magnetic measurements indicated that Ni-doped ZnO samples exhibit ferromagnetic behavior at room temperature, which is possibly related to the presence of point defects [29]. Dianwu Wu et al were successfully prepared Ni-doped ZnO rod arrays on glass substrate from the aqueous solution. They observed that densities, diameters, and lengths of the rods can easily be well controlled through the concentrations of dopants, and the dopant Ni ions were incorporated into the wurtzite structure of ZnO crystal. Room temperature photoluminescence spectrum of rod arrays show a strong emission band at 410 nm, and the oxygen deficiencies in ZnO structures were significantly reduced with Ni doped in ZnO rod arrays. Along with that they measured field dependence of magnetization at room temperature which exhibits the obvious ferromagnetic properties [30].

R. Elilarassi and G. Chandrasekaran were synthesized Ni-doped ZnO nanoparticles having 0 at %, 2 at %, 4 at %, 6 at %, 8 at % and 10 at % of Ni by means of low temperature sol-gel method. They studied effects of Ni doping on the structural and optical properties of ZnO: Ni particles in powder sample by using various characterization techniques. They observed formation of single phase; polycrystalline and hexagonal-wurtzite structure. Their SEM images show clusters of particles in nanosizes and some particles in the form of thin rods. The FTIR spectra confirm the formation of tetrahedral coordination of the oxygen ions surrounding the zinc ions and a shift in the frequency of bands brings out Ni doping in ZnO. The optical absorption spectra show a shift in the position of band edge towards lower energy. The estimated band gap is found to decrease with higher nickel doping. Also they observed that the nanoparticles of ZnO:

Ni exhibit room temperature ferromagnetic behaviour [31]. Chuanwei Cheng et al have been synthesized Diluted magnetic semiconductors $Zn_{1-x}Ni_xO$ nanorods with nominal Ni doping concentrations of $x=0$ at %, 1 at %, 5 at %, and 10 at % by a simple hydrothermal route. Their XRD and high-resolution TEM characterizations indicated that the as-prepared samples were single crystalline wurtzite structure and no metallic Ni or other secondary phases were found in the nanorods. The field dependence of magnetization (M–H curve) measured at room temperature exhibited the ferromagnetic characteristic. The saturation magnetization and coercive field (HC) were obtained to be 0.4emu/g and ~ 72 Oe for $ZnO_{0.95}Ni_{0.05}O$ nanorods [32].

Guangqing Pei et al have been successfully synthesized Polycrystalline $Zn_{1-x}Ni_xO$ diluted magnetic semiconductors by an auto-combustion method. Their X-ray diffraction measurements indicated that the 5 at% Ni-doped ZnO had the pure wurtzite structure. Refinements of cell parameters from powder diffraction data revealed that the cell parameters of $Zn_{0.95}Ni_{0.05}O$ were a little bit larger than ZnO. Transmission electron microscopy observation showed that the as-synthesized powders were of the size ~ 60 nm. Also they studied Magnetic investigations which showed that the nanocrystalline $Zn_{0.95}Ni_{0.05}O$ possessed room temperature ferromagnetism with the saturation magnetic moment of 0.1 emu/g (0.29 mB/Ni²⁺)[33].

R.N. Gayen et al were synthesized Ni-doped zinc oxide (Ni: ZnO) nanorods by incorporating nickel in vertically aligned ZnO nanorods. They observed that Ni was evaporated onto ZnO nanorods and the composite structure was subjected to rapid thermal annealing for dispersing Ni in ZnO nanorods. Their optical study shows that band gap decreased with increasing amount of Ni incorporation and origin of the photoluminescence peak at ~ 400 nm was related to the defect levels introduced due to substitution of Ni²⁺ in the Zn²⁺ site with annealing. The Raman spectra indicated the presence of the characteristic peak at ~ 436 cm⁻¹ which was identified as high frequency branch of E₂ mode of ZnO [34].

Xiaolu Yan et al have been deposited the transparent thin films of undoped, Mn-doped, and Ni-doped zinc oxide (ZnO) on glass substrates via sol–gel technique using zinc acetate dehydrate, nickel chloride, and manganese chloride as precursors. The structural properties and morphologies of the deposited undoped and doped ZnO thin films have been investigated by using various characterization techniques. The analyzed results indicate that the obtained films are of good crystal quality and have smooth surfaces, which have a pure hexagonal wurtzite ZnO structure without any Mn or Ni related phases. The band gap energy was estimated by Tauc's method and found to be 3.28, 3.26, and 3.34 eV for ZnO, Ni-doped ZnO, and Mn-doped ZnO thin films at room temperature, respectively. Room temperature photoluminescence is observed for the ZnO, Ni-doped ZnO, and Mn-doped ZnO thin films [35].

Snure, Kumar and Tiwari reported a detailed study aimed on understanding the origin of ferromagnetism in Ni doped ZnO thin films. They used pulsed laser deposition technique to deposit Ni doped (5 at %) ZnO films on saffire (0001) substrates under different oxygen pressure ranging from 10⁻⁶ to 0.1 Torr and observed that the magnetism in Ni doped ZnO thin films [36]. D A Schwartz et al studied the preparation of spin coated nickel doped zinc oxide nanocrystalline thin films using high quality colloidal diluted magnetic semiconductors. They observed that these films show robust ferromagnetism with Curie temperature above 350°K and 300°K saturation moments up to 0.1 Bohr magnetons per nickel [37].

Quantum dots of Ni-doped ZnO are proved to be good DMS materials with ferromagnetism up to 350°K [38-40]. Cong et al [41-42] have studied the nanoparticles of Ni-doped ZnO prepared by archeological phase reaction-precursor method and given experimental demonstration of magnetic phases in the film.

Although there are many experimental reports on ZnO based DMS exhibiting room temperature ferromagnetism, the origin of the ferromagnetism is still controversial [43]. Early studies explained that the magneto-optical effect in DMS was directly related to the interactions between the d electrons of transition metal ions and the s and p electrons of host semiconductors [44]. Room temperature

ferromagnetic magnetization behavior of TM doped ZnO has been studied in terms concentration of transition metal, post annealing condition and co-dopant used [45-49]. However, more recent studies proposed that defects like oxygen vacancies give rise to ferromagnetic ordering in oxide based DMS [50].

A considerable research effort has recently been focused on studying transition metal-doped one-dimensional (1D) ZnO nano/microstructures (such as wires, rods, and tubes) due to their potential use in producing nano/micro scale spintronics devices [51]. Among the transition metal ions, Ni is the most efficient doping elements to improve and tune the optical, electrical and magnetic properties of ZnO materials [52]. Ni is also very much unstable metal in the ZnO matrix, hence it has the tendency to form clusters of metallic Ni or NiO [53]. Nickel is a silvery-white metal with a slight golden tinge that takes a high polish. Its Curie temperature is 355 °C, meaning that bulk nickel is non-magnetic above this temperature. The unit cell of nickel is a face centered cube with the lattice parameter of 0.352 nm giving an atomic radius of 0.124 nm.

The ferromagnetism in Ni doped ZnO is not well established yet. It also appears that processing parameters which affect the magnetic properties of the samples are not well optimized, particularly for thin film samples. Also the variations of critical temperature (T_c) and magnetization with concentration of Ni in the thin film have not been established very well. The reason for the formation of ferromagnetism in wide band gap semiconductors is still unclear.

There are various methods to fabricate one-dimensional transition metal-doped ZnO materials. These techniques include chemical vapor deposition [54], hydrothermal method [55] thermal evaporation [56] and spray pyrolysis technique [57]. Among these, the chemical bath is especially suitable, since it has proved to be a simple and inexpensive method, particularly useful for large area applications.

3. Conclusion

The Ni doped ZnO thin films have been synthesized by various deposition methods. The variations in structural, optical and magnetical properties of ZnO thin films have been studied as a function doping concentration, period of deposition and annealing temperature. The investigation of these properties showed that properties are sensitive to impurity doping like Nickel.

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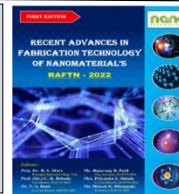
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**Recent Advances in Fabrication Technology of
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Electro-chromic materials: Potential candidate for supercapacitor Applications

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KEYWORDS

Electro-chromic materials
 Supercapacitor
 Metal oxides
 Polymers
 Viologens

ABSTRACT

Supercapacitors are electrochemical devices which having a features like higher energy density, higher power density, higher capacitance, longer life and higher stability. The electro-chromic materials are used in electrodes in supercapacitor. The electro-chromic materials such as metal oxides, conducting polymers, viologens and coordination complexes are used in supercapacitors. Nowadays researchers from physics, chemistry, material science and nanotechnology used these materials as potential candidates in Supercapacitor application. The electro-chromic materials are materials that changes colors on applying electrical potential, so it used in color chromatography.

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1. Introduction

The growing cost of fuels, pollution, worldwide warming and geopolitical concerns are among the problem connected with the dependence of modern societies on fossil fuels. Reducing those troubles is an important goal that can be achieved through developing other energy sources and storage technologies. As a result, recently, there has been a growing hobby in excessive power and high electricity density storage structures. a more widespread use of renewable sources and a better efficiency of transportation structures are two important goals to be pursued to overcome this problem. Energy storage structures (ESS) are vital things to deal with the intermittent nature of renewable power sources and increase the power transmitted into the grid from structures such as wind and solar power. In addition, an increase in the efficiency of a vehicle requires kinetic power to be stored somewhere every time the vehicle slows down or stops. Although these operations have been successfully performed with batteries on a low-power scale. New methods for efficiency enhancement will require large amount of power that can only be provided via other energy storage technologies such as supercapacitors. Those have attracted significant attention due to their excessive power capabilities and long cycle-lifestyles, giving a very good chance to build more advanced hybrid ESRs, for both on-board and stationary applications [1-3].

Supercapacitors are devices capable of managing high power rates compared to batteries. Although supercapacitors provide hundred to many thousand times better power inside the same volume, they are not able to store the same amount of charge as batteries do, which is usually 3–30 instances lower. This makes supercapacitors capable for those applications in which power bursts are wanted, but high electricity storage capacity is not required. Supercapacitors can also be included within a battery-based ESS to decouple the power and electricity characteristics of the ESS, accordingly improving the sizing at the same time as pleasant the power and strength necessities, and probably enlarging its lifetime. The power output of supercapacitors is higher than that of electrolytic capacitors [2]. Depending on the storage mechanism or cell configuration, electric double-layer capacitors (EDLC), Pseudocapacitors, and hybrid capacitors can be distinguished. EDLCs are based on excessive specific-surface area (41000 m²/g) nanoporous

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materials as active electrode materials, leading to a massive capacitance in comparison with electrostatic capacitors. The electrodes are usually made of nanoporous carbon materials thanks to their availability, existing industrial production and comparatively low cost [3].

Pseudocapacitors are based on conducting polymers or metal oxide-based electrodes, and sometimes a functionalized porous carbons, combining electrostatic and pseudocapacitive charge storage mechanisms. These materials can hold much better specific capacitance values as compared to EDLCs, with the charge storage mechanism relying on fast redox reactions occurring on the electrode surface however not inside the bulk like in batteries. However, like within the case of batteries, redox reactions can lead to mechanical changes making the electrodes swell and shrink, giving upward push to poor mechanical balance [4]. Consequently, lower cycle lifestyles is an important deficiency of pseudocapacitive materials. Finally, hybrid capacitors are composed of an EDLC electrode and a pseudocapacitive or battery type electrode, combining the properties of both systems and leading to an intermediate performance in some cases. A good example of such device is lithium-ion capacitors [5].

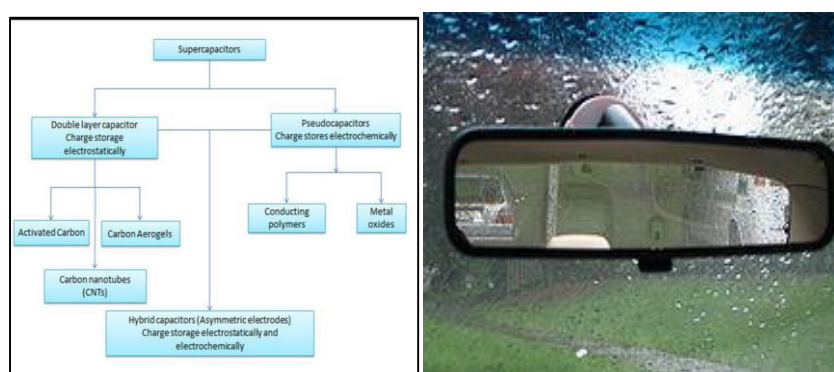


Fig. 1 (a) Type of supercapacitor, (b) Rare view mirror

Electrochromic materials are materials that change colour upon application of an electrical potential. Electrochromic material changes colour in a persistent but reversible manner by an electrochemical reaction, and the phenomenon is called electrochromism. Electrochromism is the reversible and visible change in transmittance or reflectance associated with an electrochemically induced oxidation-reduction reaction. When more than two redox states are electrochemically available, the electrochromic material may exhibit several colours and may be termed a polyelectrochromic or can be said to possess multicolour-electrochromism. Although materials are considered to be electrochromic when light is modulated by reflectance or absorbance in the visible region of electromagnetic spectrum-colour changes are perceptible to the human eye-recent interest in electrochromic devices. A minor electric current affects this optical change at a low DC potential of a fraction of a volt to a few volts [6].

Electrochromism is a process in which the colour or light of an object changes as a voltage is applied. By doing so, a bright electrochromic window can block infrared light quickly and as needed. The ability to control the apparent light exposure nearby can increase energy efficiency in a building, reducing the energy needed to cool in summer and heat in winter. As colour change persists and energy needs to be used only to make the change, electrochromic materials control the amount of light and temperature allowed to pass through the surface, usually bright windows [7]. One popular application is in the automotive industry, where it is used to automatically type rear-view mirrors in various lighting conditions. The separation of the electrochromic panel changes from transparent to light. The voltage is applied to all running electrodes, and the ion flows from the ion storage layer, through the electrolyte, to the electrochromic layer. The state of electrochromism occurs in other mutations of iron oxides that drive both electricity and ions, such as tungsten trioxide (WO_3) [8].

2. Electrochromic Materials for Supercapacitors:

Supercapacitors and batteries are often associated with faradic reactions on the electrode surface and mass, respectively. When an excessive reaction occurs with a transfer, some electrode material will change color and return. This phenomenon is known as electrochromism. If you assume that an electrochromic process occurs when a charge is inserted or discharged, electrochromic devices may be integrated with storage charge devices. Here we emphasize the combination of energy conservation and electrochromism, achieving both advantages in these two different effects, as the electrochromic device and the thin film supercapacitor or battery, the operating life of the electrochromic device is related to the capacitor time.

3. Types of Electrochromic Materials:

They are chromophores and affect a surface's optical colour or opacity when applied to voltage. Tungsten oxides (WO_3) are the most extensively studied and well-known electrochromic material among metal oxides. Other include molybdenum, titanium and niobium oxides, which are less effective optically. For organic materials, viologens have been commercialized on a small scale. Various conducting polymers are also of interest, including polypyrrole, PEDOT and polyaniline. Viologen is used in conjunction with titanium dioxide to create small digital displays.

3.1. Metal Oxides

Tungsten oxide is the most widely read metal oxide of the EC application. It is a semiconductor of the indirect band gap and exhibits the divisive and intercalation properties of H^+ , Li^+ , Na^+ , and K^+ under discrimination that may elicit an EC response. The renewable EC structure of WO_3 is due to the formation of tungsten bronze (M_xWO_3) according to the following equation: M corresponds to H, Li, etc. Also, cathodic separation resulted in the insertion of metal ions and electron injections, leading to a blue colour with a low x value due to CT inter valence between nearby W^{5+} and W^{6+} sites [9]. The ion insertion increases the lattice of WO_3 , and the embedded electrons reduce the tungsten centre in a low oxidation state, thereby modulating the visible structures.

3.2. Metal complexes

Metal complexes are another class of EC materials that use metal ions and ligands. Metal (II, III) hexacyanoferrate (II, III), more commonly known as PB, is a complex compound and blue colour that has long been used as an EC material [11-12]. PB can be electrically reduced to Everett salt colour or colourless Prussian white (PW) [13], metal (II) hexacyanoferrate (II) [14], or can be mixed entirely with Prussian yellow (PY), metal (III) hexacyanoferrate (III), or composed of oxidized only in Berlin green, which is a combination of (1: 2) for PB and PY [15].

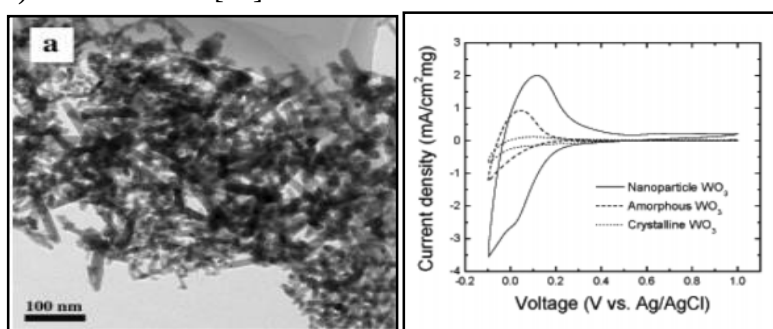


Fig. 2 (a) TEM image of HWCVD-generated WO_3 nanoparticle, (b) CVs of the WO_3 films deposited by electrophoresis [10, 11]

3.3. Organic molecules and conducting polymers

Specific organic molecules and CPs are organic EC materials. Viologen is an organic EC material and has attracted significant research interest due to low operational driving voltage for visual colour changes, high contrast, switchable EC property, and easy cell construction. Bipyridiliums (viologens) are organic EC molecules that remain transparent in the stable dicationic state following one-electron reduction change

into highly coloured in the radical cation state. Many polyviologens and N-substituted viologens, such as heptyl viologen, have been used as thin films for EC applications [16].

3.4. Conducting Polymers

Disturbed metal oxides with barriers show difficulties such as slow change times and colour efficiency; hence they face stiff competition from polymer materials that have long been the focus and low cost, fast preparation process and excellent electrochemical properties [17]. Polyaniline (PANI) films are usually prepared from robust aniline solutions to acids and have been extensively tested using electrochromism and supercapacitors. Several redox methods have been suggested, including protonation/deprotonation or anion ingress/egress. PANI films show the following colour changes as the probability varies: clear leucoemeraldine to emerald yellow-green to dark black pernigraniline, with power ranging from 0.2 to 1.0 V vs SCE [18].

3.5. Coordination complexes

Coordination complexes, called metal–organic frameworks (MOFs), are used as carbon and template sources. They have designable framework structures modularly built from transition-metal clusters as nodes and organic ligands as struts. Intriguing examples of MOFs include Al-based porous coordination polymers (Al-PCPs) MOF-5, ZIF-8, and IRMOF-1/3/8. On the other hand, MgO, Ni(OH)₂, inorganic salts of Zn(NO₃)₂·6H₂O and Mg(NO₃)₂·4H₂O can also serve as hard and soft templates. Noteworthy that coordination complexes can repeat coordination entities extending in different dimensions, explicitly forming porous frameworks, which thereby prefer to result in nonporous carbons featuring ordered porous structures or narrow pore size distributions [19].

4. Conclusions

The features like high energy density, high power density, high specific capacitance, longer life and high stability of the electro-chromic materials like such as metal oxides, conducting polymers, viologens and coordination complexes makes the potential candidates for supercapacitor applications. Nowadays researchers from physics, chemistry, material science and nanotechnology also used these materials in various applications like Li-ion batteries, Hydrogen evolution reaction and Oxygen evolution reaction.

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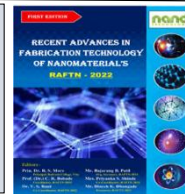
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A Review: Activated carbon from biowaste materials a good candidate for supercapacitor application

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KEYWORDS

Biowaste materials,
 Activated carbons,
 Supercapacitor.

ABSTRACT

Bio-derived activated carbon is readily used because it exhibits high surface area, excellent electrical conductivity, high stability, environment-friendly nature, and easy availability. All of these properties make it a unique and a perfect applicant for energy storage devices. Biowastes such as corncobs, coconut shells, peanut shells, oil seeds and bamboo are utilized as precursors in manufacturing porous carbon. The use of bio materials is preferred because of their abundance and biodegradable nature. The production of porous carbon was carried out through various synthesis techniques with the help of acid, primarily KOH, as the active substance. The ambient temperature for conducting materials is 400 °C–800 °C approximately. Food wastes like peels and shells are among the most significant biowaste sources alongside farm waste like rice husks, coconut shells, etc. This paper aims to extensively review all of the research conducted for Bio-waste utilization and its conversion to carbon for further use in super capacitance applications.

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1. Introduction

In comparison with fuel cells and batteries, supercapacitors generally possess relatively higher power densities, more reliable safety, and better stability, while the energy density is in a limited range (5–10 Wh.kg⁻¹) [1,2]. Thus, the development of high-performance electrode materials is the basic requirement for the development of supercapacitors at present and in the future. Carbonaceous materials with porous structure have been regarded as promising electrode materials for supercapacitors and been intensively investigated because of their outstanding characteristics such as tenable morphology, stability, electrical conductivity, and functionality [3,4]. It is very important to develop and utilize renewable resources for the production of porous carbon materials for supercapacitor applications. Biomass, particularly agricultural and forestry biomass materials, is a promising carbon precursor for preparing porous carbons with renewable nature, natural abundance, and environmental friendliness [5–7]. Supercapacitors are generally classified into two types based on their storage mechanism: the electrochemical double layer capacitors (EDLCs) and pseudo capacitors. EDLCs store charges via reversible ion adsorption at the electrode–electrolyte interface, while pseudo capacitors store charges via redox reaction [9]. The performance of biomass activated carbons as the electrode materials for supercapacitors depends mainly on their specific surface area, pore size distribution, and functional groups. Therefore, in order to obtain highly available biomass-derived carbons in supercapacitor applications, it is necessary to develop porous carbons with rich functional groups and more reasonable pore structures.

ELDCs are the devices that can charge rapidly and release energy as and when needed. They have a much longer life than batteries. Their main components are a pair of electrodes with a large surface area. Electrodes made with carbon nanospheres make for a perfect material for supercapacitor electrodes due to

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their large surface area [8]. Lots of biomass-based active electrode materials have been prepared through hydrothermal carbonization, chemical or physical activation. For example, Jiang et al. provided a summary of recent progress on the well-design of biomass-derived carbon materials, focusing on morphologies, surface chemistry and synthesis method for their applications in supercapacitors, lithium- and sodium-ion batteries [10]. They can thus store more charge and provide energy for a long duration. By developing electrodes from biowaste materials, these “cells” can be sustainable. Thus, supercapacitors made of biowaste materials would be a perfect solution for both disposal of bio-waste and energy storage.

2. Carbon from Bio-Wastes as an Excellent Material for EDLC

During the past decade, researchers have shown an increased interest in the use of porous carbon materials as electrodes in high-capacity supercapacitors [29]. Several carbon-based materials have been investigated for use as electrodes in supercapacitors because of their outstanding electrical conductivity and high specific surface area. The most investigated carbon-based materials widely reported include activated carbons [30–32], carbon aerogels [33–35], graphene [36–40], and nano-sized carbons [41–43]. These materials are popular because of the ease of accessibility processability, non-toxicity, high chemical stability, and wide temperature range. Activated carbon has received considerable critical attention because of its high porosity and surface area [44].

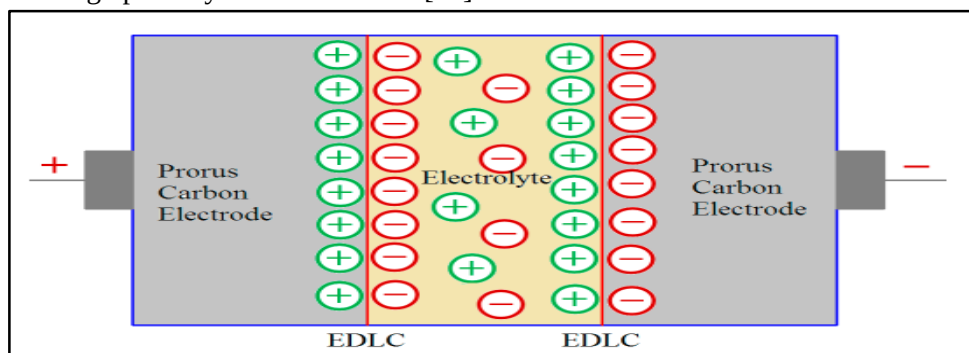


Fig1. Schematic illustrating a basic EDLC supercapacitor

This review focuses on providing a summary of the latest advances in electrode materials derived from biowaste for supercapacitors. Furthermore, we briefly discuss and compare the electrochemical performance (charge storage capacity, energy/power densities, and cyclic stability) of supercapacitors.

2.1 Table BET specific surface areas for different biowaste

Bio wastes	Activation method	BET (m ² /g)	Ref.
Almond shell	Physical, steam, 850 °C/30 min	601	[45]
Apricot stone	Chemical, ZnCl ₂	814	[46]
Bagasse	Chemical, ZnCl ₂	923	[47]
Bamboo	Chemical, KOH	1533	[48]
Coconut shell	Physical, steam, 1000 °C/120 min	1926	[54]
Palm kernel shell	Chemical, KOH	217	[49]
Peanut hull	Physical, steam, 600 °C/2 h	253	[50]
Pistacio-nut shell	Physical, CO ₂ , 900 °C/30 min	778	[51]
Rice husk	Chemical, ZnCl ₂	927	[47]
Sugarcane bagasse	Physical, steam, 900 °C/2 h	320	[52]
Tea	Chemical, KOH	2532	[53]
Hazelnut bagasse	Chemical, KOH	1642	[55]

2.2. Precursors in biomass-derived materials

In recent years, biomass-based materials or by-products have been utilized as a sustainable precursor to prepare carbon nanomaterials for energy storage catkins [11], rice [12], orange peel [13], sugar cane bagasse [14], rice stem [15], coconut shell [16], sunflower stalk [17], tamarind seed coat [18],

almonds [19], etc. Biomass can be used as a precursor of functional carbon attributing to two main aspects. From element perspective, the synthesized functional materials mainly composed of carbon element, and biomass is a carbon-rich material. Besides, other element such as H, O, N and S can be removal by thermal conversion to some extent [20]. The synthesis of activated electrode materials usually composes of carbonization and activation which can be completed in either two-phase or a single phase. The carbonization of a kind of biomass usually happens at temperature between 400°C and 900° C using nitrogen as protective gas. Activation is a process of transforming biochar into functional materials by pyrolysis at relative high temperature in a tube furnace or a microwave. Physical and chemical activation are the most common used to adjust pore structure and graphitization degree. Physical activation is consisted of two stages which carbonization at low temperature in a protective gas and activation at high temperature with using CO₂ or steam as activating agents. During a special activation phase, the biomass reacts with gas at high temperature to form porous texture. Porous texture with hierarchical micro/meso/macro-pores can reduce the diffusion distance for electrolyte ions and decrease the electrical resistance of active biochar materials. Yoshizawa et al. prepared porous active carbon by physical activation means using coconut-shell [21].

2.3. Chemical Activation methods for bio-waste materials

For chemical activation, it usually includes three stages: Firstly, the natural precursor is pyrolyzed at low temperature, then immersed in a chemical activating agents' solution such as NaOH, KOH, ZnCl₂, H₃PO₄, heated in a protective atmosphere (e.g., N₂) at temperature that commonly ranging from 500 to 800° C [22]. As a result, lots of channels and pores are formed in the carbon skeleton, which enable electrolyte ions transfer quickly and store efficiently [23]. Among chemical activating agents, KOH is the most generally applied in chemical activation. Wang et al. prepared celtuce leaves-based active carbon by KOH activated method [24].

3. Result Analysis

3.1. Biowaste carbon cyclic voltammetry double layer energy storage mechanism.

They used a one-step thermal treatment combined with pyrolysis and steam activation to produce porous carbon. The ratio of mesopore to total pore volume ($V_{\text{meso}}/V_{\text{total}}$) was reported to be greater than 75%. Using a three-electrode setup, the cyclic voltammetry (Figure 1a) shows a quasi-rectangular shape, which is perfect for the double layer energy storage mechanism. The specific capacitance values ranged from 209–228 F/g at 5 mV/s depending on the activation, water flow rate, and activation time. Galvanostatic charge/discharge cycling plots (Figure 1b) show negligible voltage drops, indicating that these carbons exhibit good electric conductivity [29].

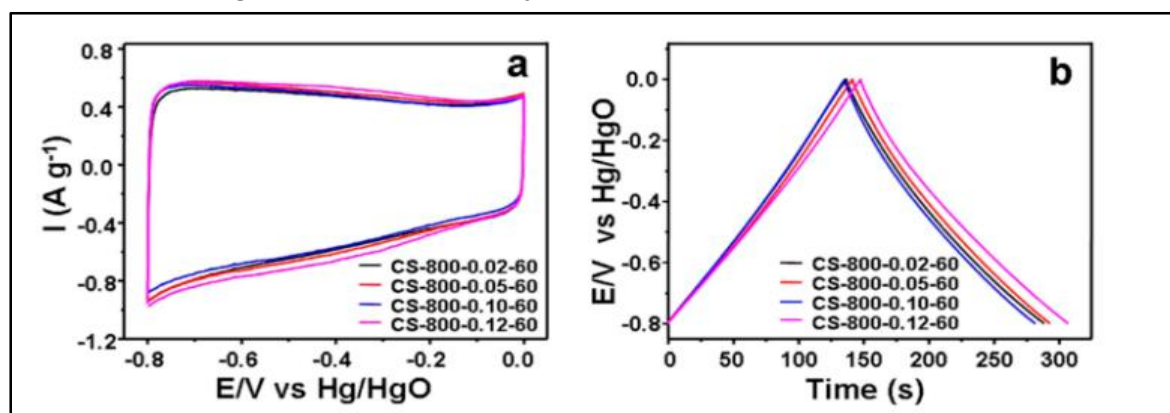
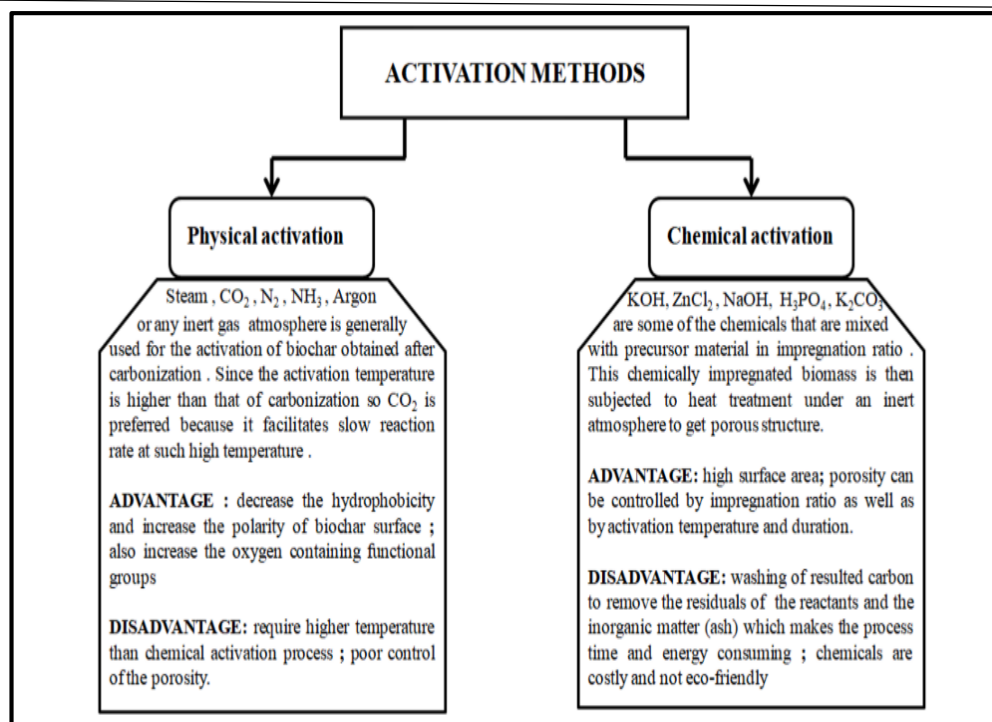


Fig. 1: Cyclic voltammetry double layer energy storage mechanism

The CV (a) and GCD (b) curves of the carbon materials of CS-800-0.02-60, CS-800-0.05-60, CS-800-0.10-60, and CS-800-0.12-60 tested with a three-electrode setup in 6 mol/L KOH. at 5 mV/s and 0.5 A/g. (Reprinted (adapted) with permission from [56].



3.2. Hydrothermal pre-treatment on sugarcane & its FESEM images

Malik Wahid et al. [57] employed hydrothermal pre-treatment on sugarcane bagasse to prepare a three-dimensional (3D) interconnected, conducting, and high surface area carbon nanochannel. The hydrothermal pre-processing is depicted in Figure 2. Samples were prepared with different synthesis protocols (pyrolyzed temperature and atmosphere). Figure 3 shows FESEM images of different carbon forms synthesized from different synthesis protocols with the same basic sugarcane bagasse precursor at 800 °C pyrolysis.

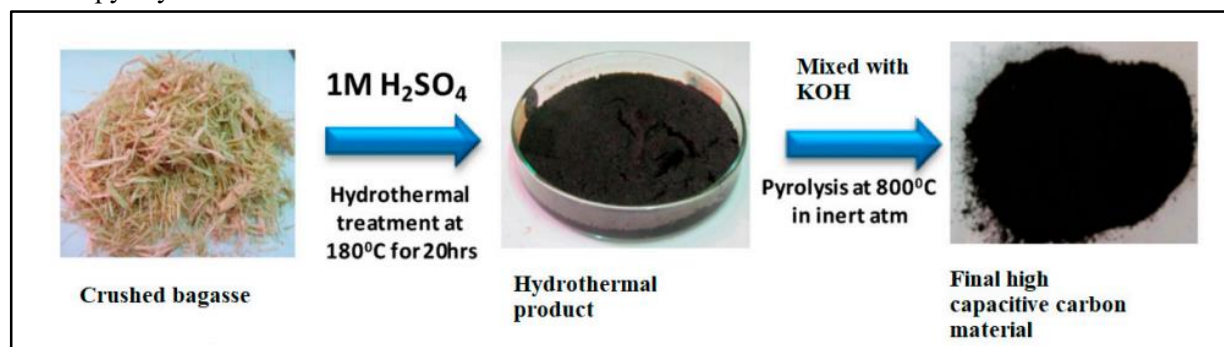


Fig. 2 Synthesis of high-capacitive carbon material by hydrothermal pre-processing followed by inert atmosphere KOH activation pyrolysis. (Reprinted (adapted) with permission from [57])

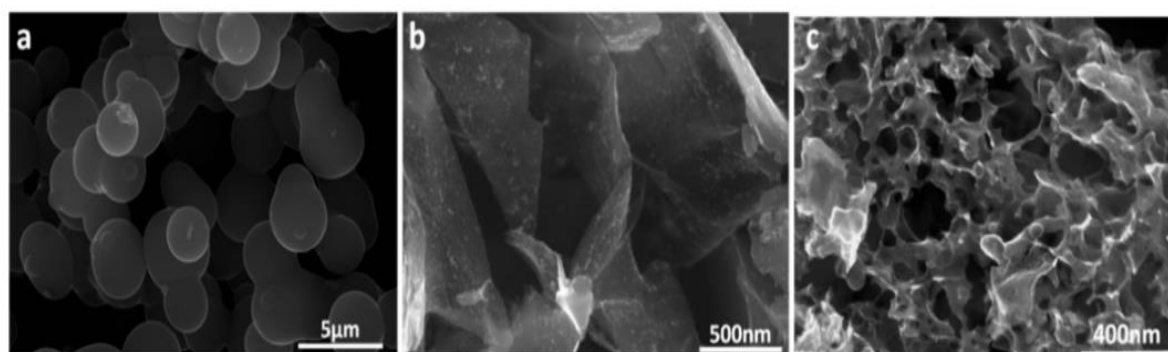


Fig.3: FESEM images of different carbon forms synthesized from different synthesis protocols with the same basic sugarcane bagasse precursor at 800 °C pyrolysis: (a) BHC (sample prepared by initial hydrolysis step followed by direct pyrolysis), (b) BAC (samples prepared by simple activation), and (c) BHAC (hydro-thermally treated and activated sample) (Reprinted (adapted) with permission from [57].

3.3. Biowaste-derived AC/MnO₂-based composite for supercapacitor electrodes

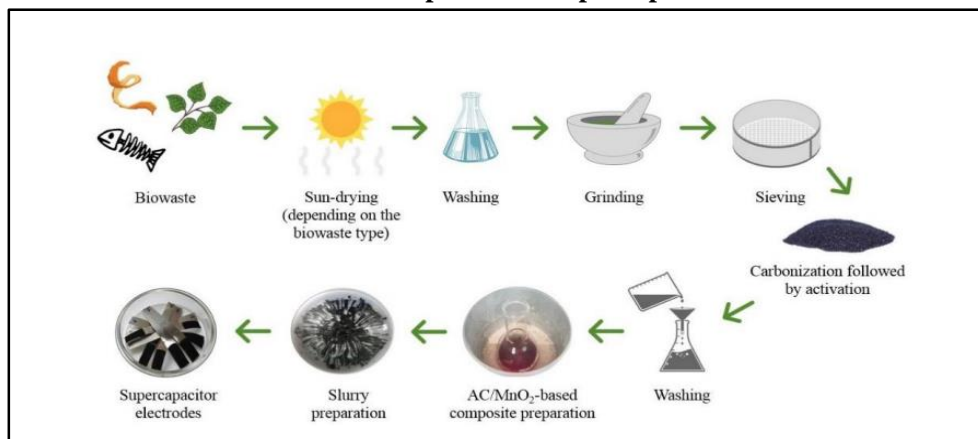
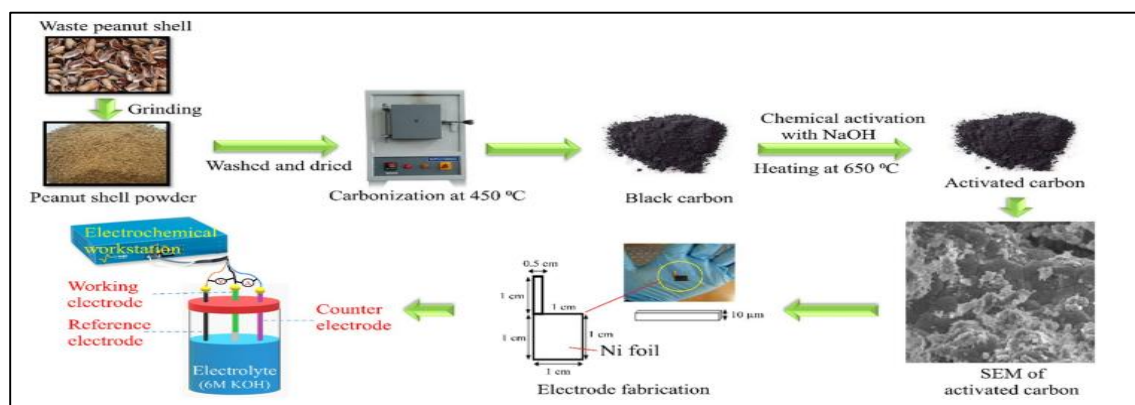


Fig.4: Scheme of preparation of biowaste-derived AC/MnO₂-based composite for supercapacitor electrodes [66]

Figure 4 shows the preparation scheme of biowaste-derived AC/MnO₂-based composite for supercapacitor electrodes. The biowaste is dried (depending on the type), washed with water or other solutions to remove dirt, and dried to remove moisture. Then, the waste is ground, sieved, and carbonized. The carbon is physically or chemically activated, neutralized, and dried; depending on the method or material, the raw materials may be activated in one step. Depending on the method, a composite is created, washed, and the moisture is removed. To create an electrode, slurry is prepared, and depending on the method of application, supercapacitor electrodes are made [66]



3.4. Fabrication of activated carbon electrodes derived from peanut shell for high-performance supercapacitors

Derived activated carbon from peanut shell waste material via a chemical activation method using NaOH as an activating agent at 1:2 and 1:3 impregnation ratios. The BET and SEM analyses suggest that there is an enhancement of surface area from 584 to 826 m²/g with an increase of impregnation ratio. This study shows that the impregnation ratio has a huge impact on the surface area of activated carbon through the chemical activation process. Furthermore, electrochemical measurements indicate an increase of specific capacitance with an excellent efficiency of 98% up to 1000 cycles. The obtained specific

capacitance of 263 F/g at 10 mV/s and 290 F/g at 0.2 A/g for 1:3 NaOH-activated sample is significant. Results indicate that the activated carbon derived from peanut shell waste material could mitigate the energy demand as an electrode material for supercapacitors [72].

3.5. Plant-based biomass

However, the chemical compositions content is different from various plants organs. For example, seed teguments of arecaceae (coconut, areca-nut, etc.) contain percent of carbohydrate polymers as high as 65% [25]. A novel method recently has been widely applied that dissolving cellulose in alkaline solutions. It mainly consists of 3 essential alcohol types: p-coumaroyl, coniferyl, and sinapyl [26]. Part of heteroatom doping in the electrode material can enhance its wettability and pseudo capacitance. Lin et al. prepared lignin-based hierarchical porous carbon (LHPC) by a simple chemical activation method [27]. First, lignin was mixed with KOH solution and solidified. Then the mixture composites were calcined. The obtained LHPC consisted of a 3D network decorating with the hierarchical mesopores and micropores on carbon walls. Furthermore, LHPC had a good capacitance performance (165 F g at 0.05 A g⁻¹) outstanding cycling stability (97% over 5000s) when investigated as supercapacitor electrode. Hemicellulose is a major constituent in the cell wall of plant-based biomass. It is polysaccharide and mainly composed of glucose, arabinose, and galactose and relative lower degree of polymerization compared with that of cellulose [28]. So obtained hemicellulose-derived carbon samples exhibited excellent electrochemical performance, which is attributed to abundant micropores and oxygen functionalities.

4. Conclusion

The demand for renewable energy sources worldwide has gained tremendous research attention over the past decades. The development and optimization of novel materials towards energy storage is essential to the push to provide clean energy through renewable sources. Materials derived from waste and for that matter biowaste have continuously gained penetration into the field of supercapacitor technology. In this review, we gathered different activated carbons derived from biowaste for electrochemical energy storage systems, discussing the various performance parameters and storage mechanisms of the various types of supercapacitors. The Peanut shell carbon electrode shows a specific capacitance as high as 378 F·g⁻¹ and good cycle stability. These results suggest that microporous carbon electrodes made from peanut shells have a potentially broad application as electrochemical capacitor electrode material. High value-added porous carbon materials derived from biowaste corncob residue were prepared by green and low-cost steam activation without pre-carbonization. As corncob residue is a cheap, abundant, widely available and sustainable biological resource, the resultant porous carbons can be industrially produced at a high efficiency/cost ratio. Biomass offers opportunities for making flexible electrodes. This will open up a new research area. With continual research on this research topic, there could be great opportunities to achieve practical applications of biochar materials in the fields of renewable energy conversion and storage.

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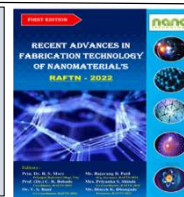
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Synthesis methods for metal-organic framework (MOF)

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KEYWORDS

Metal-organic frameworks, Synthesis methods

ABSTRACT

Metal-organic frameworks (MOFs) are porous crystalline materials constructed of metal centers and organic linkers, creating 1D, 2D, or 3D well-organized frameworks with high surface areas. The study of MOFs has become one of the main topics for research in many fields, due to the broad potential applications projected for these materials in various areas. It is well known that synthesis methods dictate the structure and properties and performance of the resulting MOFs. This chapter provides a completely up-to-date overview of the synthesis methods for MOFs. Using different synthesis methods, the size and crystal morphology can be manipulated.

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1. Introduction

Porous materials are solid compounds with an ordered and/or disordered pore structure, volume, and large surface area. These combined with some of their distinctive chemistries make them a special class of chemical and engineering materials. Over the past few decades, porous materials have become one of the leading research fields in chemistry, physics, materials science, and engineering. The diversity in the pore orientation and dimensionality, combined with the variety in pore shapes and sizes, makes the porous materials highly interesting and vastly studied. The IUPAC defines porous materials according to the pore dimensions and classifies them as materials with dimensions less than 2 nm pore as microporous materials, materials ranging from 2 to 50 nm as mesoporous materials, and materials with pores larger than 50 nm as microporous materials [1]. Porous materials have shown great applications in some industries, such as oil and gas processing, industrial catalysis, adsorption/separation, and fine chemical industries [2]. They are also being recognized and explored in the research fields of water treatment, sustained release of drugs, and fuel cells, in the recent decade [3].

Among all porous materials, zeolites are the most famous microporous materials. Chemically, the acidity of zeolites is adjustable, in addition to their high-quality pore channel selectivity and hydrothermal stability. These help the research value of zeolites in industrial applications like petroleum processing. However, the inorganic nature of zeolites limits their adjustability in chemical properties and designability in pore structures and sizes, which restricts the further development and applications of zeolites [2]. For decades, there have been research efforts trying to combine various metal centers and functional organic molecules into porous structures for the regulation of physical and chemical properties. This effort has resulted in the development of hybrid porous crystalline materials formed by the coordination of inorganic metal centers and organic linkers in the 1990s. This new type of porous material is commonly called the metal-organic framework (MOF) [4]. Ever since their discovery, MOFs have received significant attention from scientists, engineers, and technologists because of their versatility in structures and chemistries. Since the synthesis of MOFs directly influences the crystallization of the MOF structure and therefore dictates its properties and functional performance, extensive work and thousands of research papers are published

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on the development of synthesis methods. The goal of this chapter is to provide an up-to-date overview of the synthesis methods of MOFs reported so far and to provide empirical guidance for developing a synthesis strategy for MOF materials aiming for specific properties. We show how the size and crystal morphology can be controlled by different synthesis methods, the effect of metal doping on MOF crystals during synthesis and the mechanisms of crystallization.

2. Synthesis methods of MOFs

The synthesis of MOFs is determined by many factors like reaction time and temperature, the solvent used, the nature of the metal ions and the organic ligands, the presence of counterions, the size of the nodes, their structural characteristics, and the kinetics of the crystallization, which should lead to crystal growth and nucleation. Mostly, the synthesis of the MOFs is done in the liquid phase by mixing solutions of the metal salt and the ligand. Its reactivity, solubility, and redox potential dictate the choice of solvent. The solvent plays an important role in determining the activation energy and thermodynamics of each reaction. In a few cases, difficulties in single-crystal growth have been encountered, nonetheless, solid-state synthetic methods have been used. To grow crystals of MOFs, slow evaporation of the reaction solution has been used often. Mostly, MOFs are synthesized under solvo (hydro) thermal conditions at a high temperature and pressure. This is the ‘classic’ method for synthesising MOFs. Other alternative synthetic methods, such as mechanochemical, electrochemical, microwave, and sonochemical methods, have been developed in recent years. These methods are low-cost, faster, and yield cleaner products [5].

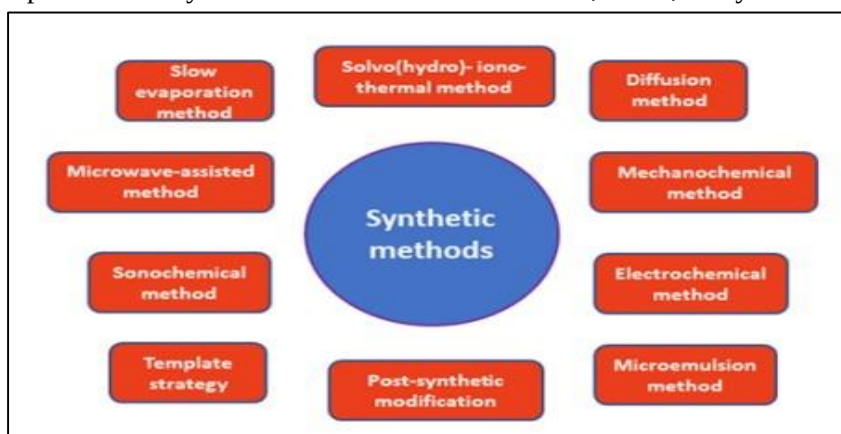


Fig. 1 Synthetic methods used to obtain MOFs

2.1. Slow Evaporation and Diffusion Methods

Both methods can be performed at room temperature. In the slow evaporation method, solutions of the reagents are mixed and evaporated slowly, and when a critical concentration is achieved for nucleation and crystal growth, the crystals are formed. To accelerate the process, mixtures of low boiling point solvents are used [6].

In the diffusion method, the reagent solutions are placed one on top of the other, separated by a layer of solvent. Gels are also used as crystallization and diffusion media in some cases. Crystals are formed in the intersection between the layers, after the moderate diffusion of the precipitate solvent into the separate layer. The diffusion method is used especially when the products are not very soluble [7].

2.2. Solvo (Hydro)-Thermal and Iono-Thermal Method

Solvo(hydro)thermal reactions are carried out in closed vessels under autogenous pressure above the boiling point of the solvent. Most of the MOFs reported so far, have been synthesized using solvo(hydro)thermal conditions [8]. The reactions are usually carried out in polar solvents using closed vessels (autoclaves) at temperatures in the range of 50–260 °C, and require long periods (hours and sometimes days). For reactions at high temperatures above 400 °C, Teflon-lined autoclaves are used. To facilitate the bond formation and to ensure proper crystallization, the temperature of the reactions is

increased, especially if kinetically inert ions are used. The morphology of the crystals is also affected by the temperature, whereas longer reaction times may cause the decomposition of the final product [9]. The cooling speed rate affects crystal growth, and it should be very slow. Mostly high boiling point solvents are used. The most common solvents are diethyl formamide (DEF) and dimethyl formamide (DMF). In solvo (hydro)thermal conditions, the initial reagents may undergo some chemical transformations, which cannot occur under milder synthetic conditions, which leads to new ligands formation. Ionothermal synthesis uses ionic liquids as solvents and can be considered a type of solvo(hydro)thermal method. Unlike the conventional organic solvents, the ionic liquids are environment-friendly reagents, because of their high solubility for organic molecules, high thermal stability, low vapour pressure, and nonflammability, which makes them excellent reagents for the synthesis of MOFs and other materials (i.e., zeolites and chalcogenides). Ionic liquids provide both anions and cations as counterions and as templates for the frameworks of MOFs and have been vastly explored in recent years as alternative methods for the synthesis of MOFs [10].

2.3. Microwave-Assisted Method

The Microwave-Assisted method is often used to synthesise organic and nanoporous inorganic materials. Lately, the method was used for the synthesis of metal clusters and MOFs [11]. The method is advantageous because the reaction time required is short, and the cost is also low. The microwave-assisted synthesis method produces crystals with improved physical properties, requiring a much shorter reaction time than conventional hydrothermal synthesis. The microwaves facilitate the motion of molecules by adjusting the concentration and the temperature of the reaction appropriately, leading to nucleation and formation of crystals with a controlled shape and size [12].

2.4. Mechanochemical Method

The mechanochemical method uses mechanical forces like automatic ball mills or manual grinding of the reagents, to form coordination bonds, instead of a solvent. In some cases, a small amount of solvent may be added to the solid reaction mixture and succeeded to obtain one-dimensional, two-dimensional, and three-dimensional coordination polymers. This method motivates the mass transfer, reduces particle size, heats, and locally melts the reagents; therefore, the reaction takes less time. It is an environment-friendly method, which produces high-purity and high-efficiency materials in short reaction times [13]. The mechanochemical method is an alternative to the high temperature and pressure solvo(hydro)thermal synthesis. The disadvantage of this method is it isolates amorphous products, which makes it unsuitable for single-crystal X-ray structural studies.

2.5. Electrochemical Method

The Electrochemical method is used on an industrial scale for the synthesis of MOF powders. The anodic dissolution provides metal ions into reaction mixtures which contain electrolytes and organic ligands. The advantages of this method are the less temperatures required for the reaction and faster synthesis under milder conditions, unlike the solvothermal method. Many MOFs have been synthesized using this method in an electrochemical cell, and the influence of reaction parameters on their yield and texture properties has been studied [14].

2.6. Sonochemical Method

In the sonochemical method, the molecules are chemically transformed under high-energy ultrasonic radiation (20 kHz–10 MHz). The bubbles formed when a reaction solution is irradiated with ultrasound radiation create local hot spots of a short life with a high temperature and pressure, which promote chemical reactions and the immediate formation of crystallization nuclei. High-quality crystals of MOF-5 and MOF-177 with a size of 5–25 μm and 5–20 μm , respectively, were prepared using the sonochemical method in the presence of 1-methyl-2-pyrrolidone as a solvent, in a substantially reduced reaction time [15].

2.7. Microemulsion Method

The method is widely used in the preparation of nanoparticles and has recently been used to synthesize MOFs [16]. Water microemulsions have water droplets of nanometer size, immobilized on the organic phase by a surfactant. The micelles of the microemulsions control the crystal growth and kinetics of nucleation. The size and number of micelles in the microemulsion can be adjusted by varying the water-to-surfactant ratio and the type of surfactant. The advantage of this method is the dimensions of the nanoscale materials can be controlled, and the disadvantage is the surfactants used are environmental pollutants.

3. Post-Synthetic Modification

The Post-Synthetic modification method requires the introduction of desired functional groups into the MOFs after the synthesis (PSM, Post Synthetic Modification). It is a process of chemical transformation of the MOFs after their isolation. This method is used to prepare isostructural MOFs with different physical and chemical properties [17]. The post-synthetic modification involves the replacement of the primary structural units of the MOFs (BBR, Building Block Replacement), like solvent-assisted ligand exchange (SALE, Solvent-assisted Linker Exchange), replacement of the metal nodes, and non-bridging ligands. An exchange of the organic ligands may occur in the SALE process, enhancing the performance of the MOF. In the BBR reactions, the heterogeneous exchange of ligands or metal ions by breaking and forming chemical bonds within the original MOF takes place. Such methods are used when the desired MOF is not achieved by direct synthesis, putting into use the pores or nodes within the MOFs, and enhancing desired functional properties such as catalysis, ionic conductivity, selective gas adsorption, and redox. BBR reactions are only observed on the outer surface of MOF crystals [18]. Post-synthetic modification reactions may create defects in the MOFs by replacing metal nodes or by missing organic linkers. Such defects can also be generated during the traditional synthesis of MOFs and the crystallization process and crystal growth. Mixed-metal MOFs which contain at least two metal ions in their framework can be prepared by using the post-synthetic methods, as well as by using metal ligands and possess new properties and activities because of the second metal ion present in the MOF. Structural defects are often related to important material properties, and therefore, defect engineering has been applied to modify and functionalize MOFs for applications in catalysis, magnetic materials, gas sorption, luminescence, and separation and storage [19].

4. Template Strategies

The template molecules used in the reaction mixture can obtain novel MOFs, which are difficult to synthesize using traditional methods. Small organic molecules, including organic solvents, organic amines, carboxylic acids, ion liquids and surfactants are the widely used template molecules. All of these organic compounds affect the synthesis and crystallization of the MOF. For example, the crystallization of the MOF is affected by the solvent polarity and solubility, the pH of the reaction solution and the deprotonation of the organic ligands is adjusted by the organic amines, carboxylate compounds act as ligands and fill the pores present in the MOF, When the aromatic heterocyclic compounds are protonated, they act as counterions and as weak organic bases, ion liquids act as counterions and solvents, and surfactants form micelles in solvents, which regulate the shape and size of the MOFs. Other molecules, which may act as templates, are coordination compounds, polyoxometalates, block co-polymers, MOFs, polystyrene spheres, substrates such as graphene oxide, and rarely biomacromolecules. The template synthesis strategy is used for the preparation of hierarchically porous materials, with mesoporous and microporous channels for hosting large molecules such as proteins and enzymes. Nevertheless, the reticular chemistry strategy is the common synthetic approach for MOFs, by extending the length of ligands to obtain MOFs of variable pore size but with the same topology [20].

5. Conclusion

MOFs, have high surface areas, uniform, versatile, and tuneable pores, and tailorable physicochemical properties, which are useful for a broad range of potential applications in various areas. Hundreds of new MOFs have been synthesized successfully since the discovery of the first MOF structure in the 1990s. In the past two decades, much attention has been paid to developing methods to control the morphology and size of MOF crystals to tailor the structural properties and performance of MOF materials. These research efforts have developed effective synthesis methods which are capable of controlling the morphology and size of MOF crystals through various mechanisms. This review chapter has highlighted several successful synthesis methods for MOF crystal formation and growth. It remains a significant challenge to fully utilize the unique properties and functionalities of the chemically versatile MOFs and realize their application potential in various identified areas. There have been significant achievements in the performance development and structure optimization of MOFs, it is predicted that further progress can be made with more fundamental research and industrial application of MOFs.

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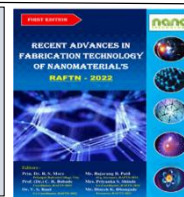
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Chemically Synthesized SnO₂-ZnO Nanocomposite Thin Films for Gas Sensing Application

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KEYWORDS

Chemical Synthesis
SnO₂-ZnO Nanocomposite,
Gas sensing,
Porous nature

ABSTRACT

Nanostructured material have attracted considerable research interest over the recent decades because of their potential application in material science and nanotechnology. Among all the nanomaterial's, the nanocomposites have attracted considerable attention in recent year. In particular metal oxide like SnO₂-ZnO have great potential application in development of gas sensors. Highly sensitive and selective gas sensor can be developed by using Nanocomposite SnO₂-SnO synthesized by Sol-gel method shows approximately 90% sensitivity at 300 °C operating temperature. The Material also shows better response and recovery time is 6-8 and 16-30 sec respectively. Present work focus on the introduction of Nanocomposite SnO₂-ZnO material and collective literature survey of synthesis methods of material, sensitivity, concentration, operating temperature, response time, recovery time etc. Successive ionic layered adsorption and reaction method is superior method for the deposition of SnO₂-ZnO Nanocomposite thin films.

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1. Introduction

Material Science is an interdisciplinary field concerned with the understanding and application of the properties of matter. In which material physics which emphasizes the use of physics to describe material properties. It grew out of an amalgam of solid-state physics, metallurgy and chemistry. Material Science examines the structure of aerial from the atomic scales, all the way up to the macro scale. Characterization is the way materials scientist examine the structure of a material.

Bulk Material refer to dry solid substances that are typically found in powder, granular or lumpy forms. With a bulk material, the particle components are too small to be counted individually and these material are typically stored in heaps or within silos. Ex. Sand, Gravel, Cement, Minerals, Coals, Plastics pellets, Coffee, Sugar, Salt. Bulk materials are present almost everywhere, especially when it comes to industrial processes. Approximately 70% all industrial processes. Depending on the size of the bulk material particles, conveying system vary in design and components vary in design and components.

Nanomaterials is defined as the material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. With nanoscale defined as length range approximately from 1nm to 100nm. The discrete pieces of material, and nanostructured material, which have internal or surface or surface structure on the nanoscale. Nanomaterials research takes a materials science based approach to nanotechnology, leveraging advances in material metrology and synthesis which have been developed in supports of micro fabrication research. Nanomaterial makes full use of their far lower scale and excellent characteristics than regular device and ideally become the core of gas sensor manufacturing material. [1] The material properties of nanostructure are different from the bulk due to the high surface area over volume ratio and possible appearance of quantum effects at the nanoscale. Nanomaterial have a low bulk density. This comes along with a typically high technical effectiveness

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caused by high specific area and change of reactivity, respectively. These characteristics together allow a wide dispersive use by a low mass application of the substance. Nanocomposite is a multiphase solid material where one of the phase has one, two or three dimensions of less than 100 nanometers (nm) or structure having nano-scale repeat distances between the different phase that make up the material. Ex. Nanoparticles, nanorods, nanofibers, and carbon-nanotubes. Thin film of nanocomposite material is used to determine low concentration of gases (ppm).

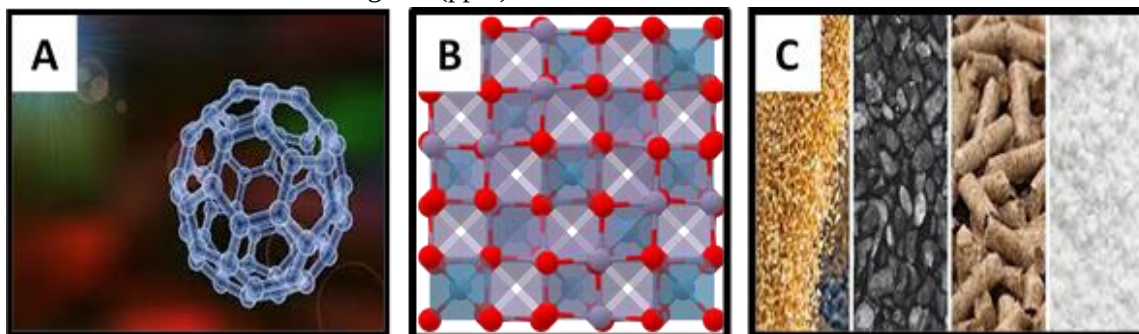


Fig.1. (A). Nanomaterial, (B) Nanocomposite, (c) bulk material

G. Korotcenkov et al. [2] they synthesized peculiarities of SnO_2 thin film by spray pyrolysis method. Prepared thin film is used for the gas sensing application. They demonstrated that active spray pyrolysis from SnCl_4 -water solution. The SnO_2 film has structure form quasi-mono-crystalline type to a very porous one. Sarbani Basu, et al. [3]. They fabricated pure and fluorine tin oxide thin film by using the sol-gel technique. They fabricated pure and nanocrystalline F-doped resistive gas sensor with Ag constant. They resulted that the optical band gap for pure SnO_2 film is 3.45 eV. From the electrical investigation they resulted that resistivity off F-doped film decreases by more than 118 time in magnitude compared with great significance for gas sensor fabrication and application, pure SnO_2 film. The gas sensor gives low resistance and quick response time (10sec) and recovery time (13sec). V.V Sysoev et al. [4] they were grown SnO_2 nano-wires and nano-belts by using the vapor-solid method. They used ceramic substrates for preparation. They conclude that SnO_2 NP 3-D network layers have superior sensitivity.

Junjie Qi, et al. [5]. They synthesized pure and In-doped ZnO nano-belets by chemical vapor deposition method. This ZnO nanoblets gas sensor can successfully distinguish acetone and ethanol. They conclude that demonstrate the potential application of In-doped nanoblets for fabrication high performance gas sensors.(paper 53). Jong-Woo Kim et al [6]. They fabricated micro patterned Df-ZnO NF flexible gas sensor by using PDMS rubbing technique. The operating temperature of the sensor was optimized at 270oC. They observed that sensor response at rising time 25.0s, decay time14.1s. the result are important for the development of nanomaterial based sensor device. They successfully improved the performance in NO_2 sensing. Luis.F.da Silva et al. [7] Prepared ZnO- SnO_2 material with composition $(100-x)\text{ZnO}$ (x) SnO_2 , where x= 0, 30, 50,70, by hydrothermal method. They reported that ZnO- SnO_2 is good material for ozone gas sensing. The illustrated that concentration level is 20ppb and the response time is 13 sec and recovery time 90 sec. and operating temperature of sensing material is 26^oc. Byung-Sam Min. et al [8]. They used SnO_2 , ZnO, Ag, Cu, In, Pd, Ru and carbon black for investigation. They fabricated SnO_2 -ZnO this film for detecting toluene gas. The sensitivity of toluene gas is in concentration range 1-2000 ppm. The good sensitivity of various gases at operating temperature 150-450 °C they conclude that at operating temperature 300°C toluene gas is detect. This thick film semiconductor gas sensor is fabricated with SnO_2 /20% and ZnO/1%, Cu/5%. (Paper 49) Madhukar Poloju, et. al [9]. They synthesized Pure SnO_2 , ZnO nanoparticles thin film and SnO_2 /ZnO Core/shell Nano composite by sol-gel technique. They resulted that highly crystalline material area formed. They concluded that fabricated film has porous morphology. The gas sensing results show that SnO_2 / ZnO film shows a high selectivity, sensitivity and also good stability. They conclude SnO_2 /ZnO has fast response towards the isopropanol at the operating temperature 300°C.

2. Structures

2.1. Tin Oxide (SnO_2)

Tin Oxide (SnO_2) is the inorganic compound with the formula SnO_2 , the mineral form of SnO_2 is called Cassiterite, and this is the main ore of tin. With many other names, this oxide of tin is an important material in tin chemistry. It is a colorless, diamagnetic, amphoteric solid. The properties of tin oxide density is 6.95 g/cm^3 , melting point is 1690°C , boiling point is about $1,800\text{--}1900^\circ\text{C}$. Tin Oxide is insoluble in water and refractive index is $2.006 n_D$. Tin Oxide crystallizes with the rutile structure. Hydrated form of SnO_2 has been described as stannic acid. In Tin Oxide Tin atom is six coordinate and the Oxygen atom three coordinate. SnO_2 is usually regarded as an oxygen-deficient n-type semiconductor. Lattice constant of Tin Oxide $a=4.737\text{\AA}$, $c=3.185\text{\AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$. Tin oxide is used as a catalyst for the oxidation of aromatic compounds in the synthesis of aromatic compounds in the synthesis of carboxylic acid anhydrides. It is used for the ceramic glazes, dyes, polishing, glass coatings, gas sensing. SnO_2 is used in sensors of combustible gases.

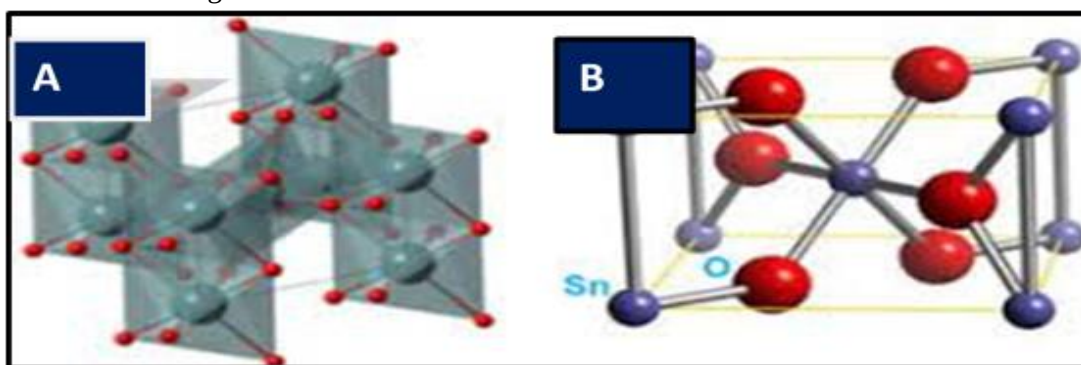


Fig 2. (A). 3D structure of SnO_2 fig (B). Cassiterite

G. Tournier et al. [11]. They synthesized thick film SnO_2 by using CVD method at high temperature is about $(500\text{--}600)^\circ\text{C}$ under the working condition, hydrogen concentration as low as 250 ppb. This hydrogen sensor has good electrical result. They concluded that response and recovery time to use this hydrogen sensor in special industrial applications.

2.2. Zinc Oxide (ZnO)

Zinc oxide is an inorganic compound with the formula ZnO . It is a white powder that is insoluble in water. ZnO is used as an additive in numerous materials and products including cosmetics, food supplements, rubbers, plastics, Ceramics, glass cement, lubricants, paints, ointments, pigments, foods, batteries, ferrites, fire retardants. Most zinc oxide is produced synthetically. ZnO appears like white solid. Molar mass is 81.406 g/mol , it is odorless, density is 5.606 g/cm^3 , melting point $1,974^\circ\text{C}$, boiling point is $2,360^\circ\text{C}$, band gap is 3.3 eV . Crystal structure is Wurtzite and the lattice constant $a=3.2495\text{\AA}$, $c=5.2069\text{\AA}$. Co-ordination geometry is tetrahedral. Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zincblende. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. The application of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as precursor to other zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties. Consequently, it is added into materials and products including plastics, ceramics, glass, cement. Rubber, lubricants, paints, adhesive, sealants, concrete manufacturing, pigments, foods, batteries, ferrites, fire retardants, etc.

Wang et al. [12]. They synthesized on a ZnO thin film by simple hydrothermal route. They fabricated gas sensor from ZnO nanorod arrays for gas sensing properties to NH_3 , CO and H_2 . They

observed that ZnO has highly sensitive and reversible response to H₂ at low temperature. They observed promising results for large scale fabrication of cost effective and high performance gas sensors.

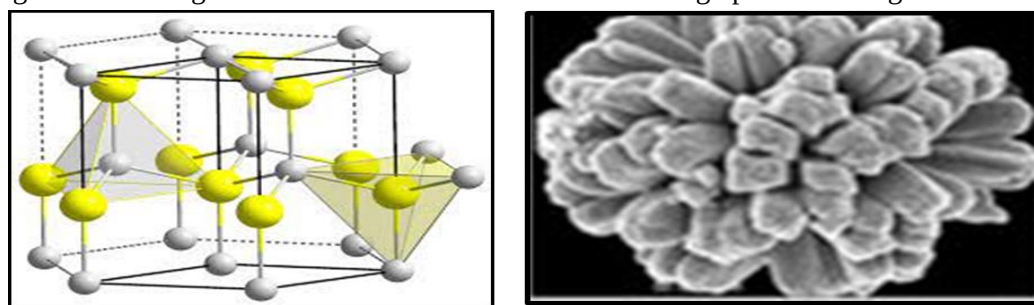


Fig 3. (a) Structure of ZnO, (b) structure of SnO₂-ZnO nanoparticle [13]

2.3. SnO₂-ZnO

One-dimensional (1D) semiconductor metal oxide nanostructures have attracted increasing attention in electrochemistry, optics, magnetic, and gas sensing fields for the good properties. N-type low dimensional semiconductor oxide such as SnO₂ ZnO have been known for the detection of inflammable or toxic gases. The improved gas sensing properties are attributed to the size of grains and pronounced electron transfer between the compound nanostructures and the absorbed oxygen species as well as to the hetero-junctions of the ZnO nanoparticles to SnO₂ nanoparticles, which provide additional reaction rooms.

In vast area of gas sensing using nanostructure most of gas sensor are based on photo crystalline tin oxide (SnO₂) and Zinc oxide (ZnO) system that are removed for their high sensitivity and chemical stability. R. H. Bari, et al. [14]. They synthesized SnO₂-ZnO nanocomposite thin film by using spray pyrolysis technique. They concluded that the structural and micro structural properties confirm that the prepared thin film are nanostructured in nature and SnO₂-ZnO thin film was most sensitive to ethanol gas and exhibit the sensitivity is about 63%. Sensor has good selectivity to ethanol against LPG, CO₂, H₂, NH₃, and H₂S. They observed that nanostructure SnO₂-ZnO nanocomposites thin films exhibit rapid response-recovery and which is one of the main features of this sensor.

3. Gas sensor

3.1. Type of gas sensor

Electrochemical gas detectors work by allowing gases to diffuse through a porous membrane to an electrode where is either chemically oxidized or reduced. Electrochemical gas detectors are used in a wide variety of environments such as refineries, as turbine, chemical plants, underground gas storage facilities, and more.

Catalytic bead sensors are commonly used to measure combustible gases that present as explosion hazard when concentrations are between the lower explosion limit (LEL) and upper explosion limit (UEL). The measurable concentration ranges are typically from a few hundred ppm to a few volume percent. Such sensors are inexpensive and robust, but require a minimum of a few percent oxygen in the atmosphere to be tested and they can be poisoned or inhibited by compounds such as silicones, mineral acids, chlorinated organic compounds, and sulfur compounds.

Photoionization detectors (PIDs) use a high-photon-energy UV lamp to ionize chemical in the sample gas. If the compound has an ionization energy blow that of the lamp photons, an electron will be injected, and the resulting current is proportional to the concentration of the compound. The common lamp photon energies include 10.0eV, 10.6eV, and 11.7eV; the standard 10.6eV lamp lasts for years. The major advantages of PIDs are their excellent sensitivity and simplicity of use; the main limitation is that measurements are not compound-specific. Recently fixed, hand-held and miniature clothing-clipped PIDs are widely used for industrial hygiene, hazmat, and environmental monitoring.

Infrared (IR) point sensors use radiation passing through a known volume of gas; energy form the sensor beam is absorbed at certain wavelengths, depending on the properties of the specific gas. This type

of sensor is advantageous because it does not have to be placed into the gas to detect it and can be used for remote sensing. The sensor would be high level of carbon monoxide or other abnormal gases in vehicle exhaust and even be integrated with vehicle electronic system to notify drivers.

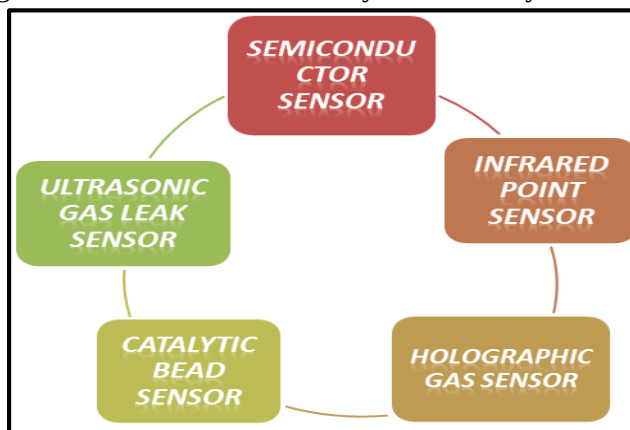


Fig. 5 types of sensor

Semiconductor Sensor, also known as metal oxide-semiconductor (MOS) sensors, detects gases by a chemical reaction that takes place when the gas comes in direct contact with the sensor. Tin dioxide is the most common material used in semiconductor sensor and the electrical resistance in the sensor is decreased when it comes in the contact with the monitored gas. semiconductor sensors are commonly used to detect hydrogen, oxygen, alcohol vapor and harmful gases such as carbon monoxide. One of the most common uses for semiconductor sensor is in carbon monoxide sensors.

Ultrasonic gas leak detectors are not gas detectors per se. they detect the acoustic emission created when a pressured gas expands in a low pressure area through a small orifice. They use acoustic sensors to detect changes in the background noise of its environment. Ultrasonic gas leak detectors cannot measure gas concentration, but the device is able to determine the leak rate of an escaping gas because the ultrasonic sound level depends on the gas pressure and size of the leak.

Holographic gas sensor use light reflection to detect changes in a polymer film matrix containing a hologram. Science holograms reflect light at certain wavelength, a change in their composition can generate a colorful reflection indicating the presence of a gas molecule. However, holographic sensors require illumination sources such as white light or lasers, and an observer or CCD detector

Literature survey

Zhaoua Wang et al. [17]. They prepared Sb-doped SnO₂ covered ZnO nano-heterojunction by using a microwave hydrothermal method. if they studied the morphology and gas sensor performance of SnO₂-ZnO NHs with Sb doping, they observed that gas sensor response higher as the concentration of Sb doping increased they concluded that Sb-doped SnO₂ ZnO NHs can be applied to design novel gas sensors with high performance at low gas concentration. Sun-Woo-Choi, et al.[18]. They investigated that sensing mechanism operating in SnO₂-ZnO- C-S NWs that are particularly ultrasensitive for the detection of trace amounts of reducing gases. They used two-step method for synthesizing of C-S NWs and for SnO₂ nanowires prepared by vapour-liquid-solid-growth and ZnO shell deposited by ALD.

Sr. No.	Material	Method	Sensitivity/ Concentration (%), (ppm)	Operating Temperature °C	Response time (Sec)	Recovery time (Sec)	Ref. No.
1	ZnO-SnO ₂	Spray pyrolysis	0.1-50 ppm	200	80-144	30-80	[19]
2	SnO ₂ -Zno	SILAR	56.93%	275	40	65	[20]

3	ZnO-SnO ₂ (100-x)ZnO; (x)SnO ₂	Hydrothermal	20ppm	26	13	90	[3]
4	SnO ₂ -ZnO	Sol-gel	20ppm	70	120	70	[21]
5	SnO ₂ -ZnO	Spray pyrolysis	-	450	37	57	[22]
6	SnO ₂	Co- precipitation Route	1000 ppm-1200 ppm	400	10-30	600-1200	[23]
7	SnO ₂ .NP _s	Sol-gel	0.5% , 1.7ppm	200-250	8-14	25	[24]
8	SnO ₂	Thermal evaporation	90%	200	43	18	[25]
9	pd/SnO ₂ /RGO	One-pot- Route	26% , 5ppm	Room temp.	420	3000	[26]
10	ZnO	SILAR	5.6%	250	100	150	[27]
11	ZnO [Zn(CH ₃ COO) 2.2H ₂ O;99%]	Sol-gel route	90%	300	6-8	16-30	[28]
12	ZnO-H	Electro spinning method	8384%	200	572	65	[29]
13	B- SnO ₂ @ZnO HNSs	Two step hydrothermal method	90%	150	<60	<60	[30]
14	ZnO-SnO ₂	Electro spinning method	50ppm	250	18	32	[31]
15	ZnO-SnO ₂	Sol-gel	50-2000 ppm	175-275	7	-	[32]

4. Application

SnO₂ has the special properties such as chemical stability, biocompatibility, eco-friendly, easy preparation, low isoelectric point, SnO₂ are commonly used in a range of applications and also zinc oxide (ZnO) has properties as high conductivity, electron mobility, stability against photo-corrosion and availability at low-cost. Due to such properties SnO₂ and ZnO has application such as photo catalyst, gas sensing, water splitting, antimicrobial etc.

4.1. Photocatalyst

Sitan Chen, Fenning Liu et al. [33] they fabricated branch-like SnO₂@ZnO hetero-junction Photo catalyst by simple two-step Hydrothermal process. They illustrated that photo catalytic efficiency of ZnO and SnO₂ are about 90% and 55% respectively. They investigated that optical properties of as prepared sample by UV-visible diffuse reflectance, the absorption edges of ZnO and SnO₂ were determine to be 394 and 335nm. Corresponding to band gap energies of 3.2 and 3.7eV. The appearance of two kind of characteristics absorption bank confirms that the TZNCs photo catalyst is a composite material which is composed of SnO₂ and ZnO. Aaron dodd, Allan Mckinley, et al. [34] they prepared nanocrystalline SnO₂-ZnO powder by a co-precipitation method. They found that the reactant mixture underwent chemical reaction during milling, they studies that mechanochemical reactance of anhydrous, chloride. Precursors with Na₂CO₃ has been investigated as a means of manufacturing nanocrystalline SnO₂-ZnO photocatalysis they gave result the temperature must sufficiently high to minimize undesirable interaction between the

oxide nanoparticle and the wash water. Alexandru Enesca, et al. [35] they synthesized mono-component bi-component and hybrid thin film containing metal oxide and copper sulfide were obtained by spray pyrolysis deposition. They concluded that the evolution of photo-catalytic properties in methylene blue and methyl orange solution show that the Zn-Cu-Sn sample reaches highest efficiency due to the triple contribution.



Fig. 6. Application of $\text{SnO}_2\text{-ZnO}$

4.2. Gas Sensor

B.M. Sargar, et al. [20] prepared a thin film of $\text{SnO}_2\text{-ZnO}$ nano-composite at room temperature by the successive ionic layer adsorption and reaction (SILAR) method. They observed that ZnO has cauliflower shape and SnO_2 has distributed agglomerated nanoparticle-like morphology. They reported that $\text{SnO}_2\text{-ZnO}$ thin film are good material for ethanol gas. they illustrated the sensitivity of $\text{SnO}_2\text{-ZnO}$ thin film is 56.93% at the operating temperature 275°C with concentration of 24ppm. Diyu Fu et al. [36]. Fabricated SnO_2/ZnO net-like, two-dimensional hetero-nanostructure. The $\text{SnO}_2\text{-ZnO}$ hetero-nanostructure detect H_2S gas at 100 ppm concentration at a working temperature 100°C . $\text{SnO}_2\text{-ZnO}$ is very dominant material for H_2S gas. They used facile method for fabrication. H_2S gas is very harmful for health of human being. Dilip L, Kamble et al., [37] synthesized SnO_2 thin film by Spray pyrolysis technique. They illustrated that its application in gas sensing. They performed synthesized SnO_2 Sensor for sensing of NO_2 gas. Its response and recovery time is 48-244 sec. and 100-46 sec. respectively. The gas is response at 150°C for NO_2 gas response.

4.3. Water splitting

Jihyun Baek et al. [38] they fabricated a $\text{BiVO}_4/\text{WO}_3/\text{SnO}_2$ based double double-heterojunction photoanode on an FTO/ glass substrate by using a facile Sol-gel spin-coating process. They demonstrated a bias-free solar water splitting (STH of $\sim 3.5\%$) by constructing a tandem PEC device with a PSC. Alexander N. Bondarchuk et al. [39] they prepared hematite-photo-electrodes on highly-conductive and porous nature SnO_2 ceramic substrate. They used AA_CVD technique. They resulted that application of conductive and porous ceramics as substrate for photo-catalytic material. Advantages of the preparation is ceramic substrates is easier and cheaper, this is important for fabrication of large area photo-electrodes for practical application.

4.4. Supper capacitor

Awais Ali, et al [40]. They synthesized a honeycomb-like ZnO/SnO_2 nanocomposite on nickel by single-step hydrothermal route. They observed that maximum energy density of $47.28 \text{ W h kg}^{-1}$ and maximum power density of $10.445 \text{ kW kg}^{-1}$. They resulted that the ZnO/SnO_2 nanocomposite is a promising electrode may be expanded greatly to other efficient energy storage systems. Their investigation demonstrate that the as synthesized ZnO/SnO_2 nanocomposite could be a good competitor as an electrode material in high-performance electrochemical energy storage application. Chirag Mevada, et al. [41] they synthesized tin oxide (SnO_2) nanoparticles by using precipitation method at room temperature. They were resulted that the formation of a tetragonal rutile crystal of spherical shape SnO_2 nanoparticles with an average size of 20.40 nm. They confirmed that the oxidation state of Sn^{4+} with an energy gap of 8.5eV.

Capacitance retention rate of 94.7% after 5000 cycles at a current density of 20 A/g for total mass loading of 10mg cm⁻² in hydro gel polymer electrolyte.

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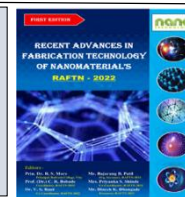
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Recent Advances in Fabrication Technology of Nanomaterials

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Metal oxide-based supercapacitor: A review

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KEYWORDS

Supercapacitor
Metal oxides
 In_2O_3
 Co_3O_4
 NiO
 Bi_2O_4
 Fe_3O_4
 V_2O_5

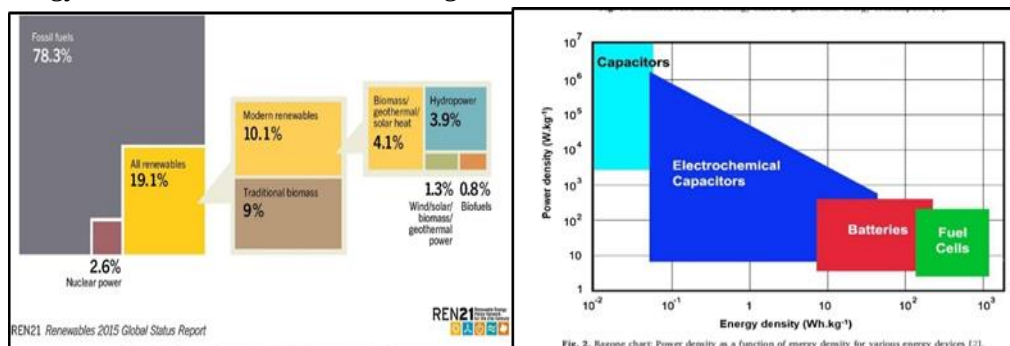
ABSTRACT

In the current scenario of the growing world, the requirement of non – conventional energy sources having high density & power has very much increased. Supercapacitors are showing successful energy storage devices having long life cycles, high specific capacitance & power densities. Supercapacitor performance is decided with help of electrode materials. Among the different materials of supercapacitor electrodes, in recent years research is focusing on the synthesis of metal oxides/ hydroxides and their composites, carbon metals, and polymers. Metal oxides such as In_2O_3 , Co_3O_4 , NiO , Bi_2O_4 , Fe_3O_4 , V_2O_5 etc. were widely used as supercapacitor electrode materials for storing energy. In the given paper, we are exploring the detail of metal oxide material for supercapacitor electrodes & their composites with a simple chemical method. We also explained the basic parameters involved in supercapacitor studies and the advantages of the electrochemical deposition technique through analysis of the literature.

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1. Introduction

Limited sources of fossil fuels along with growing population and technology development put the mankind in front of an energy problem. Increasing pollution forces us to think about energy and the approach to energy management. There are two main types of energy sources, fully controllable power plants (nuclear power stations, incineration plants, fossil fuels, biomass, geothermal) and renewable energy sources, which are non-dispatchable (wind and solar energy). The world human population cannot use only renewable energy sources, at least in the near future. The share of renewable energy among other types of energy sources in 2015 is shown in Fig. 1.



In the ideal case, renewable energy should cover 100% of world energy consumption, but it is only a theoretical idea that is not possible to be achieved. We should however increase the proportion of renewable energy sources in the world energy production as fast as possible. Energy from renewable energy sources needs to be (due to its non-dispatch ability) stored and used when needed. Energy storage

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and accumulation is the key part of renewable energy sources utilization. Use of batteries or special hydropower plants is the only way how can we today store the energy from renewable energy sources. There are other experimental alternatives – storing energy in superconducting magnetic energy storage systems (SMES), which store it in a magnetic field created by the flow of current in a superconducting coil that has been cryogenically cooled to a temperature below its superconducting critical temperature. There are also other energy storage systems still in the phase of basic research, so they cannot be considered as regular energy storage systems. Another important step to decreasing pollution and keeping sustainable development of population is reducing emissions produced by combustion engine vehicles and replacing them with electric vehicles. Autonomy electric vehicles, which do not have connection to the electrical grid, also need to store electric energy in batteries. Using batteries, especially lithium-ion batteries, is a widely discussed and technologically developed topic. Supercapacitors could be considered as an alternative to conventional batteries for electric vehicles.

This paper is related to supercapacitors, it provides their brief description, operation principles, types and recent development. Electrochemical capacitors, also named supercapacitors or ultracapacitors, are electrical components that are able to store and accommodate certain amounts of energy. The development of supercapacitors started in the 50 s of the 20th century. First experiments started between 50 s and 70 s and were conducted by US companies General Electric (GE) and Standard Oil of Ohio (SOHIO). These first electrochemical supercapacitors reached the capacity around 1F. This type of supercapacitors was patented in 1971 by SOHIO. The first supercapacitor named “Gold Cap” was released to the commercial market in 1982 by Panasonic and had high equivalent series resistance (ESR). In 1982, first electric double-layer capacitor (EDLC) supercapacitor was developed for military purposes by the Pinnacle Research Institute (PRI). This first EDLC supercapacitor already had a low ESR. After ten years, in 1992, Maxwell Laboratories introduced to the commercial market a wide range of EDLC supercapacitors with low ESR named “BoostCap” with nominal capacity of 1 kF. Since 2007, the development of novel hybrid-supercapacitors took place. This kind of supercapacitors should reach higher nominal voltage along with higher volumetric and gravimetric energy density than conventional EDLC supercapacitors. Most of today’s supercapacitors have capacity over several thousand Farads and can provide charge-discharge currents in the range from tenths to hundredths of Amperes. Their main advantage from the application point of view is extremely high current (in comparison to batteries) that they are able to operate with. Thanks to this characteristic property, supercapacitors fill the void gap among energy storage devices between batteries (accumulators) and common capacitors (see Fig. 2 below). Supercapacitors are used in applications, where is need to store or release huge amount of energy in a very short time. Nowadays, the supercapacitors are used primarily in Hybrid Electric Vehicles (HEV), Electric Vehicles (EV) and Fuel Cell Vehicles (FCV) like passenger cars, trains, trolleybuses. Another area of supercapacitors’ use are electronic devices as Uninterruptible Power Supplies (UPS) and volatile memory backups in PCs. Third area of use are energy harvesting systems, solar arrays or wind turbines, where supercapacitors play a supplementary role next to conventional batteries [1–14]. Especially the application of supercapacitors in automotive industry brings many advantages. Supercapacitors can be used to increase the efficiency of hybrid electric vehicles in several ways. Today’s hybrid vehicles typically turn off the engine completely when the car stops, and then very efficiently start it again using energy stored in supercapacitors. There are over 600 thousands HEVs that use supercapacitors in their stop-start systems. Some supercapacitor manufacturers designed replacements for conventional vehicle batteries using supercapacitors connected across a smaller lead acid battery. The concept of their application is in the moments when the power demand peaks, such as starting a car, and they decrease the overall energy consumption from the batteries. Batteries last much longer when the discharge is small and steady. Supercapacitors in this “hybrid lead-acid battery” configuration essentially smooth out the energy demands on the battery.

A large number of review articles including a special issue by The Electrochemical society [15-27]. The capacitance of a device is largely dependent on the characteristics of the electrode material;

particularly, the surface area and the pore-size distribution [28]. The operating voltage of supercapacitors is usually dependent on electrolyte stability. Aqueous electrolytes, such as acids (e.g., H_2SO_4) and alkalis (e.g., KOH) have the advantage of high ionic conductivity (up to 1 S cm^{-1}), low cost and wide acceptance however; they have the inherent disadvantage of a relatively low decomposition voltage of 1.23 V [29]. Non-aqueous electrolytes allow the use of cell operating voltages above 2.5 V . Non-aqueous electrolyte mixtures such as propylene carbonate or acetonitrile, containing dissolved quaternary alkyl ammonium salts have been employed in many commercial supercapacitors. The electrical resistivity of non-aqueous electrolytes is, however, at least an order of magnitude higher than that of aqueous electrolytes and therefore the resulting capacitors generally have a high internal resistance [28]. In supercapacitors, a number of sources contribute to the internal resistance and are collectively measured and referred to as the equivalent series resistance, or ESR. Contributors to the ESR of supercapacitors include: (i) electronic resistance of the electrode material, (ii) the interfacial resistance between the electrode and the current collector, (iii) the ionic (diffusion) resistance of ions moving in small pores, (iv) The ionic resistance of ions moving through the separator, and (v) the electrolyte resistance [30]. The required electrode properties of supercapacitor electrode material arise from a combination of chemical and physical properties, namely: high conductivity, high surface area range (1 to $> 2000 \text{ m}^2 \text{ g}^{-1}$), good corrosion resistance, high temperature stability, controlled pore structure, process ability and compatibility and relatively low cost. It has been possible to generate high surface area materials exhibiting Faradaic electrochemical as well as electrical double layer type responses. Among the several transition metal oxides and carbon aerogels studied for capacitor response, the only oxide that has been widely researched and known for its superior electrochemical capacitor response to date is the various crystallographic and morphological forms of ruthenium oxide [31]. Unfortunately, the expensive nature of ruthenium has limited the technological viability of this material. Consequently, the field of supercapacitor has not witnessed many advances.

Many chemically deposited metal oxide thin films including ruthenium oxide, iridium oxide, manganese oxide, cobalt oxide, nickel oxide, tin oxide, iron oxide, perovskites, ferrites, etc. have been applied in supercapacitors. The thin film deposition methods involving the growth from solution are called as chemical methods. Here, a fluid surface precursor undergoes a chemical change at a solid surface, leaving a solid layer. In chemical deposition the solutions contain precursor molecules for a variety of elements in the thin film of interest. These methods are inexpensive and enable the synthesis of film materials with complex chemical compositions [32]. Depending on applications, one would prefer thin films which have a special texture, low grain boundary density, or smooth surfaces. The methods usually have low operating temperature. Apart from the obvious advantages in terms of energy saving, the low deposition temperature avoids high temperature effects such as inter diffusion, contamination and dopant redistribution. They offer mysterious morphologies of the thin films which can be easily controlled by preparative parameters. Unlike physical deposition methods, they do not require high quality target and/or substrates nor do they require vacuum at any stage, which is a great advantage if the methods are used for industrial applications. Chemical methods include electrodeposition, chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), electroless deposition, anodization, spray pyrolysis, liquid phase epitaxy, spin coating, dip drying, etc. This review presents the survey of supercapacitive performance of chemically deposited metal oxide thin film electrode materials. The supercapacitors have exhibited the specific capacitance (Sc) values between 50 and 1100 F g^{-1} , which are quite comparable with bulk electrode values. Therefore, it is likely that these metal oxide thin films will continue to play a major role in supercapacitor technology.

2. Metal Oxides:

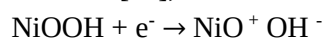
2.1. Cobalt oxide (Co_3O_4) based supercapacitors

Liu et al. [33] reported that Co_3O_4 and CoO_x are for promising materials for supercapacitors due to their intercalative pseudocapacitance properties. Lin et al. [34] obtained a maximum Sc of 291 F g^{-1}

using CoOx aerogel calcined at 423 K. Srinivasan and Weidner [35] reported Co_3O_4 film used as a positive electrode exhibited capacitor-like behavior. Wang et al. [36] reported $\text{Co}(\text{OH})_2$ electrode exhibits about 280 F g^{-1} as a single electrode capacitance. The cobalt oxide electrode has been found to have good efficiency and long-term performance and the good corrosion stability [37,38]. The MWNTs/ Co_3O_4 composites show high capacitor property, and their best specific capacitance is up to 200.98 F g^{-1} which is significantly greater than that of pure MWNTs (90.1 F g^{-1}) [65]. A room temperature, simple and low cost SILAR method for the cobalt oxide film on to copper substrate was developed [39]. Cobalt oxide films were deposited from the cationic precursor CoCl_2 complexed with liquor ammonia solution and the H_2O_2 as anionic precursor showed Sc of 165 F g^{-1} in 1.0 M KOH . Binary hydrous cobalt-nickel oxide with an amorphous structure, denoted as $\text{a}-(\text{Co} + \text{Ni})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ was anodically deposited at $+0.75 \text{ V}$ [40]. This deposit with very rough morphology and many small spherical grains aggregated to form the larger oxide particles exhibited Sc of 730 F g^{-1} in 1 M NaOH . The pseudocapacitance of hydrous oxides mainly came from the electrochemical energy stored by the faradaic redox transitions of interfacial oxyanion species [40, 41]. Similarly, cobalt nickel layered double hydroxides ($\text{Co}_x\text{Ni}_{1-x}\text{LDHs}$) were deposited onto stainless steel electrodes by the potentiostatic deposition method [42]. The $\text{Co}_x\text{Ni}_{1-x}\text{LDHs}$ in 1 M KOH electrolyte showed that $\text{Co}_{0.72}\text{Ni}_{0.28}\text{LDHs}$ had the highest specific capacitance value, 2104 F g^{-1} , which is also the highest yet reported value for oxide materials in general. The porous structure with inter-particles spaces increases the electrochemically active sites and therefore, can improve utilization of the LDHs.

2.2. Nickel oxide (NiO) based supercapacitors

Nickel oxide films have been prepared by thermal treatment of electrodeposited $\text{Ni}(\text{OH})_2$ [43-44], sol-gel [46-49] and electrostatic spray deposition [50]. Nickel oxide films synthesized by electrochemical precipitation of $\text{Ni}(\text{OH})_2$ were heat-treated in air [51]. The non-stoichiometric nickel oxide (Ni_{1-x}O) approached the stoichiometric NiO structure with increasing heat-treatment temperature due to the defect healing effect. The defective nature of the nickel oxide could be utilized to improve its specific capacitance. The Sc was from 200 to 278 F g^{-1} in 1 M KOH within 0.5 V potential windows. The cubic NiO films with different morphologies were prepared by hydrothermal and electrodeposition methods on ITO-coated glass and Ti foil [52]. The Sc of about 148 F g^{-1} was obtained for the electrodeposited film at 100 mV s^{-1} scan rate. Using SILAR method, ITO assisted mesoporous and amorphous nickel hydroxide electrodes of $120 \text{ m}^2 \text{ g}^{-1}$ surface area (pore-size distribution centered 12 nm) were synthesized [53]. The supercapacitive characteristics in 1.0 M LiCl electrolyte showed the Sc of 85 F g^{-1} . Decreasing trend of supercapacitor value with electrode mass due to the starvation of active sites reacted with ions was observed. Due to the slight phase change from nickel hydroxide to oxide through the intermediate stage of NiOOH , the redox peak was gradually reduced and caused collapse of its intrinsic lattice structure and showed diminution of its capacitance as follows [54];



Liu and Anderson [47] used the sol-gel method to fabricate a porous NiO electrode with a thickness of around 0.4 mm on nickel foil. Srinivasan and Weidner [43] utilized the cathodic precipitation method to fabricate NiO onto gold substrates. Comparative supercapacitor studies on nickel and graphite substrates have been carried out [55]. Thin NiO films were obtained by post-heating of the corresponding precursor films of nickel hydroxide ($\text{Ni}(\text{OH})_2$) cathodically deposited onto graphite and nickel foils. The specific capacitances of the NiO films on nickel foil and graphite were 135, and 195 F g^{-1} , respectively. Electrochemically deposited Nickel and cobalt mixed oxides onto CNT film substrate showed Sc value of 840 F g^{-1} at the discharge current density of 10 mA cm^{-2} in 1.0 M KOH electrolyte [56].

2.3. Indium oxide (In_2O_3) based supercapacitors

Electrodes of different morphologies, i.e. nanospheres (NSs) and nanorods (NRs), made by chemically depositing indium oxide on indium-tin oxide substrates were investigated for their electrochemical supercapacitive properties [57]. The presence of nanosized pores and voids in In_2O_3 electrode of NRs caused increase in redox reaction active sites, and ultimately, inner and outer charges

than that of NSs In_2O_3 electrode. The calculated active sites suggested that the change in surface morphology from NS to NR increased the number of redox reaction sites from 0.02 to 0.3. The Sc values calculated for In_2O_3 electrodes composed of NRs and NSs were 104.9 and 7.6 F g^{-1} , in 1 M Na_2SO_4 , respectively at a constant discharge current density of 8 A/g. Electrodeposition of nanorods of indium oxide of average length of about 250 nm and an average diameter of about 50 nm was carried out by Prasad et al. [58]. The In_2O_3 electrodes in 1 M Na_2SO_3 electrolyte showed Sc of 190 F g^{-1} at a scan rate of 10 mV s^{-1} . There was minimal decrease in Sc for 1000 cycles, indicating stability of In_2O_3 for long-term capacitor applications.

2.4. Bismuth oxide (Bi_2O_3) based supercapacitors

Polycrystalline monoclinic Bi_2O_3 thin films were grown on copper substrates at room temperature by electrodeposition [59]. Though the Bi_2O_3 films are crystalline with a monoclinic crystal structure, they are capable of giving a specific capacitance of 98 F g^{-1} . Typical cyclic voltammograms of Bi_2O_3 electrode deposited on copper substrate in 1 M NaOH electrolyte at scan rate of 100 mV s^{-1} is shown in Fig. 3 [59]. It is seen that the specific and interfacial capacitances decrease from 98 F g^{-1} and 0.022 F cm^2 to 60 F g^{-1} and 0.012 F cm^2 , respectively, as the scan rate is increased from 20 to 200 mV s^{-1} . The decrease in capacitance has been attributed to the presence of inner active sites that cannot sustain the redox transitions completely at higher scan rates.

2.5. Iron oxide (Fe_3O_4) based supercapacitor

An aqueous Fe_3O_4 (magnetite) supercapacitors based on powder form and mixed with carbon black have been studied [64-65]. Large capacitances have been reported in alkali sulfites and sulfate solutions. In particular, the capacitance of the Fe_3O_4 was found to be sensitive to the anion species but not to either alkaline cations or electrolyte $\text{pH} < 11$. These behaviors suggest a capacitance mechanism is different from that of either RuO_2 or MnO_2 . Wang et al. [64] have reported the capacitance mechanisms of an electroplated magnetite thin film electrode in Na_2SO_3 , Na_2SO_4 , and KOH aqueous solutions using electrochemical quartz-crystal microbalance (EQCM) analysis and X-ray photoelectron spectroscopy (XPS), and other electrochemical characterizations [66]. The oxide film exhibited granular morphology with high porosity with an average crystallite size of 12 nm. The Fe_3O_4 electrode exhibited Sc of 170, 25, and 3 F g^{-1} in aqueous 1.0 M Na_2SO_3 , Na_2SO_4 , and KOH, respectively. Strong specific adsorption of the anion species was evidenced in all solutions. Experimental results indicate that, in Na_2SO_3 , the capacitive current of magnetite electrode originate from the combination of electric double layer capacitance (EDLC) and the pseudo capacitance that involves successive reduction of the specifically adsorbed sulfite anions, from SO_3^{2-} through, e.g., S^{2-} , and vice versa. In Na_2SO_4 , the current is due entirely to EDLC. The lowest capacitance of magnetite observed in KOH is attributed to the formation of an insulating layer on the magnetite surface.

2.6. Vanadium oxide (V_2O_5) based supercapacitors

Recently, amorphous vanadium oxides (V_2O_5) have received a lot of attention as electrode materials for supercapacitors in aqueous and organic electrolytes. Lee and Goodenough prepared amorphous V_2O_5 by quenching V_2O_5 powders heated at 1183 K and reported its supercapacitive behavior in KCl aqueous electrolyte with c of 350 F g^{-1} [60]. They proposed that the K^+ ions in the KCl aqueous electrolyte were responsible for the supercapacitive redox reaction of amorphous V_2O_5 . V_2O_5 is also known to have electrochemical redox reactions with Li ions in an organic electrolyte as in lithium secondary batteries [61]. Passerini et al. prepared a sol-gel-derived thin film of V_2O_5 aerogel on a Hastelloy felt substrate and reported a specific energy of 10 Wh/kg with respect to the total mass of a unit cell in LiClO_4 in propylene carbonate [62]. An amorphous and hydrous vanadium oxide ($\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) thin film of approximate 6- nm thickness was electrochemically prepared onto a carbon nanotube (CNT) film substrate with a three-dimensional porous structure on a nanometer scale for supercapacitor application [63]. From C-V and galvanostatic discharging experiments in an organic electrolyte (LiClO_4 in propylene carbonate), the $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}/\text{CNT}$ film electrode showed Sc of 910 F g^{-1} at a potential scan rate of 10 mV s^{-1} and a

specific capacity of 540 mAh/g at a current density of 10 A/g. The improved Sc of $V_2O_5 \cdot xH_2O$ in the $V_2O_5 \cdot xH_2O$ /CNT film electrode has been attributed to its electrode construction comprising a very thin film of $V_2O_5 \cdot xH_2O$ on the conductive CNT film substrate with a three-dimensional nanoporous structure.

4. Conclusion

(i) Simple chemical methods such as electrodeposition, spray pyrolysis, chemical deposition, spin coating, dip dry etc. have been employed to deposit metal oxide thin films. (ii) For most of the systems, only specific capacitance (Sc) values have been reported and the values of interfacial capacitance, specific energy and specific power are not studied. (iii) In general, stability of electrodes has been reported only for 1000 cycles. (iv) No asymmetric devices formed. (v) Amongst the metal oxide materials, only NiO and Co_3O_4 thin film-based systems have been paid more attention.

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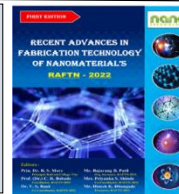
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Ni-Co nanoferrites: A Potential Candidate for Wave Absorption Application

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1. Introduction

Ferrites are a kind of magnetic material that finds wide applications in various fields. Ferrites are ceramic magnetic materials having the main constituent is iron oxides. Ferrites are usually described by the formula $M-(Fe_2O_4)$, where M represents any metal ion with 2+ valency. By heating a mixture of the oxides of constituent metal with high temperatures, ferrites are produced. In ferrite, adjacent magnetic moments are of unequal magnitudes aligned in antiparallel direction. These material shows both magnetic and dielectric properties. For electromagnetic wave loss, it has both electrical loss and magnetic loss. They can be magnetized or attracted to a magnet, which means ferrites are ferrimagnetic type. Also they have excellent corrosion resistance. It is used electronics, telecommunications, capacitors and computers because of their electrical and magnetic properties. For the production the most convenient and successful method is ceramic method, but also this method has some limitations [1]. Ferrites are hard, brittle, iron-containing and gray or black in appearance and polycrystalline material. Most of the ferrites are not electrically conductive. The resistivity of ferrites is very much higher than that of the ferromagnetic metals and the unit of resistivity is ohm-meter. The density of ferrite magnets is about $5g/cm^3$. The important properties of ferrites are magnetic permeability and high electrical resistance. In formation of ferrites having formula $M-Fe_{(2)}O_{(4)}$, here metal ion and iron possess oxidation states of +2 and +3.

Nickel ferrites is one the versatile and technological soft ferrites because of its ferromagnetic properties such as, low conductivity, and thus lower eddy current losses, catalytic behavior, high stability, etc. [2]. It is one of the most important spinel ferrite which finds application in the fabrication of soft magnets and low loss materials at high frequencies. Nickel ferrite have cubic spinel structure. The method which is most suitable for preparation of Ni- ferrite is sol-gel auto combustion method [3]. Sivakumar et al. [4] Prepare nickel ferrite ($NiFe_2O_4$) nanoparticles by a polyvinyl alcohol (PVA) assisted sol-gel auto-combustion method. From SEM and TEM images they confirm that particles have spherical shape, uniform distribution and narrow size. They found that, the nickel ferrite nanocrystal obtained have ferromagnetic property with saturation magnetization (M_s) 51.3 and 47.23 emu g^{-1} . Sen et al. [5] synthesized Ni-ferrite nanoparticles using sol-gel method with urea as a fuel. XRD analysis tell that, formation of single phase Ni-ferrite with $Fd-3m$ space group. From above work they observe the UV-visible spectra indicate the band gap of sample is 5.5eV.

Cobalt has high melting point ($1493^\circ C$) and high thermo stability .it is a semi-hard type of ferrite with chemical formula $CoFe_2O_4$. Semi-hard means the substance can be considered as between soft and hard materials .cobalt ferrite has inverse spinel structure. They has widely studied due to its high electromagnetic performance, excellent chemical stability, mechanical hardness, high coercivity [6]. Mostly it is used to enhance the scope of materials in biomedical field. To prepare cobalt ferrite, various precipitation agents have been used of specific size and shape. Najeehah et al. [7] synthesized cobalt ferrite ($CoFe_2O_4$) using sol-gel auto combustion method and they observed cubic spinel structure having

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crystalline size 35.3nm. the VsM analysis reveals ferromagnetic behaviour have high saturation magnetization which is 62.79emu/g acceptable for different electromechanical and electrical devices.

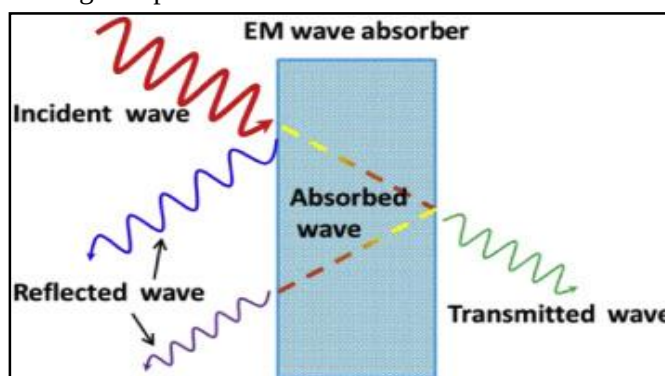


Fig.1 Electromagnetic wave absorption [11]

Ferrite help in achieving high magnetic permeability, low energy loss and a good frequency. Ferrite nanoparticles are excellent physical and chemical properties and good absorption bandwidth. Sol-gel method is most suitable method to prepare the Ni-Co ferrite. Because of this, we choose the material $\text{NiCoFe}_2\text{O}_4$ for the application of wave absorption.

2. Historical background

Before the birth of Jesus Christ the discovery of Ferrite material is abundant, human kind discovered stones that are attract the iron. These stone 1st found in district Magnesia in Asia Minor that's why this stones name become magnetite (Fe_3O_4). Kato and Takei [12] found the magnetic metal oxide in 1930. Ferrites also called the ferrimagnetism iron, cobalt and nickel materials are ferromagnetism. In 1932, Japan's Kata and Takei, who were researchers in chemistry made by chance, two great discoveries regarding ferrites. They discovered that a solid solution of magnetite and cobalt ferrite was strongly magnetized at -300°C .

TDK was founded in 1935 with the aim of commercializing ferrite, Japan's original invention. TDK's ferrite cores were used as antenna cores. The steady progress of soft ferrites which has been made since production was started in 1936, especially has been the results of the consistent efforts made by many workers in chemistry. The value of ferrites as materials for ultrahigh frequency application not realized until 1940, when ferrites were systematically studied by Snoek et al. [13] for applications in devices that send, receive and manipulate electromagnetic signals at radio frequency, microwave and millimeter wave frequencies.

In 1947, J. L. Snoek [14] published the book, *New Developments in Ferromagnetic Materials*. Studies done by Snoek and others at Phillips laboratories in the Netherlands led to magnet ceramics with strong magnetic properties, high electrical resistivity, and low relaxation losses. At about same time, in 1948, L. Neel announced his celebrated theoretical contribution of ferrimagnetism. This deal with the basic phenomenon of "Spin-Spin interaction" taking place in the magnetic sub lattices in ferrites. The stage was now set for the development of microwave ferrite devices. Public attention was through aroused as to the importance of ferrites after the 1950's because new application such as radio, television, carrier telephony and microwave devices were rapidly expanding. The invention of hexagonal ferrite magnets such as the barium and strontium ferrite by Went et al. [15] in 1952. The spinel type ferrite magnet with composition of $\text{Fe}_3\text{O}_4 \cdot \text{CoFe}_2\text{O}_4$ was mass produced as a commercial magnet but was discontinued about 1955. This magnet was replaced by the hexagonal type barium ferrite magnet and strontium ferrite magnet since about 1953. The great achievements were concentrated in the years from 1935 to 1970. Golden age of ferrites can be referred for this 35 year period-the time during great development seen in science and technology of ferrite.

The first international conference on ferrites (ICF), was held in Japan in 1970. However, in Japan the unit price of production of high-performance Nd-Fe-B alloy magnets has become lower since about 1992. This has resulted in an increase in the production of ferrite magnets, which has gradually decreased. A decrease in the output of Japanese banded ferrite magnets also has occurred since about 1992 [16].

3. Types of ferrite

According to the magnetic properties, ferrites are classified into two types; Soft and Hard Ferrites.

3.1. Hard ferrite

Without becoming demagnetized, hard ferrites can withstand an external applied magnetic field. i.e. hard ferrites have high coercivity. Also they have low corrosion tendency. Due to low cost of raw material, hard ferrite core is the cheapest magnet type. These ferrite magnets have very good electrical isolation effects. Low tensile strength and high breakability are the disadvantages of hard ferrite. This type of ferrite core is used for making permanent magnets which can be used in motors and speakers. Examples of hard ferrites are Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) and Cobalt ferrite (CoFe_2O_4).

3.2. Soft ferrite

Soft ferrites are not permanent magnets. These are also called as transformer ferrites, because they change the voltage from primary to secondary windings. They have low coercivity, so they act as conductors of magnetic field by changing their magnetization. Soft ferrite cores are used to make ferrite cores for high frequency applications like inductors and transformers. Soft ferrite materials can be shaped in various shapes (toroids, C shapes, E shapes and curved shapes). High resistivity, high permeability, flexibility in choice of core shapes and low cost are the advantages of the soft ferrites. The most common soft ferrites are Manganese-zinc ferrite (MnZn).

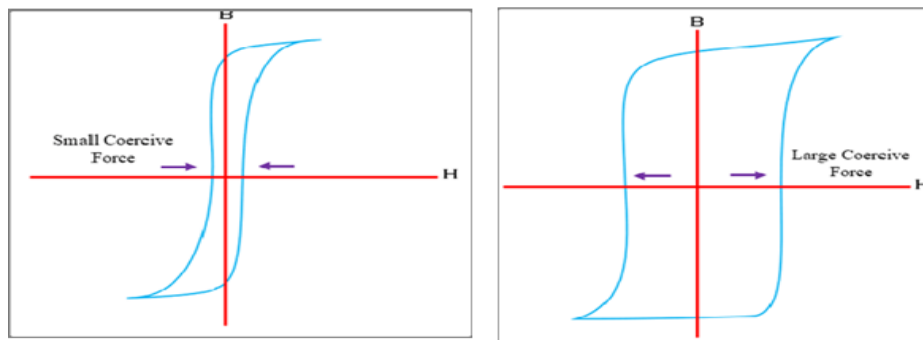


Fig.2 B-H curve for ferrites (a) soft ferrites and (b) hard ferrites

4. Structure of Ferrite

Based on crystal structure, ferrites can be divided into three groups, such as spinel ferrites, Hexagonal ferrites and Garnet ferrites.

4.1. Spinel ferrites

Several ferrites have a spinel type of structure with formula AB_2O_4 . Where, A and B are metal ions. This formula includes the combination of a trivalent cation B (Fe) and divalent metallic cation A (A = Mn, Mg, Co, Ni, Zn). [17].

One unit of ferrite consists of 32 closely packed oxygen atoms, with 64 divalent tetrahedral sites and 32 trivalent octahedral sites. B cation occupies one-eighth of tetrahedral holes and A cation can occupy one-half of octahedral sites. Particularly, A^{2+} and Fe^{3+} occupy 8 tetrahedral and 16 octahedral sites. Based on the position of cation, a spinel ferrite structure can be classified into 3 groups. Such as normal, inverse and mixed [19].

4.2. Hexagonal ferrites

The hexagonal ferrites are ferrimagnetic materials and their magnetic properties are intrinsically associate to their crystalline structure. According to their chemical composition and crystal structure hexagonal ferrites divided into six different types such as, M ($\text{AFe}_{12}\text{O}_{19}$), W ($\text{AMe}_2\text{Fe}_{16}\text{O}_{27}$), X ($\text{A}_2\text{Me}_2\text{Fe}_{28}\text{O}_{46}$), Y ($\text{A}_2\text{Me}_2\text{F}_{12}\text{O}_{22}$), Z ($\text{A}_3\text{Me}_{12}\text{Fe}_{24}\text{O}_{41}$) and U ($\text{A}_4\text{Me}_2\text{Fe}_{36}\text{O}_{60}$) [20]. Where, A is a divalent transition metal.

In a crystal structure; all the related compounds can be understood as a stacking of three basic block units, S, R and T [19]. The crystal structure of barium hexaferrite has space group $\text{P6}_3/\text{mmc}$. The unit cell formula for given structure described as RSR^*S^* , the * indicates that the corresponding sub-unit.

4.3. Garnet ferrites

Garnet ferrite have chemical formula $\text{M}_3(\text{Fe}_5\text{O}_{12})$, where M is yttrium or rare-earth ion. They have structure of the silicate mineral garnet. yttrium iron garnet (YIG) is one of the most common iron garnet.

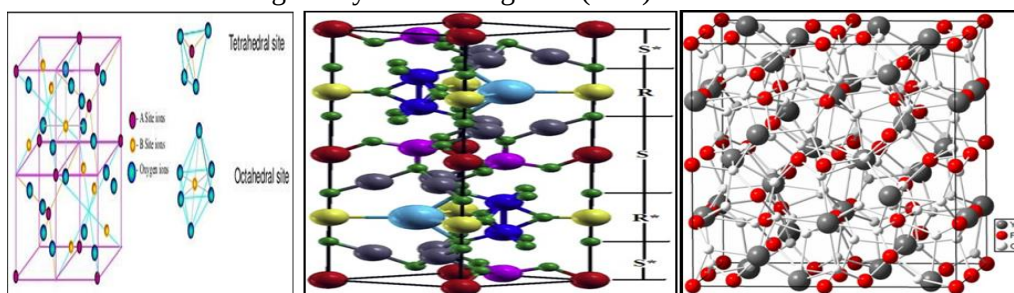


Fig. 2 Structure of spinel ferrite (AB_2O_4) [18], **Fig. 3** Crystal structure of barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) [21], Fig. 4 Crystal structure of Yttrium Iron Garnet (YIG) [22].

In a crystal structure, garnet ferrites have three crystallographic lattice (a, b, c) sites. Among three lattice 24Fe^{3+} ions occupy tetrahedral site, 24R^{3+} ions on the dodecahedral sites, 16Fe^{3+} ions occupy octahedral sites and oxygen ions goes on the interstitial sites [23]. YIG is a versatile ceramic material which has high melting point, large resistivity, high thermal stability and high thermal conductivity. Garnets like YIG have high crystalline quality.

5. Literature review

Gangothri S. Kumar et al. [24] prepared $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x=0.02, 0.04$ and 0.06M) by sol-gel auto-combustion method. They found that, when nickel concentration increases from 0.02 to 0.06M then average crystalline size decreases from 31 to 27nm. From the microstructural parameter they confirm the cubic spinel phase structure of prepared sample. They observed two Raman bands at 486.87cm^{-1} (E_g) and 696.96cm^{-1} (A_{1g}). Using transition metal as substituted metal nitrates this work give effective results. Dong-Hwang Chen et al. [25] produce NiFe_2O_4 prepared by calcining gel precursors with different molar ratios. They observed that the resultant nickel ferrite nanoparticles might be super magnetic and reflecting. Detailed information of the synthesis and characterization of nickel cobalt ferrite by sol-gel method for wave absorption is summarized in following table.

Sr. no.	Material	Method	Synthesis condition	Result	Frequency Range	Ref. No.
1	$\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0.5$)	Heat treatment method	Precursors are dissolved in 75ml of de-ionized water each separately.	On heating upto 600°C, the nanoparticles of Ni-Co ferrite formed stable cubic spinel structure.	-	[26]
2	$\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$	Aerosol method	Proportions of cobalt, nickel and iron nitrates	Particle of 10nm size of Ni-Co	-	[27]

	(x=0, 0.2, 0.4, 0.6, 0.8 and 1.0)		dissolved in water	ferrite have prepared.		
3	$\text{Ni}_{0.30}\text{Zn}_{0.65}\text{Fe}_2\text{O}_4$ Nickel zinc ferrite	Glyoxylate precursor method	Ni(II):Zn(II):Fe(III)=0.35:0.65:2 this combination decomposed at 325°C.	At 400°C Ni-Zn mixed spinel ferrite is formed.	-	[28]
4	ZnF_2O_4 Zinc ferrite	Sol-gel method	Sample sintering at three temperatures (400°C, 600°C, 800°C) for 2h.	Semispherical shaped nanostructure with size 70.71nm-92.03nm.	Max. microwave absorbance at 9GHz.	[29]
5	$\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (x=0.2, 0.4, 0.6, 0.8) Mn-Zn ferrite	Oxalate co-precipitation technique	- Temperature of metal ions maintained at 450°C. - Precipitates dried in oven at 100°C for 8 hours.	- Mn-Zn ferrites synthesized at 450°C. - Cubic spinel structure with crystalline size varies from 11nm to 30nm.	Micro wave oven operated at frequency.	[30]
6	$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ Cobalt zinc ferrite	High energy ball milling	- Powder crushed for 2 hours. - Then sintered at 1250°C for 10 hours.	A high magnetic permeability and losses obtained from ferrite with zinc content.	24.5 dB at 8.6 GHz.	[31]
7	Cobalt ferrite	Sol-gel method	- Co nitrate and Fe nitrate stirred for an hour. - Then mixture was left stirring for 24hours.	Crosslinker and chelating agent to have crucial effect on particle size.	-	[32]
8	MgFe_2O_4 Magnesium ferrite	Polymerization method	Polymerized by treatment at 100°C for 24h, 150°C for 24h, and 200°C for 24hours.	MgFe_2O_4 having n-type semiconducting property.	-	[33]
9	$\text{SrFe}_{12}\text{O}_{19}$ and Fe_3O_4 Strontium and iron oxide.	Co-precipitation method	- Precursor washed and then dried at 100°C. - Calcinated at different temperature from 600 to 900°C for 1hour.	- Sample calcinated at 900°C showed formation of $\text{SrFe}_{12}\text{O}_{19}$. - Spinel/hexagonal structure were synthesized.	400MHz to 32Ghz	[34]

10	$\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Nickel zinc ferrite	Solution combustion synthesis (SCS) technique	Reactant heated at 100°C with magnetic stirring at 300rpm.	- Crystalline size between 44 to 81nm. - The zinc addition increased lattice parameter and decrease crystalline size.	In x band with 8-12 GHz.	[35]
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5. Applications of ferrites

Ferrites prepared in the configuration of nanoparticles has unlock advanced and intresting research field. Ever since the discovery of ferrites have been playing an important role in various application such as biomedical, supercapacitor, catalyst, magnetic resonance imaging (MRI) and gas sensors. This applications are briefly described below.

5.1. Biomedical and Nanowhisiker

Hajar Q. Alijani et al. [36] synthesized the various nanostructures with well-organized characteristics and biomedical applicability with greener method. Spinel nickel ferrite (NiFe_2O_4) nanowhiskers with rod-like structures were synthesized. Nanowhisiker is a type of nanofiber crystal with diameter of less than 100nm. They have various applications in filtration, food packaging, diagnosis, drug delivery, gene delivery, cancer therapy and cell scaffolding. In this study, nickel ferrite nano whiskers were eco friendly synthesized using aqueous extract of rosemary. The toxicity of Ni-ferrite nanowhiskers was improved against leishmania major promastigotes by increasing concentration of nickel ferrite. NoppakunSanpo et al. [37] prepared transition metals of nickel, copper, chromium and zinc were substituted in cobalt ferrite nanoparticles using sol-gel method. They observed cubic spinel structure and shows irregular morphology with crystalline size in range of 40-50nm. Among all of the nanoparticles copper-substituted cobalt ferrite have effective contact biomedical property. The substitution of copper and zinc in cobalt ferrite improved antibacterial activity against *E. coli*.

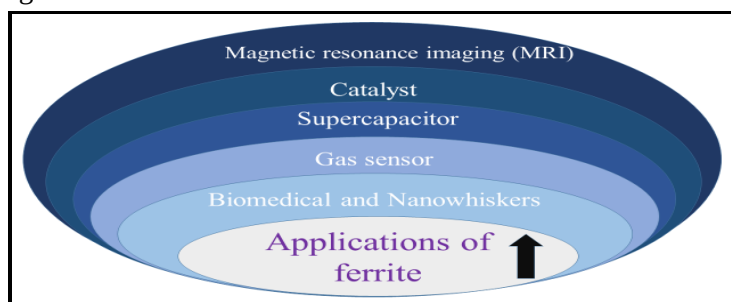


Fig. 5 Applications of Ferrites

5.2. Gas sensor

Florin Tudorache et al. [38] studies structure and gas sensing properties of nickel-cobalt ferrite ($\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$). This paper related to the characterization and preparation of Ni-Co ferrite thin films for gas sensor application. They found that the formation of Fe^{2+} species in presence of Co^{2+} ions in octahedral sites. They investigated the sensitivity to some reducing vapor gases such as acetone, liquefied petroleum gas (LPG), ethyl alcohol and methyl alcohol. They observed that the thin films with $x=0.75$ shows high sensitivity to ethyl alcohol and for $x=0.25$ thin films exhibit high sensitivity to acetone. It was clear that, all thin films are gas sensitive. This sensitivity mostly depends on gas concentration and temperature. Shankaran et al. [39] synthesized $\text{Co}_{0.87}\text{Ni}_{0.13}\text{Fe}_2\text{O}_4$ nanoparticles from metallurgical wastes and improved gas sensing response of nickel doped cobalt ferrite. In this work, nanoparticle pellets used to sense liquefied petroleum gas (LPG) and result are compared with undoped cobalt ferrite. $\text{Co}_{0.87}\text{Ni}_{0.13}\text{Fe}_2\text{O}_4$ sensor shows speedy response recovery time, high sensing response and long-term stability. The LPG gas

sensing performance of Ni-Co ferrite sensors calculated by determining the gas sensing response at a constant gas concentration of 5000 ppm. P. Durga Prasad et al. [40] prepared cobalt ferrite (CoFe_2O_4) using electrospinning technique. Magnetic hysteresis loops of CoFe_2O_4 shows ferromagnetic nature, coercivity of 948 Oe and maximum saturation magnetization of 76.5 emu/g. they investigated that, the sensing response of cobalt ferrite towards ammonia was much better than other gases such as methanol, 2-propanol, acetone, ethanol. Also cobalt ferrite fibre have ability to sense very low concentration of ammonia.

5.3. Supercapacitor

Bharadwaj et al. [41] studied and prepared $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ - activated carbon composite using sol-gel method for the application of super-capacitance. They observed magnetization of 2.9 emu/g and coercivity of 442.015 Oe shows a soft ferromagnetic nature. The NCFO-AC composite show specific capacitance of 1242.5 F/g in presence of external magnetic field and in absence magnetic field it exhibited only 574.9 F/g. the composite show capacitance retention of 98.34% after 10,000 cycles reveals high stability. S. Martinez-Vargas et al. [42] studied the use of cobalt ferrite nanoparticles for fabrication of supercapacitors. When they are synthesized with concentrations of cobalt 0.25 and 33 mol% then they found that, the cobalt ferrite have quasi-spherical shapes. When cobalt concentration increases from 0 to 33 mol%, then the capacitance was enhanced from 77.8-337.1 Fg^{-1} but also discharge times from 1650 to 4957 s. The discharge time and enhancement of capacitance was associated to the electrical conductivity of the anodes and increase of the surface area.

5.4. Catalyst

Razlescu et al. [43] prepared $\text{Ni}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$ spinell ferrites using sol-gel self-combustion method. In the catalytic combustion of acetone, benzene and propane, the catalytic properties of ferrite nanopowders were tested. The $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ has spinel structure and it has helpful effect on catalytic activities. They found that the scandium substituted Ni-Co ferrite is most active catalyst and can be a good candidate for catalytic combustion of acetone or propane. Charanjit et al. [44] studies exploration of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles as catalysts for reduction of 4-nitrophenol and photo-oxidative degradation. They found the ordered cubic spinel structure with spherical particle having crystallite size 4-6nm. For reduction of 4-nitrophenol to 4-aminophenol $\text{Co}_{0.4}\text{Ni}_{0.6}\text{Fe}_2\text{O}_4$ shows the best catalytic activity in presence of NaBH_4 . They observed cobalt ferrite was found to be catalytically inactive in this work. Also NiFe_2O_4 and $\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ observed to be best catalyst.

5.5. Magnetic resonance imaging (MRI)

Huixia Wu et al. [45] synthesized cobalt ferrite magnetic hybrids using solvothermal method. These cobalt ferrite prepared at 180°C based on high hydrophilicity and superparamagnetic property. Investigated for biomedical applications. They observed that the anticancer drug doxorubicin (DOX) can be loaded onto the hybrids. CoFe_2O_4 -180 hybrid shows low cytotoxicity and hemolytic activity and good MRI enhancement effect on cancer cells. Therefore, CoFe_2O_4 -180 hybrids have good stability to be used as MRI contrast agent and anticancer drug delivery systems. Arshad et al. [46] studied cobalt ferrite as contrast agent for MRI experiment. They prepared cobalt ferrite and iron oxide nanoparticles using co-precipitation method. MRI experiment performed at MRI diagnostic center at Rawalpindi at low field MRI unit (0.35 Tesla) using spin echo, the MRI images of stomach and liver of rabbits were taken with $\text{TE}=15\text{ms}$ and $\text{TR}=400\text{ms}$. They found that, the high signal intensity is induced from cobalt ferrites compared to iron oxides.

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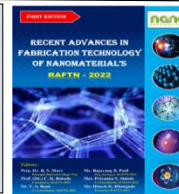
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Temperature Domain Thermal Conductivity Engineering of One-Dimensional Silicon Square Nanowire

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KEYWORDS

Thermal Conductivity;
 Dynamics Simulation;
 1D Nanostructures,
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 Nanoscale Nanomaterials.

ABSTRACT

For investigation of thermal conductivity in nanoscale nanomaterials, various experimental methods and theoretical predictions are considered. Nowadays, rising up of modelling and simulation is because it is a critical tool for researchers which allow optimizing designs without complications and the significant cost of nanofabrication processes. Thermal conductivity is a critical parameter to enhance the performance of thermoelectric devices. Silicon square nanowire (SiSqNw) is scalable thermoelectric material. Engineering thermal conductivity at nanoscale dimensions is more challenging. In this paper, the length of the simulation cell taken is 29.3618 nm and the empirical interatomic potential used for Si-Si interaction is Stillinger-Weber potential. Thermal conductivity of silicon square nanowire at temperature of 0.001K to 10,000K varied logarithmically is calculated by nonequilibrium molecular dynamics simulation (NEMD). At 300 K temperature, thermal conductivity of silicon square nanowire (SiSqNw) is 2.75451 W/mK. The dependence of novel properties of silicon square nanowire such as accumulative kinetic energy, average temperature, and thermal conductivity on temperature is studied.

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1. Introduction

At nanoscale level and in real experiments which are difficult to perform, the molecular dynamics (MD) simulation is an alternative to predict the thermal conductivity, to unveil the mechanism and factors affecting heat conduction in nanowires [1]. The MD has become a valuable and promising tool in the field of thermal science and plays an important role in predicting thermophysical properties of materials from atomic/molecular viewpoint. Molecular dynamics simulation is used for solids within the classical limit which shows temperatures higher than the Debye temperature [2]. High thermal conductivity reduce device temperatures by removing heat to improve performance of nanoelectronics and optoelectronics, while low thermal conductivity is useful in thermoelectric for improving the figures of merit ZT of material. $ZT = S^2 \sigma T / k$ Where S is Seebeck coefficient, σ is electronic conductivity, T is temperature, k is thermal conductivity [3]. Thermal conductivity is utmost important thermophysical property for thermal management and thermoelectric applications[4].

Low thermal conductivity is of particular interest in thermoelectric applications [5]. The efficiency of thermoelectric devices depends upon the thermal conductivity which converts heat energy to electricity [6] Because of a higher surface to volume ratio, a significant reduction of the thermal conductivity is observed in nanowires [7]. The thermal conductivity of silicon nanowires is about two orders of magnitude smaller than that of bulk crystals due to the strong surface inelastic scatterings [8]. Nonequilibrium molecular dynamics simulation is based on Fourier law of heat conduction which expresses thermal conductivity as the ratio of heat flux to temperature gradient [4].

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Semiconducting silicon nanowires attracted great attention in recent years due to their excellent electrical and mechanical properties and potential applications in many areas solar cell [9], field effect transistors[10], lithium ion batteries. Thermal conductivity of SiSqNw within a temperature domain of 0.001K to 10,000K is not studied yet. So, the present work investigates the thermal conductivities of SiSqNw at different excitation temperature.

This study also investigates the dependence of thermal properties of SiSqNw on a) time domain accumulative kinetic energy at different temperature; (b) position domain average temperature at different excitation temperature; (c)time domain average temperature in the silicon square nanowire at different excitation temperature;(d) time domain kinetic energy at different temperature; (e) kinetic energy dependent thermal conductivity of the silicon square nanowire; (f) temperature dependent thermal conductivity of the silicon square nanowire.

2. Methodology

By using Stillinger-Weber inter atomic potential [11] model for Silicon and Nonequilibrium molecular dynamics simulation, time dependent positions $r_i(t)$ of silicon nanowire and velocities $v_i(t)$ of the nanowire atoms are calculated.

The Thermal conductivity is calculated using heat flux J to form temperature gradient. The heat flux J continuously transfer energy from hot bath to cold bath[12]

$$J = \frac{\sum_{N transfer} \frac{1}{2}(m_h v_h^2 - m_c v_c^2)}{t transfer} \quad (1)$$

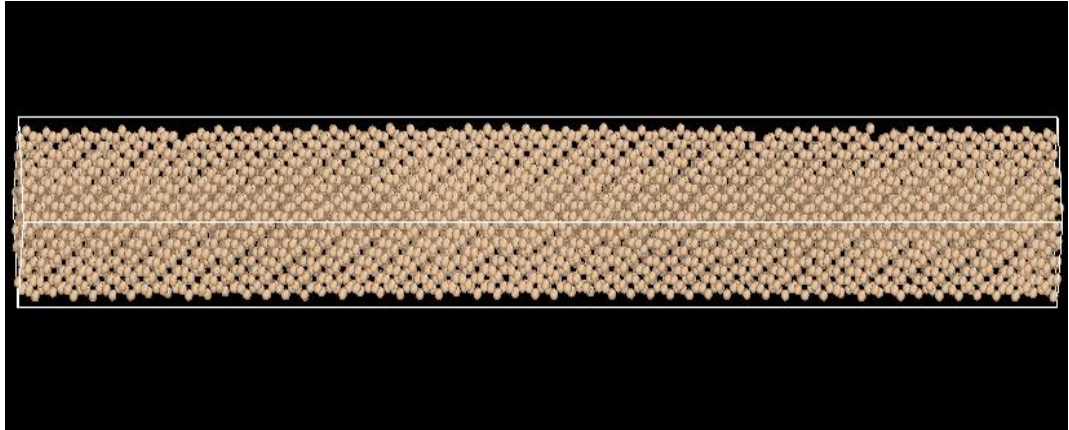


Fig.1 Silicon square nanowire directed along z direction

The heat flux is imposed by a velocity swapping technique. Atoms with the largest K.E. (i.e. hottest) in the heat sink are exchanged with those with lowest K.E.(i.e., Coolest in the heat source). The simulation cell is divided into even number of bins. The temperature of each bin and its temperature gradient is calculated by averaging the atomic K.E. over time as well as overall the atoms in the bin. The temperature $T_{MD}(z)$ of a bin along the z-direction (i.e. the direction of heat flux) at every time step is determined from statistical mechanics equipartition theorem as

$$T_{MD(z)} = \frac{1}{3n_k k_B} \sum_{i=1}^{n_k} m_i v_i^2 \quad (2)$$

Where k_B is the Boltzmann constant, n_k is the number of atoms in the bins about z and m_i and v_i are the mass and velocity of individual atoms i respectively [13]. Position domain average temperature at different excitation temperature is used to calculate temperature gradient $\frac{\partial T}{\partial x}$. Thermal conductivity λ is calculated by Fourier's law

$$\lambda = \frac{J}{2A \frac{\partial T}{\partial x}} \quad (6)$$

Where, J is heat flux and $\frac{\partial T}{\partial x}$ is temperature gradient.

3. Simulation Set Up

For this NEMD simulation, silicon square nanowire is orientated along the z [001] direction. In NEMD method the simulation cell length in the transport direction is supposed to be sample length as in real experiment [14]. Here periodic boundary condition is along z direction and free boundary condition is along X and Y directions. In this study, the length of the simulation cells is 29.3618 nm. The cell parameter of Si is 0.543737037nm. Along the transport direction, simulation cell has 24 bins of silicon material. To calculate thermal conductivity, simulation cell is divided into 24 bins along z [001] axis. The cross-sectional area of the simulation cell is (5 x 5 x 54-unit cells) which gives 10800 atoms. The effective size of transport is 14.6809 nm. Hot and cold heat baths have 3 bins. Non-equilibrium molecular dynamics (NEMD) simulations is performed using inhouse code via Nano-HUB [15]. For the thermalization run, the initial temperature of the system is 300 K and thermalization has been done for 10,000 MD steps, which equilibrate the system to the desired temperature. The time for MD is 2 fs. Next temperature ranges from 0.001K to 10,000 K is applied to both heat baths. The temperature of the heat bath is maintained at particular temperature for every cycle of the simulation through re-scaling the velocity of the atoms in that region to fit the Boltzmann distribution for the specific temperature. Interatomic potential used is Stillinger-Weber potential and 40,000 MD time steps are used to run simulation. First 20,000-time steps are used to achieve steady state of the heat transport and remaining 20,000-time steps are used to run thermal conductivity calculations.

4. Results and Discussions

Figure 2 depicts the simulated atomic trajectories of SiSqNw is visualized within excited temperature range with the help of OVITO [16]. From Atomic trajectories, It can be seen that as temperature increases atoms of SiSqNw are disordered more with respect to earlier one. At 10000K atoms of SiSqNw crosses it's own boundary.

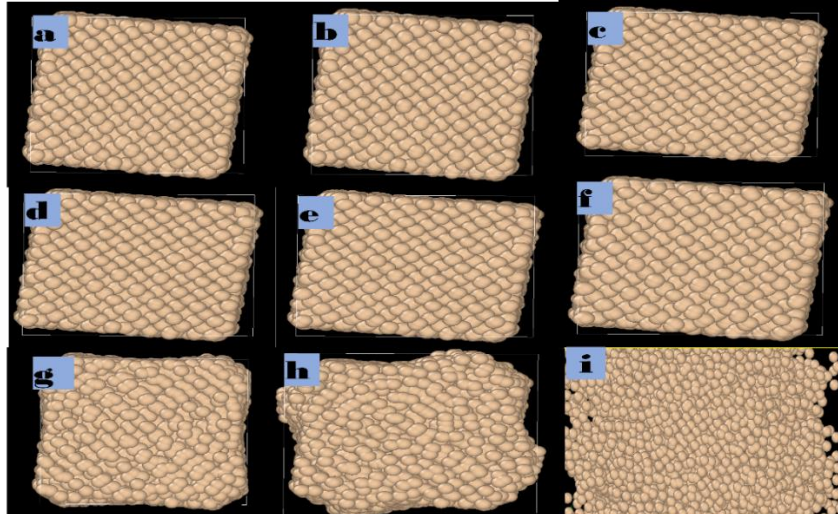


Fig. 2 Atomic trajectories of SiSqNw at temperature of a)0.001K, b)0.01K, c)0.1K, d)1K, e)10K, f)100K, g)300K, h)1000K, i)10000K

In order to validate the computational model of SiSqNw the simulation is carried out and shown in Fig. 3. The accumulative kinetic energy is found to be low at lower temperature and found to be increased at higher temperature. Furthermore, sudden change in the accumulative kinetic energy is observed for all scanned temperature range and become saturated after some time. The average temperature in units of Kelvin versus position in units of angstrom is plotted at differing temperature ranges from 0.001K to 10000K for the simulated system. At the cold bin and Hot bin, the temperature is nonlinear due to size effect [17]. In order to avoid edge effect, middle linear portion has been used to extract temperature gradient for the determination of thermal conductivity using following equation $\lambda =$

$\frac{J}{2A\partial T/\partial x}$. The factor 2 in the denominator is used to account for the periodicity of the system [18]. The average temperature in units of Kelvin versus time in units of picoseconds at different temperature range of 0.001K to 10000K are calculated for system. The linear behavior is observed at higher temperature whereas non-linear behavior is observed at lower temperature. The kinetic energy in units of Kcal/mol versus time in units of picoseconds is plotted at different excitation temperature. From the simulation, it is observed that the thermal conductivity of material is decreased as the kinetic energy is increased. Further increase in the kinetic energy, a sudden increase in the thermal conductivity is observed. In addition to this the thermal conductivity is found to decrease at higher kinetic energy. Thermal conductivity is found to decrease with increase in temperature upto 1K and again thermal conductivity rises upto 300K. From 300K temperature, thermal conductivity decreases upto 10,000K temperature. This is due to the fact that at low temperature, k is proportional to T^3 while phonon mean free path is constant. Above 300K, thermal conductivity starts to decline. This is because heat capacity is constant at high temperatures whereas thermal conductivity is inversely proportional to temperature.

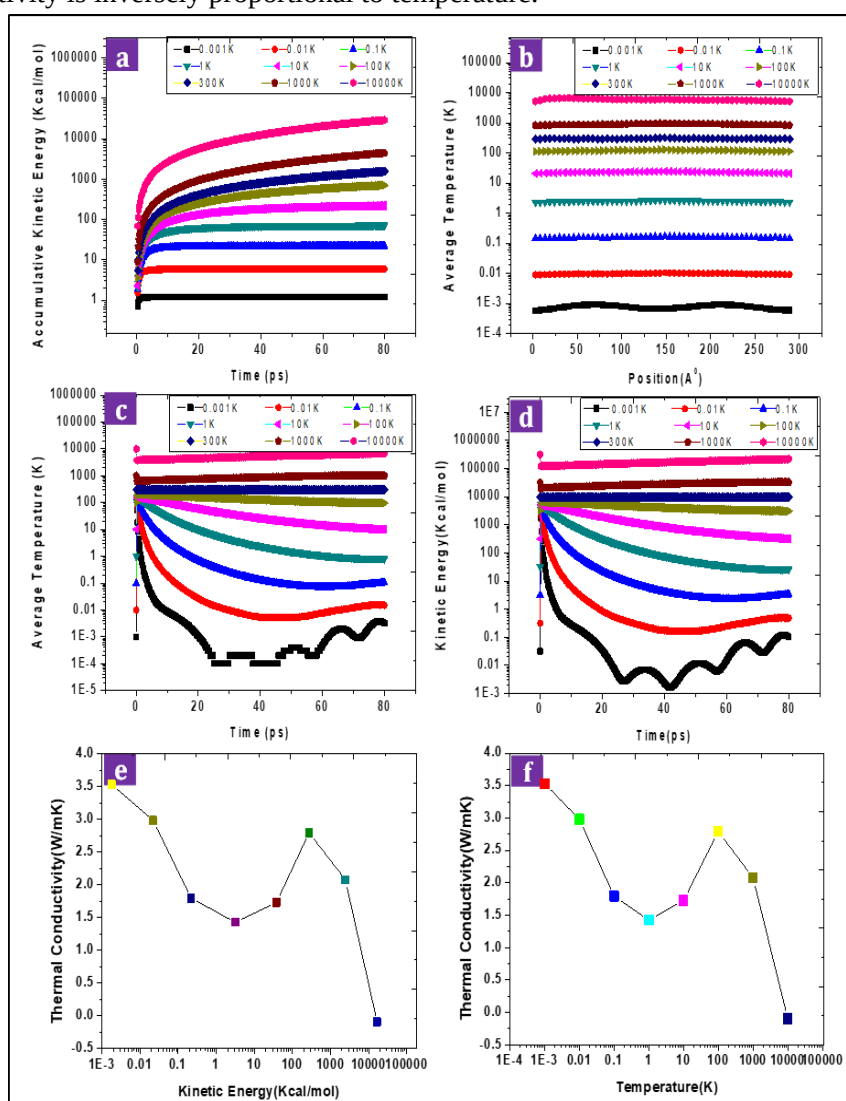


Fig. 3: Thermal properties of Silicon Square Nanowire. (a) time domain accumulative kinetic energy at different temperature; (b) Position domain average temperature at different excitation temperature; (c) Time domain average temperature in the Silicon Square Nanowire at different excitation temperature; (d) time domain kinetic energy at different temperature; (e) kinetic energy dependent thermal conductivity of the Silicon Square Nanowire; (f) temperature dependent thermal conductivity of the Silicon Square Nanowire.

5. Conclusions

In this chapter, non-equilibrium molecular dynamics simulations are performed to explore the thermal conductivity engineering of SiSqNw at a temperature range of 0.01K to 10000K. The thermal conductivity of silicon square nanowire increases with rise in temperature from 1K upto 300K and then considerably decreases. This is due to the fact that at low temperature, k is proportional to T^3 while phonon mean free path is constant. Above 300K, thermal conductivity starts to decline. This is because heat capacity is constant at high temperatures whereas thermal conductivity is inversely proportional to temperature. At 300 K temperature, thermal conductivity of SiSqNw is 2.75451 W/mK. Low thermal conductivity is useful for researchers in thermoelectric applications. This chapter paves the way to better understand thermal management.

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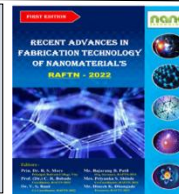
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Anti-microbial properties of copper Doped zinc oxide Nanoparticles

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1. Introduction

In recent years, among metal oxide NPs, a lot of research focused on zinc oxide, because it has strange, chemical, optical, magnetic and mechanical Properties. Zinc oxide is an Inorganic Compound with the Formula ZnO. It is white powder that is insoluble in water. Zinc oxide is most studied material in metal oxides. Zinc oxide can called multifunctional material because of their unique physical and chemical properties like high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability. In material science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. ZnO shows huge band gap energy of 3.3 eV along with high excitation energy of about 60 eV and high thermal and mechanical stability at room temperature make it attractive for potential use in electronics, optoelectronics and laser technology. Zinc oxide is a material which, under ordinary circumstances, has a small oxygen deficiency. This lack of chemical makes ZnO and n-type doped with a aluminium, gallium or indium is transparent and conductive (transparency~90%, lowest resistivity~ $10^{-4}\Omega\text{cm}$).

The Piezo and Pyroelectric properties of ZnO So it can be used as sensor, converter, energy generator and photo catalyst in hydrogen production because of their hardness, rigidity and piezoelectric constant it play important role in ceramics industry, while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicine and in pre-ecological system. Zinc oxide is widely used in many areas because of their chemical and physical properties. The powder ZnO is used as additive in numerous material and products including ceramics, glass, paints, ointments, plastics, cement, rubber (e.g. Car tyres), lubricants, Sealants, pigments, food(source of Zn nutrients), batteries and fire retardants. An antimicrobial is an agent that kills microorganisms or stops their growth. Antimicrobial medicines can be grouped according to the microorganisms they act primarily against. For example, antibiotics are used against bacteria, and antifungal are used against fungi.

1.1. Antimicrobial Properties

Antimicrobial activity can be defined as a collection as a collective term for all active principles (agents) that inhibit the growth of bacteria, prevent the formation of microbial colonies, and may destroy microorganisms. Nanoparticles is a small principle that ranges 1 to 100 nanometres in size. Antimicrobial activity of any compound can be defined as the mechanism which help in destruction or inhibition of bacterial growth as per The American Heritage Medical Dictionary 2007[1].Antimicrobial Activity of silver, gold, copper and zinc nanoparticles have been demonstrated by some scientists across the world. When compared to chemically synthesized nanoparticles, the biogenic nanoparticles show higher antimicrobial activity. The utilization of metal and metal-oxide nanoparticles for antimicrobial performance is attracting much attention, as several of these suggest superior activity towards resistant microorganisms [2].The substitution of zinc in cobalt ferrite nanopowders improved significantly the antibacterial activity against E. coli and S. aureus. The antibacterial activity of zinc-substituted cobalt ferrite nanopowders against E. coli was higher than S. aureus [3]. Birajdar et al. [4] studied structural, morphological and optical properties of ZnO nanoparticles synthesized by sol-gel auto combustion method to find effect of Co^{2+} ions. The absorption result spectra show that the electronic structure of ZnO

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nanoparticles can be tuned when Co^{2+} ion is doped into ZnO lattice which may give good optical properties. The energy band gap of the present system for undoped ZnO is 3.344 eV and it starts decreasing in 0.06 and 0.12 of Co^{2+} doped ZnO samples and found to be 3.253 and 3.168 eV with doping concentration. They reported that the small amount of Co^{2+} introduced ZnO metal ions nanoparticles can control structural, morphological and optical properties. Ranjith Kumar et al.[5] studied antimicrobial activities of zinc oxide nanoparticles. They synthesized zinc oxide nanoparticles using natural fuels (Honey and Cow urine) by combustion method. Gram Positive (*B. subtilis*) and Gram Negative (*E. Coli*) bacteria were tested using plate counting technique. They reported that the cow urine prepared ZnO nanoparticles shows strong antimicrobial activities as compared with honey-assisted ZnO nanoparticles.

1.2. Classification

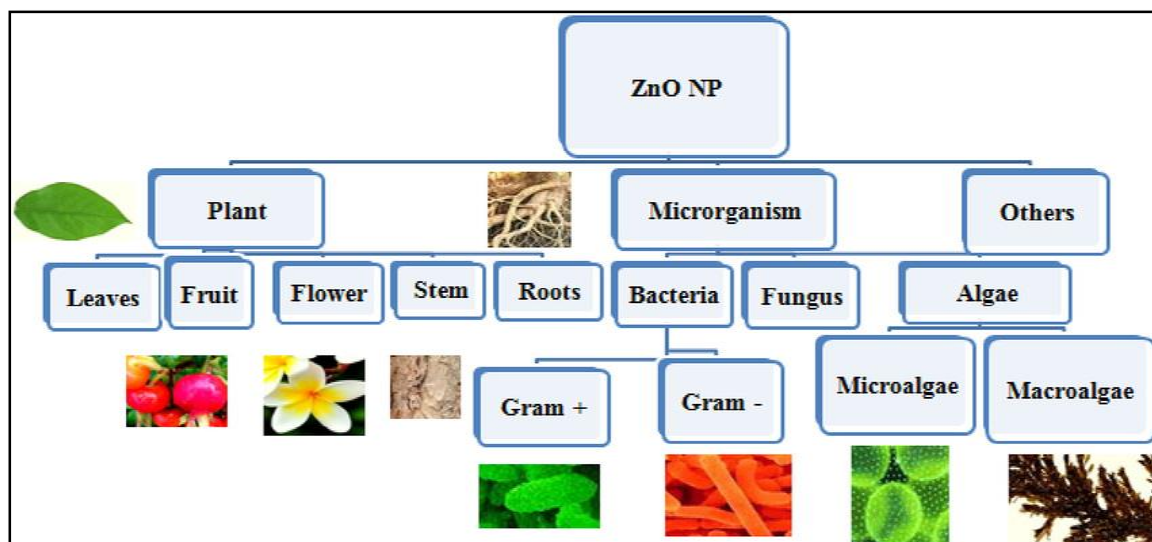


Fig-1. Classification of plant and microorganism [18]

Zinc oxide is widely used material in metal oxides, it is multifunctional material. In recent years, a lot of research focused on Zinc oxides as a nanoparticle. So we decided to use zinc oxide material nanoparticles synthesized using sol gel auto combustion method and studied its antimicrobial properties for gram positive and gram negative bacteria

2. Historical background

The history of antimicrobials begins with the observation of Pasteur and Koch, who discovered that one type of bacteria could prevent the growth of another. They did not know at that time that the reason one bacterium failed to grow was that the other bacterium was producing an antibiotic. Technically, antibiotics are only those substances that are produced by one microorganism that kill, or prevent the growth, of another microorganism. The discovery of antimicrobials like penicillin by Alexander Fleming and tetracycline paved the way for better health for million around the world. Before penicillin became a viable medical treatment in the early 1940s, no true cure for gonorrhoea, strep throat, or pneumonia existed. Patients it infected wounds often had to have a wounded limb removed, or face death from infection. Now, most of these infections can be cured easily with a short course of antimicrobials.

Antimicrobial have revolutionized medical science during the 20th century. The history of antimicrobial discovery the 20th century. The history of antimicrobial discovery has been a long and storied one culminating in strides in the fight against human disease. The term antibiotic was first used in 1942 by Selman Waksman and has collaborators in journal articles to describe any substance produced by a microorganism that is antagonistic to the growth of other microorganism (such as gastric juices and hydrogen peroxide). It also excluded synthetic antibacterial compounds such as the sulphonamides. Many antibacterial compounds are relatively small molecules with molecular weight of less than 2000 atomic

mass units. With advances in medical chemistry, most of today's antibacterials chemically are semi synthetic modifications of various natural compounds.

The first antimicrobial agent in the world war salvarsan, a remedy for syphilis that was synthesized by Ehrlich in 1910. In 1935, sulfonamides were developed by Domagk and other researchers. These drugs were synthetic compounds and had limitations in terms of safety and efficacy [6]. Since the late of 19th /early 20th century, many antimicrobial drugs have been developed and released onto the market worldwide, treating a variety of infectious diseases. They include antibacterials, antivirals, and antifungal and antiphrastic drugs. Continuing improvements have been made for antimicrobial agents in various aspects in addition to the antimicrobial spectrum and activity. The drugs have been developed to achieve better pharmacodynamics including the absorption of oral drugs, concentrations in the blood, and distribution to inflammatory focus. In addition, as antimicrobial chemotherapy has been established and matured, more importance has been attached to the drug safety. Antimicrobial agents that are associated with serious side effects have been replaced by other safer drugs [6].

1.3. ZnO nanoparticles

Zinc oxide is an inorganic compound with the molecular formula ZnO. It appears as a white powder and is nearly insoluble in water. The powder ZnO is widely used as an additive in numerous materials and products including ceramics, glass, cement, rubber (e.g., car tyres), lubricants, paints, ointments, adhesive, plastics, sealants, pigments, foods (source of Zn nutrient,) batteries, ferrites, and fire retardants. In Earth crust ZnO is present as zincite is mineral but mostly ZnO used for commercial purposes is produced synthetically [7].

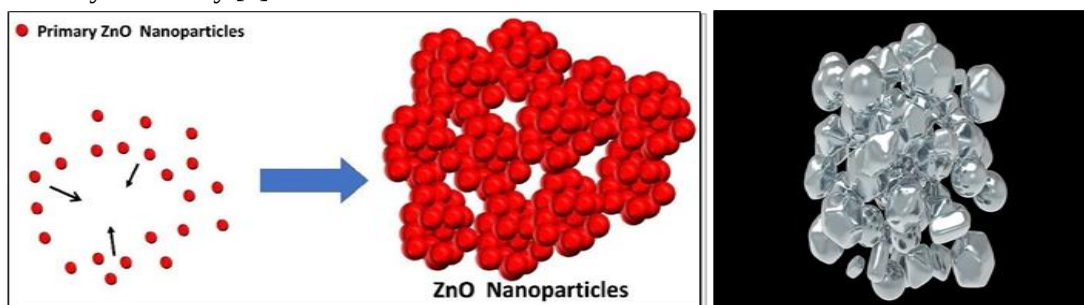


Fig. 2 Zinc oxide nanoparticles [19]

Zinc oxide nanoparticles are nanoparticles of zinc oxide (Zno) that have diameters less than 100 nanometres. They have a large surface area relative to their size and high catalytic activity. The exact physical and chemical properties of zinc oxide nanoparticles depend on the different ways they are synthesized.

Zinc oxide nanoparticles are the nanoparticles of a zinc oxide (ZnO) that have diameters less than 100 nm. They have a large surface area related to their size and high catalyst activity. The Extract physical and chemical properties of zinc oxide nanoparticles depend upon the different ways they are synthesized. Some possible ways to produce zinc oxide nanoparticles are hydrothermal method, electrochemical deposition, sol-gel method, chemical vapour deposition, thermal decomposition, combustion method, ultra sound micro wave associated combustion method, two state thermal synthesize anodization co-precipitation using a solution. Concentration pH and washing medium zinc oxide is widely gap semiconductor with an energy gap 3.37 ev at room temperature.

ZnO nanoparticles are believed to be one of the three most produced nanomaterials, along with Titanium Dioxide and Silicon Dioxide nanomaterials most common use of zinc nanoparticle is an sunscreen they are used because they effectively absorb ultraviolet light posses a large enough band gap to be completely transparent to the visible light. They are also be can investigated to kill harmful microorganism in packing uv protective material such as a textile.

1.4. Crystal Structure

Crystallization of zinc oxide exists in two types: cubic zinc-bled and hexagonal wurtzite structure. The structure of wurtzite is stable and common in ambient situations. At ambient temperature and pressure, zinc oxide is crystal in the wurtzite structure type B4[8]. Structurally, ZnO has a non-centrosymmetric wurtzite crystal structure with polar surfaces. The wurtzite structures of ZnO can be considered to be composed of two interpenetrating hexagonal close packed (hcp) sublattices of cation (Zn) and anion (O) displaced by the length of cation-anion bond in the c-direction.

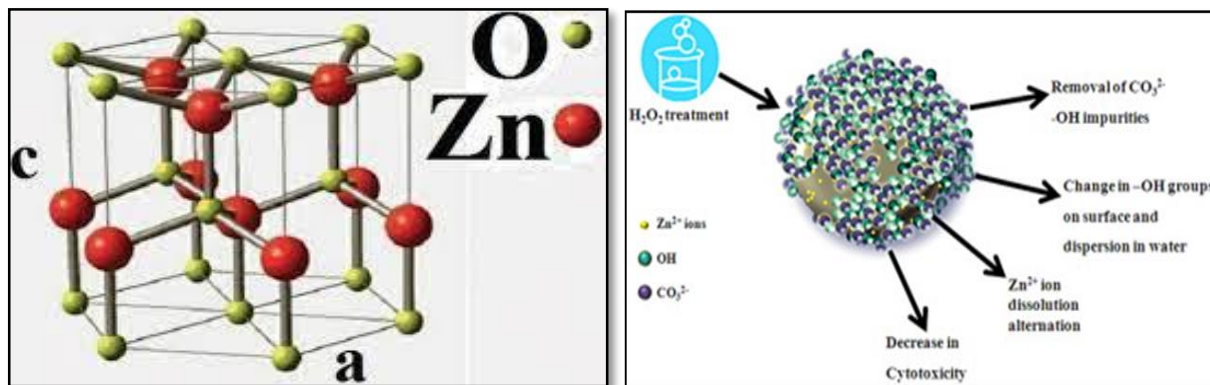


Fig. 3 Crystal structure of zinc oxide, **Fig 4.** Surface properties of Zinc oxide nanoparticles

Crystal structure of zinc oxide is lattice parameters, band structure, mechanical properties including elastic constant, piezo electric constant, lattice dynamics, vibrational process, low field and high field carrier transport is treated. The wurtzite structure has a hexagonal unit cell with a two lattice parameters a and c as a ratio $c/a = \frac{\sqrt{8}}{3} = 1.633$ (in an ideal wurtzite structure) and also begin to space group C_{6v}^4 in the schoenflies notation and $p6_3mc$ in Hermann-Mauguin notations. The structure composed two interpenetration hexagonal packed (hcp) sub lattice each consist of displayed with respect to each other along three fold c axis by amount $u = 3/8 = 0.375$.

1.5. Properties of Zinc Oxide Nanoparticles

Zinc oxide NPs have different physical properties. It should be noted that since the dimensions of semiconductor materials are continuously reduced to a nanometer or even smaller size, several physical properties fall under the effects of changes called (quantum size effects). For instance, quantum confinement rises the energy band gap of quasi, one-dimensional (Q1D) zinc oxide, which was accepted via optical radiation[8]. Zinc oxide nanoparticles are widely used in industrial processes, electronic and consumer products due to their unique optical, electronic, and structural properties that are absent in bulk ZnO. The Principal parameters of nanoparticles are their shape, size, surface characteristics and inner structure.

Zinc oxide has been great interest because excellent physical properties such as low cost, toxicity, high thermal stability, photosensitivity, advance optical properties and environmental friendly features. Therefore, ZnO has been widely used in many field such as a absorption, paint, cosmetics, superconductor catalyst as a effective photocatalyst in the degradation president organic compound catalyst support zinc oxide should be have sufficient structure to allow diffusion activity and electronic transfer. Well designed zinc oxide has high perform degraation dyes promised photocatalyst. Zinc oxide with a widely band gap energy 3.37 eV and high exciton binding energy (60mv) could absorb and larger fraction of UV spectrum to oxidised harmful substance.

H. Agarwal et al[18] studied on antibacterial action of zinc oxide nanoparticle synthesized using green route method. They synthesize green method of zinc oxide nanoparticles (ZnO NPs) and its antibacterial applications has been particularly discussed in review literature the present studied of

highlight differential nanoparticle attach to gram positive and gram negative bacteria surface and different mechanism adopted by the nanoparticles for bacterial control pharmacokinetics and applications of zinc oxide NP are discussed briefly. S. Gharpure and B. Ankamwar[1] studied synthesis and antimicrobial properties of zinc oxide nanoparticles. These review focus on different synthesis method of zinc oxide nanoparticles various analytical technology frequently used for testing antimicrobial properties, mechanism explaining antimicrobial nature of zinc oxide nanoparticle as well as different factor affecting the antimicrobial properties.

1.6. Applications

ZnO NPs have attracted intensive research efforts for their unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics. Zinc oxide nanoparticles have their own importance due to their vast area of applications. Such as gas sensor, biosensor, cosmetics, storage, optical devices, window material for displays, solar cells and drug delivery[7].

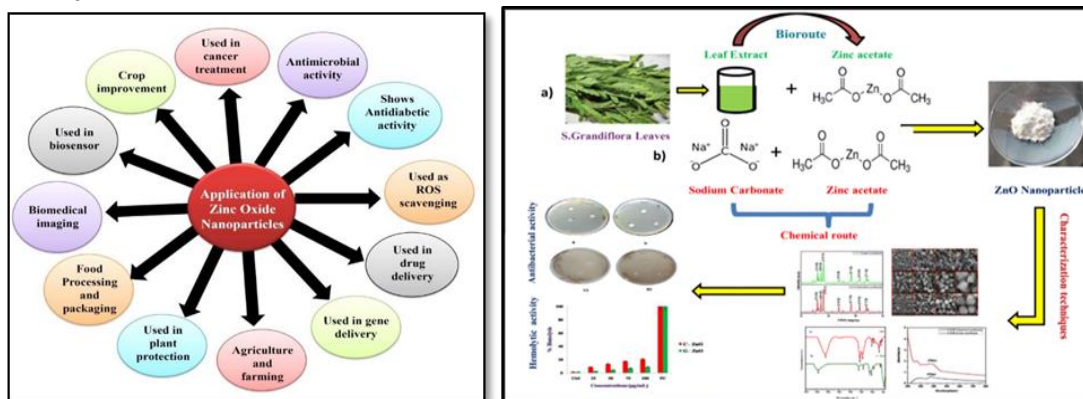


Fig. 5. Medical uses of ZnO NPs [27] **Fig. 6.** various application of ZnO nanoparticles [28].

1.6.1. ZnO as a Gas Sensor

ZnO sensors are good candidate for the detection of explosive and toxic gases. ZnO nanostructures can be synthesized by physical and chemical routes. Sensing response can be enhanced by modification of ZnO nanostructures. Sensing mechanism of ZnO sensor is depends on the adsorption/desorption of gas. Gas sensors work on the principle of transforming the gas adsorption effects on the surface of the active material into a detectable signal in terms of changed electrical, optical, thermal, mechanical, magnetic (magnetization and spin), and piezoelectric properties.

S Roy and S. Basu [34] improved zinc oxide film for gas sensor applications. Zinc oxide is a versatile material for different commercial application such as transparent electrodes, piezoelectric devices, varistors. The result of this application is good quality ZnO thin films, as produced by a modified CVD technique, developed in laboratory, showed the performance of a superior DMA sensor at an optimum operating temperature of 300°C. The selectivity for DMA in air, with respect to hydrogen, was also very good. M. S. Wagh et al[35] Modified zinc oxide thick film resistors as NH₃ gas sensor. Screen printed thick films of pure and RuO₂-doped zinc oxide were prepared. Pure zinc oxide films were also surface modified with ruthenium chloride. Gas sensing properties of the pure, doped and surface modified films were studied. The films were observed to be most sensitive to NH₃ gas.

1.6.2. Medical Uses of ZnO NPs

ZnO NPs play some potential role in CNS and perhaps during development processes of diseases through mediating neuronal excitability or even release of neurotransmitters. Some studies have indicated that ZnO NPs affected functions of different cells or tissues, biocompatibility, and neutral tissue

engineering but little information is present about influences on CNS and CNS related diseases. However, due to its targeting potential ZnO NPs have potential utility in cancer treatment [9].

1.6.3. ZnO used in Drug Delivery

Hamed mirzaei and Majid Darroudi studied zinc oxide nanoparticles by nanosynthesis and biomedical application [21] among of various applications of nanotechnology, drugs deliver has been emerged as a power for to in treatment of different diseases such as cancer NPS are one of the main system in drug delivery ,in a study et used of zinc oxide quantum dots as a drugs delievery system of targeting doxorubicin to hela cells ZnO is also known as one of will semiconductor which has good potential replacing the traditional cd related species used in biology and optical land space ZnO is known as safe matter generally ZnO has been utilised in sunscreen product in food plane packing is used as food adective has hence the luminescent properties of ZnO NPS could be used in various biological and medical applications.

1.6.4. ZnO used in Agriculture

Sidra Sabir et al. [7] studies the zinc oxide nanoparticles for Revolutionizing Agriculture Synthesis and Application. Agriculture is backbone of third world economics but unfortunately now, the agriculture sector is facing various global challenges like climate changes, urbanization, sustainable use of resources and environmental issues such as runoff, accumulation of pesticides and fertilizers; human population is increasing day by day and food demand is growing rapidly and estimated population increase in world from current level. Zinc oxide NPs have potential to boost the yield and growth of food crops. Peanut seeds were treated with different concentrations of zinc oxide nanoparticles.

The use of zinc oxide as an inorganic micronutrient fertilizer includes direct application of soils to correct the zinc deficiency, root dipping and seed coating before crop transplant but also as ingredient for foliar application of zinc. These are widely used, especially with fruit trees and grapevines.

1.6.5. ZnO used in bio sensor

S. S. Bhat et al. [31] studied ZnO nanostructures based Biosensors for Cancer and Infectious Disease Applications, Perspective, Prospects and Promises. Biosensors are the devices for detection of biological analytes which have wide applications, including biomarker detection for medical diagnostics, and pathogen and toxin detection in a specimen by binding analyte on the reactive surface. These bio-sensors are based on analytical information obtained by converting the bio recognition process into a potential signal monitoring the potential of a system at a working electrode, an accurate reference electrode, under conditions of essentially zero current flow. ZnO has been recognized as a good candidate for biosensor applications because of its high isoelectric point (IEP), cost effectiveness, nontoxicity, and chemical stability.

Liu et al [32], reported the functionalization of ZnO nanorods on transparent thermoplastic polyethane (TPU) surface, through coupling of dimercaptosuccine acid (DMSA), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide), (EDC). Lastly human serum alibumin (HSA) and brocine serum albumin (BSA) were covalently attached on the DMSA and EDC altered ZnO nanorods. Gu et al[33] showed exceptional biosensing properties of ZnO nanostructures. Tyrosinase was immobilized on the surface of gold electrode to investigate electrochemical response of ZnO nanorods for sensing phenol. They used Au-Zn alloy catalyst for the formation of ZnO nanostructures. Hydrothermal reaction were performed in grow ZnO nanorods on the surface. Finally sensor was developed through enzyme immobilization for detection of phenol.

1.6.6. ZnO used in Cancer Treatments

S. Ibraheem et al. [29] studied zinc oxide nanoparticle as Diagonstic Tool for Cancer Cells. In this study research developed as immunosensor based zinc oxide nanoparticle detector of liver cancer. Another study of interdigital electrode nanobiosesor enhanced by Aunps nanoparticle with zinc oxide NPs detecting viral oncogenes papillomavirus subtype -16 (HPV-16) by spotting viral E6 genes target as a little 1 Fm. The physical parameter includes electrostatic particle stability NPs positive and negative surface charge cancer and normal cells ability to induce ROS.

1.6.7. Zinc Oxide used in Photocatalysis

Li et al [23] also studied the photocatalytic properties of ZnO nanoparticles which were obtained in electrochemical method, method in the process of polyoxometalates (POMs) at room temperature. The experiment shows that POMs play a very important role in the formation of ZnO nanoparticles. The photocatalytic properties of ZnO determined using the example of degradation of rhodamine (RhB). Based on this study Li et al., concluded that ZnO displays high photocatalytic activity below the UV range. Ma et al.[30] demonstrated superior photocatalytic performance on ZnO nanorods and nanoflowers compared with commercial ZnO particles on methyl orange (MO). Besides organic dyes, UV-induced photocatalytic degradation of stearic acid by ZnO nanowires was also reported.

Reference:

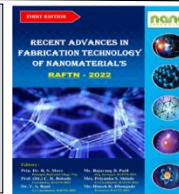
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Electrochemical Supercapacitor Performance of Electro spun Nanofibers

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KEYWORDS

Electrospinning
Nanofibers,
Energy storage,
Metal oxide,
Carbon,
Conducting polymers.

ABSTRACT

The rapid development of electric appliances and vehicles has increased the demand for energy storage systems, and this desire has sparked researchers on the next generation of high-performance, high-density energy storage devices. Future energy sustainability is currently being assured by new opportunities and solutions made possible by nanotechnology. The synthesis of metal oxides and sophisticated functional nanofibers can be done on a wide scale using one of these techniques, electrospinning, which is particularly straightforward and affordable. Particular attention is given to nanofibers in this work that have good electrochemical characteristics. Due to the intriguing confinement effects and structure-related features, one-dimensional (1D) nanostructures including nanofibers, nanorods, and nanotubes have garnered a great deal of attention. Because of their large surface areas, porosities, and quick charge transport, metal oxides with 1D nanostructures are particularly recognized as promising candidates in the applications of energy conversion and storage devices. The synthesis of pure metal oxides via electrospinning and their use in energy storage make up the three main components of this research.

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1. Introduction

Rapid population expansion and technological advancements have led to an enormous increase in the usage of fossil fuels, which not only depletes available resources but also has a negative influence on the sustainable development of world economics and ecology. Renewable energy sources are regarded to be the worthiest replacement for fossil fuel in the coming days because they are environmentally friendly and sustainable [1]. Science and technology specialists have been grappling with the problem of converting this enormous energy into electrical power for an extremely long time. Photovoltaic cells, Li-ion batteries, supercapacitors, and fuel cells are today the most efficient clean alternative energy sources [2]. The ease and sustainability of human progress in the wide spreading use of Electric vehicles (EV), flexible wearable electronic devices depend on both primary and rechargeable batteries, which can produce clean electric energy from the stored chemical energy and transform chemical energy back into electric energy. More researchers will focus on supercapacitors because of their high-power density, which efficiently satisfies people's desire for a fast-paced lifestyle [3]. Because there is a significant association between the forms, sizes, and morphology of nanomaterials and their physical/chemical properties, scientists are striving to optimize these parameters. This also suggests more stringent specifications for energy storage technologies, going beyond those that only stores energy and then deliver energy when required.

As supercapacitors operate as a bridge between batteries and electrochemical capacitors in terms of electrochemical characteristics, they are a possible alternative to batteries [4]. Nanomaterials offer significantly better ionic transport and electrical conductivity to supercapacitor. They also make it possible for all intercalation sites in the particle volume to be occupied, which results in high specific

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capacities and quick ion diffusion. Wide-ranging electrical, chemical, and physical characteristics of metal oxides make them frequently quite sensitive to changes in their chemical surroundings. Due to these characteristics, metal oxides have received much research, and the majority of commercial applications rely on oxides that are correctly organized and doped. Metal oxide nanofibers have many advantages [5]. Due to its ability to manage different energy transport methods, metal oxide nanofibers are suggested as the best material for producing sophisticated energy devices for supercapacitors. Numerous techniques are used to create nanofibrous metal oxides, such as electrospinning, top-down approaches, chemical etching, non-metal seeded gas phase growth, metal-promoted vapour growth, metal-assisted growth in liquids, and crystal structure governed nucleation in solution. Electrospinning has gained popularity due to its simplicity and low cost [6-7].

2. Supercapacitors

Supercapacitors (SCs), also referred to as ultracapacitors (UCs) or electrochemical capacitors (ECs), are devices that store electrical energy through the special separation of ionic and electronic charges at the electrode/electrolyte interface with the formation of an electric double layer (electric double layer capacitors, to be precise), where charges are separated at the nanoscale. Thinness of the double layer and exceptionally high specific surface area ($\sim 3000 \text{ m}^2 \text{ g}^{-1}$) enables these devices to have very high specific capacitances when compared with conventional electrostatic capacitors and therefore superior energy densities compared to electrostatic capacitors [8]. Additionally, SCs maintain a remarkable level of capacitive performance, with capacity retention rates up to 99% having been attained. Since SCs do not utilize a lot of electrolytes, unlike rechargeable batteries, they are extremely safe to use and simple to recycle. Safety and environmental friendliness are some other additional benefits of SCs [8-9].

Supercapacitors are built similarly as a battery and include two electrodes immersed in a liquid electrode with a separator located between them. In such a device, the capacitance value of each part shows the total capacitance of the cell [4].

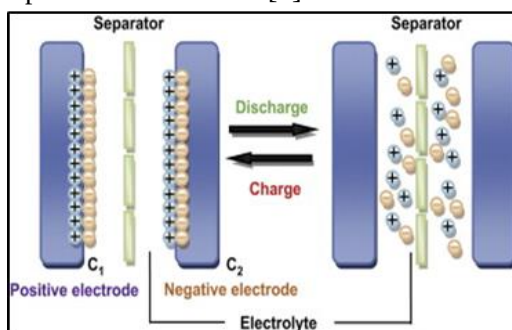


Fig. 1: Schematic process of supercapacitor performance and charging/discharging [10],

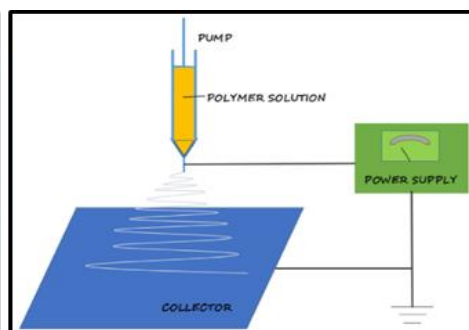


Fig. 2: Schematic diagram of an electrospinning set-up.

In terms of assembly, charge storage technique, and electrode/electrolyte materials, supercapacitors can be classified into three distinct categories. Every configuration has a different charge storage system, and as a result, each type Electric Double layer Capacitor (EDLC), Pseudo capacitor (PCs), and Hybrid Supercapacitor (HSCs) tonnes of literature [10].

3. Electrospinning

To create woven and non-woven micro/nanoscale fibers from polymeric solutions, electrospinning is a straightforward technique. Regarding the creation of electronic devices and components, this technology has garnered a lot of attention.

3.1 Working of electrospinning

The components of an electrospinning system typically include a syringe, pump, power source, and collector. The syringe is filled with a mixture of a polymer and solute material, which is then pumped via a nozzle. The surface tension of the polymeric solution is overcome by a high-voltage or high-electric field. The hemispherical surface of the polymer solution at the tip of the capillary tube starts to stretch into a form known as the Taylor cone when the electric field intensity is increased above a specific limit, known as the threshold intensity. As the solvent evaporates and the polymer solidifies at the micro/nano scale, electro spun fibers are created by plastically stretching a jet of polymeric solution. Numerous operating parameters, including surface tension, solution concentration, conductivity, viscosity, flow rate, applied voltage, and the distance between the capillary tube and the collector, affect the shape of nanofibers [11]. Nanofibers are created using a variety of electrospinning processes.

- Rotating Drum Electrospinning
- Coaxial Electrospinning
- Needleless Electrospinning
- Electrospinning with Rotating Disk
- Near-field Electrospinning

3.2 Electro spun one-dimensional nanomaterial electrodes for supercapacitors

Electro spun nanomaterials displaying electrochemical activity and large surface area are essential for electrodes of SCs, including EDLCs and pseudo capacitors. As active electrode materials in SCs, a wide range of electrochemically active electro spun nanomaterials have been created, including carbons, metal oxides, metal sulphides, metal nitrides, conducting polymers, and nanocomposites. For high capacitor performance, various architectures such as solid, porous, core–sheath, hollow and hierarchical structures have been fabricated.

3.3 Electrospun metal oxide nanofibers for supercapacitor

The development of several types of electrospun transition metal oxide nanofibers for SC electrodes has accelerated recently. Taking advantages of the large surface area and distinct reversible redox chemistry, electrospun nanofibers of pseudocapacitive transition metal oxides displayed extremely high specific capacitance values compared to CNF electrodes as EDLCs.

Among all of the electrospun transition metal oxide nanofibers, RuO_2 nanofibers display the highest capacity due to their high electronic conductivity and unique redox chemistry. For example, electrospun RuO_2 nanofibers derived from RuO_2 precursor/PVAc composite fibres possess a high electronic conductivity. To improve the transport of protons and charge storage capability, a thin hydrous RuO_2 overlayer was introduced on the surface of electrospun RuO_2 nanofibers through an electrodeposition process, which afforded a specific capacitance of 886.9 F g^{-1} in $1 \text{ M H}_2\text{SO}_4$ electrolyte solution. Hydrous RuO_2 coated electrospun RuO_2 nanofibers showed an excellent long cycle performance, which maintained 78.2% of its original capacitance after 20000 cycles [12]. B. Vidhyadharan and co-workers prepared NiO nanowire by electrospinning a mixed solution containing nickel acetate, PVA, ethanol and water, followed by a calcination process at 500°C in air. The NiO nanowires developed have 50% lower diameter $\sim 50 - 70 \text{ nm}$. NiO nanowires exhibited 670 F g^{-1} at 1 A g^{-1} current density in 6 M KOH the high degree of crystallinity improved the cycling stability and Coulombic efficiency; devices showed capacity retention of $\sim 100\%$ at the end of 1000 cycles and gave $\sim 98\%$ Coulombic efficiency. The “greener” NiO nanowires thus developed by electrospinning demonstrated beneficial electrochemical properties for fabrication of an energy storage device under super capacitive mode [13]. Copper oxide (CuO) is popular among TMO nanostructures due to its relatively low toxicity, high abundance, low cost, high environmental stability, and desirable optical, electrical, and electrochemical properties. is attracting attention. Izan and co-workers synthesized CuO nanowires, by electrospinning using an aqueous polymeric solution, with ultra-low diameters ($< 50 \text{ nm}$) and the evaluation of their electrochemical properties for fabrication of a

supercapacitor device. Supercapacitor electrodes were fabricated on nickel foam substrates using 75 wt% CuO in 15 wt% conducting carbon and 10 wt% polyvinylidene fluoride. A record specific capacitance (CS) is observed for the present electrospun CuO nanowires showed Specific capacitance $\sim 620 \text{ F g}^{-1}$ in KOH and 581 F g^{-1} in LiOH at a current density of 2 A g^{-1} with a Coulombic efficiency of $\sim 100\%$ and operational stability (98% at the end of 1000 cycles) [14]. MnO_2 is another widely studied SC electrode material due to its good redox property, natural abundance and low cost. In general, MnO_x nanofibers with a low oxidation state of Mn ($x < 2$) were usually produced by electrospinning followed by a thermal calcination process. The 1D nano-fibers provide ease of ion transport, high specific surface area and porosity beneficial for energy storage application. Teli and co-workers prepared Nanofibers (NFs) Mn_2O_3 thin films facial and cost effective single-nozzle electrospinning method. They demonstrated that the excellent performance of NF samples attributed to their high specific surface area, porosity and cable like structure, beneficial for electrolytic ion transport. The amorphous Mn_2O_3 NFs structure have high specific surface area and excellent capacitive performance as compared to crystalline Mn_2O_3 . The nanofibers exhibited 526 F g^{-1} at 0.5 m A cm^{-2} current density in $1 \text{ M aq Na}_2\text{SO}_4$ and devices showed capacity retention of 96% at the end of 1000 cycles [15]. Kumar and co-workers prepared Co_3O_4 nanofibers by electrospinning technique. The electrospun Co_3O_4 nanofibers exhibit a specific capacitance of 407 F g^{-1} at a scan rate of 5 mV s^{-1} . At a constant current density of 1 A g^{-1} , the Co_3O_4 nanofibers exhibit superior cycle stability and better capacity retention with 94% after 1000 continuous charge-discharge cycles. The improved supercapacitor performance is primarily attributable to the special nanofiber structure of the device, which offers a greater reactive surface area and permits quick ion and electron transport. Due to easy electrolyte penetration and improved use of the electroactive surface, Co_3O_4 nanofibers offer a greater specific capacitance. The Co_3O_4 nanofibers demonstrate outstanding cyclic performance, high-rate pseudo capacitance behaviour, and electrochemical stability and hence can be used as electrode material for high performance supercapacitor applications [16-17].

Wai and his team prepared Vanadium pentoxide nanofibers (VNF) and polyaniline nanofibers (PANF) nanofibers by electrospinning and rapid chemical polymerization routes. Amorphous hydrous ruthenium oxide ($\text{RuO}_2 \cdot x\text{H}_2\text{O}$), one of the transition metal oxides, displays pseudocapacitive behaviour with a large specific capacitance, but it is too expensive for practical use. Because of its layered structure and numerous vanadium oxidation states, which enable surface/bulk redox reactions and result in high capacitance in symmetric supercapacitor design, V_2O_5 is one of the appealing alternatives. The specific capacitance was calculated to be as high as 213 F g^{-1} at 10 mV s^{-1} in 3 M KCL retention with 73% loss after 2000 cycles [18]. The benefits of nano scaled TiO_2 are its low cost, high specific surface area, good physical and chemical stability, and abundance of Titanium in the Earth's crust. X. He and co-workers fabricated TiO_2 nanofiber by electrospinning technique and a post treatment by KOH. KOH treatment on NFs dramatically converted from highly resistant to conductive, making them an appropriate material for supercapacitor electrodes. The specific capacitance values ranged from 65.84 F g^{-1} (at 0.001 V s^{-1}) to 11.33 F g^{-1} (at 2 V s^{-1}) in mass and 109.73 to 18.88 mF cm^{-2} in area, respectively. The TiO_2 electrode material likely achieved the maximum specific capacitance [19].

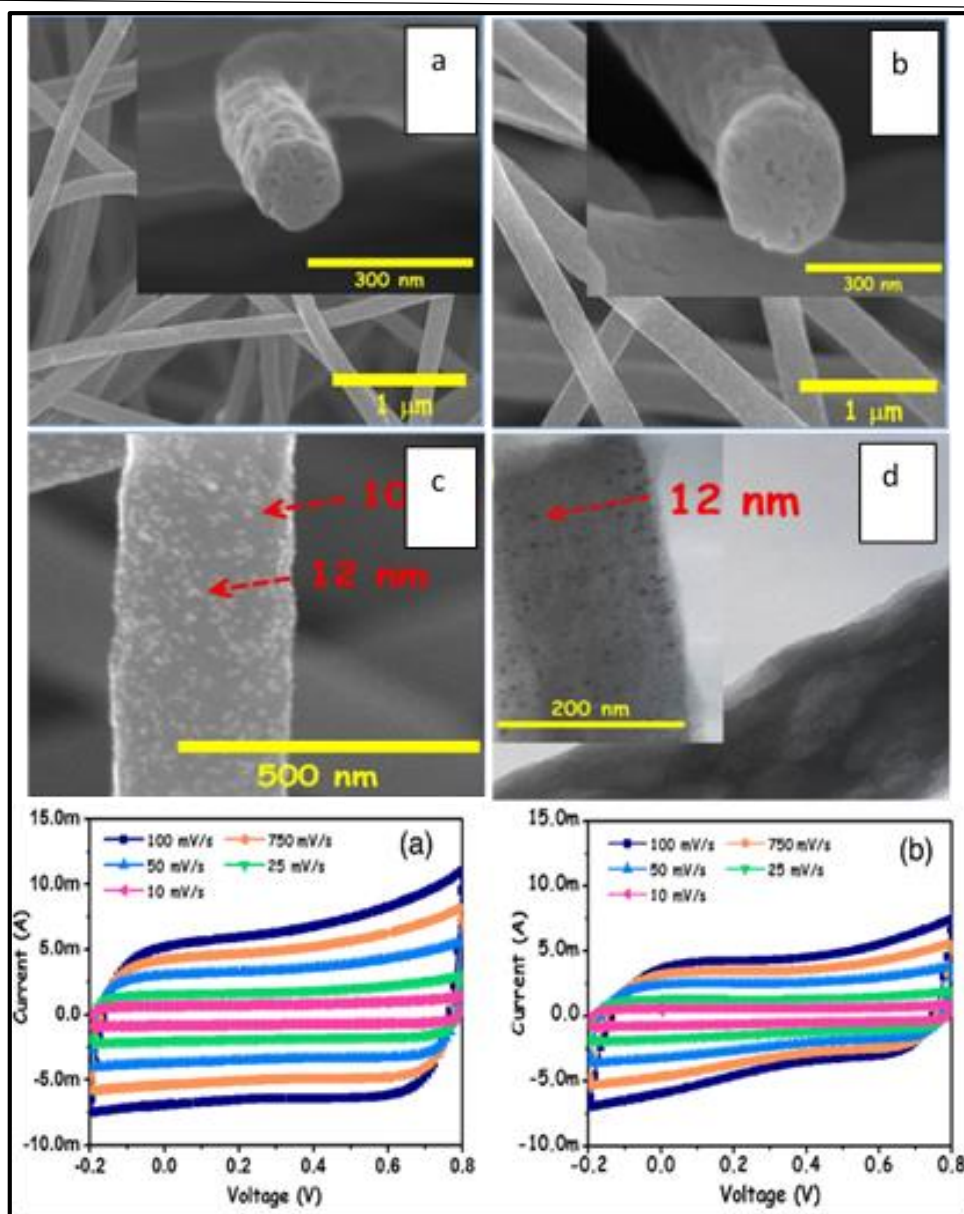


Fig. 3: FE-SEM images (a-d) and highly magnified SEM images and cyclic voltammograms of (e) PMRu (15)-ACNF, (f) PMRu(10)-ACNF [12].

Table1: Electro spun one- dimensional Metal oxides for supercapacitor.

Electrode material	Electrospinning Solution Precursor/polymer /Solvent	Applied Voltage kV	Flow rate	Morphology	Specific capacitance Fg^{-1}	Current density $\text{Ag}^1/\text{mAcm}^{-2}$	Electrolyte	Scan rate mVs^{-1}	Cycle	Ref
RuO_2 Nanofibers mat	$\text{RuCl}_3/\text{PVAc}/\text{DMF}$	12 kV	$15 \mu\text{m min}^{-1}$	Nanofibers mat	886.9 Fg^{-1}	-	-	10 mVs^{-1}	87.2% after 20000	[12]
NiO Nanowires	NiAc/PVA/Water	24 kV	0.5 mlh^{-1}	Nanowires	670 Fg^{-1}	1 Ag^1	6M KOH	-	100% after 1000	[13]
CuO wire	CuAc/PVA/Water	24 kV	0.5 mlh^{-1}	Nanowires	620 Fg^{-1}	2 Ag^1	6M KOH	5 mVs^{-1}	92% after 1000	[20]
Mn_2O_3 Nanofibers	Mn (Ac)/PVP/ethanol & distilled water	12 kV	1 mlh^{-1}	Nanofibers	526 Fg^{-1}	0.5 Ag^1	1M aq Na_2SO_4	-	96% after 1000	[15]
Co_3O_4 Nanofibers	CoAc/PVP/Ethanol	13.5 kV	0.5 mlh^{-1}	Nanofibers	407 Fg^{-1}	1 Ag^1	6M KOH	5 mVs^{-1}	94% after 1000	[17]
Vanadium Pentaoxide Nanofibers	$\text{VO}(\text{acac})_2/\text{PVP}/\text{Et}$ hanol	10 kV	1 mlh^{-1}	Nanofibers	213 Fg^{-1}	0.15 Ag^1	3M KCl	10 mVs^{-1}	27% loss after 2000	[18]
TiO_2 Nanofibers	TiCl ₄ /PVP/Ethanol	25 kV	1 mlh^{-1}	Nanofibers	65.84 Fg^{-1}	-	Na_2SO_4 aq	1 mVs^{-1}	90% after 10000	[19]

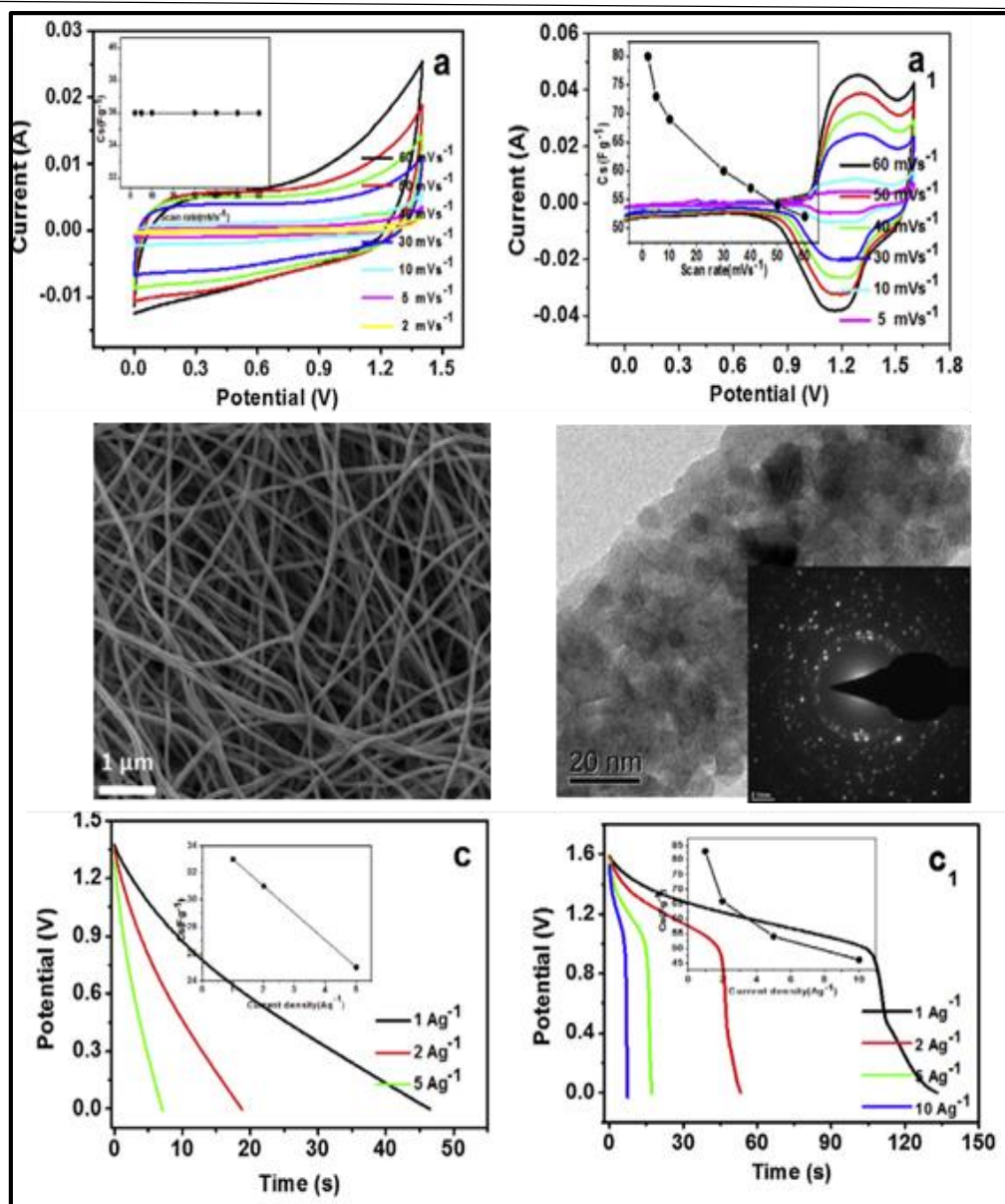


Figure 4: The CV curves of the AC//AC symmetric EDLC in 6 M KOH aqueous solution at scan rates between 2 and 60 mV s^{-1} ; inset shows variation in CS with scan rate; (a1) the CV curves of the CuO//AC asymmetric supercapacitor in 6 M KOH aqueous solution at scan rates between 5 and 60 mV s^{-1} ; inset shows variation in CS with scan rate; (b) the FESEM image of the calcined CuO nanowires; (b1) the bright field TEM images of a typical CuO nanowire; inset: SAED pattern showing highly crystalline random particles. c) the discharge curves of the AC//AC symmetric EDLC at different current densities in 6 M KOH aqueous solution; inset variation of CS of the device calculated from discharge curves; and (c1) the discharge curves of the CuO//AC asymmetric capacitor at different current densities in 6 M KOH aqueous solution; inset variation of CS of the device calculated from discharge curves [14].

4. Conclusion

This overview of electrospinning synthesis of metal oxide nanofibers can be fabricated at affordable price by simple electrospinning setup. The statistics provided represent the ongoing interest in nanofibers, which is a result of the broad range of applications for energy storage that nanofibers have demonstrated. Future electrospinning nanofiber for energy storage applications are anticipated to expand to more and more in technical domain.

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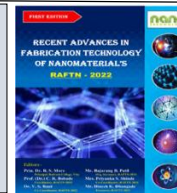
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Recent Advances in Fabrication Technology of Nanomaterials

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Photoelectrochemical Studies of Pure CdSe Thin Films - A Review

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KEYWORDS

Photoelectrochemical,
cadmium selenide,
efficiency, deposition
methods.

ABSTRACT

Concerted investigative efforts have been made concern to conversion of power from sun to produce energy. Because of easiness in junction formation and inherent storage ability photoelectrochemical cells have become a center of attention over p-n junction solar cells. For the same CdSe is widely used II-IV semiconductor with n type conductivity. Current paper presents a concise analysis on synthesis of CdSe thin films by diverse deposition methods on different substrates from an aqueous and non-aqueous medium. Further the main intend of this review is to present details of photoelectrochemical studies of CdSe photoanodes prepared by various methods.

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1. Introduction

Energy requirement of world grows up by way of development of the countries and their population. To meet this ever-rising energy demand mankind has been focused towards promising renewable energy. Amongst various renewable sources, solar energy is one of the best substitutes. Energy from sun is considered to be very cleanest, abundantly availed and inexpensive. In order to overcome the energy crisis situation and associated environmental issues, proficient use of solar energy can be one of the promising way outs. So nonstop transfer of solar energy into electrical energy is indispensable to meet the energy demand of current world. Solar cells are well-designed for solar energy conversion. For this amongst all, semiconductor liquid junction solar cells have become a point of attention. Solid junction formation process is delicate, complex and needs sophisticated amenities. This enhances overall expenditure in formation of solid junction device. As of this view point, junction fabrication in photoelectrochemical cell is awfully simple and at ease, which can be made just by immersing photoelectrode in the redox electrolyte. In contest with solid state solar cells, low efficiency of photoelectrochemical cell is a big barrier.

Among various methods of harnessing solar energy, the photoelectrochemical route is simplest one. The conversion of solar energy directly into electrical form using semiconductor photoelectrode-redox electrolyte interface is typically renowned as photoelectrochemical (PEC) solar cell as shown by Gerischer [1] low-priced, ease and simplicity in junction fabrication and in-built storage capability, these rewards of PEC cell make it more attention-grabbing in contrast with solid state cells [2].

In energy conversion process, semiconductor electrolyte interface can be employed for photoelectrochemical power conversion, photoelectrolysis and photocatalysis [3] In PEC cell, the properties of photoanode, redox electrolyte and S-L junction controls diverse factors as formation of open circuit voltage, short circuit current, charge transport diagonally the photoelectrode – redox

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electrolyte junction etc. When n-type semiconductor photoanode-redox electrolyte interface is illuminated, if $h\nu \geq E_g$, electron hole pairs are generated in depletion region, which are separated due to local electric field present at interface. Electron promoted to top of conduction band while holes in the valence band. These separated charges produce counter charge, which under open circuit condition gives open circuit voltage. When counter electrode immersed in electrolyte and connected externally to semiconductor. Holes oxidize reduced species in electrolyte. Electrons through external circuit moves to counter electrode where it reduces oxidized species in the electrolyte.

The key part of proficient solar cell is photoanode material, consequently right choice of it is decisive thing. The most important necessity in selecting photoelectrode candidate is its band gap. It must be positioned in close to maxima of visible spectrum in an attempt to ensure competent use of the solar spectrum. Binary Chalcogenides have been considered as credible contestants in solar energy conversion. Cadmium Selenide (CdSe) is a one of the most multipurpose II-VI semiconductors with band gap (1.7eV) in the vicinity of visible spectrum maxima. It has received recognizable interest of researchers for the reason that high absorption coefficient, intrinsic birefringence, direct band gap, size dependant physical and chemical properties, and luminescent properties etc. These properties uphold use of CdSe in diverse applications as solar cell, thin film transistor, light emitting diode and various electronic devices [4] etc. CdSe thin films have been grown by a variety of physical and chemical techniques such as Chemical bath deposition, thermal evaporation, electron beam evaporation, electrodeposition, spray pyrolysis, hydrothermal, successive ionic layer adsorption and reaction method [5] etc. Many researchers studied use of CdSe thin film as a photoanode in PEC cell. This paper gives a mini review on performance of photoelectrochemical studies of CdSe phototodes synthesized by different methods with different solar cell configuration.

Sr. No.	Method of Synthesis	Solar cell configuration	Illumination intensity (mW/cm ²)	Jsc (mA/cm ²)	Voc (V)	Efficiency η (%)	Fill factor	Reference
1.	Spray Pyrolysis	CdSe (TiO ₂ /FTO)/0.5 M Na ₂ S+2 M S+0.2 M KCl / Pt coated counter	1 sun , 100	14.4	0.52	2.6	35	[6]
2	Chemical-Two step method	CdSe (Nickel)/1M (NaOH+Na ₂ S+S) /platinum spiral wire	100	2-3	0.50-0.55	-	-	[7]
3.	Spray pyrolysis	CdSe(FTO)/ 1M (NaOH+Na ₂ S+S)/Graphite	20	0.708	0.32	0.50	44	[8]
4.	Arrested precipitation technique	CdSe (ITO)/ 1 M (NaOH+Na ₂ S+S)/Graphite	--	1.15	0.58	0.62	28	[9]
5.	Brush plating technique	CdSe(Titanium)/ 1 M (NaOH+Na ₂ S+S)/Graphite	80	18.2	0.56	7.43	60	[10]
6.	Thermo- chemical approach	CdSe(ITO)/1M (NaOH+Na ₂ S+S)/Graphite	80	3.41	0.32	0.473	35	[11]
7.	Dip coating	CdSe(SS)/1M (NaOH+Na ₂ S+S)/Graphite	30	0.169	0.26	0.55	36	[12]
8.	Thermal wet chemical method	Glass(ITO) CdSe/ P3HT/Al	AM 1.5	0.37	0.43	0.039	25	[13]
9.	Vacuum evaporation	CdSe(Titanium)/1M (NaOH+Na ₂ S+S)/Graphite	60	17.5	0.42	7	57	[14]
10.	Co-evaporation	CdSe(Titanium)/1M (NaOH+Na ₂ S+S)/Graphite	50	7.64	0.49	4	54	[15]
11	Non-catalytic displacement plating	CdSe/1M (NaOH+Na ₂ S+S)/Graphite	60	2	0.45	1.02	34	[16]
12	Pulse plating	CdSe(Titanium)/1M (NaOH+Na ₂ S+S)/Graphite	—	22.35	0.39	6.57	40	[17]
13	Chemical Bath deposition	CdSe (FTO) /1M (NaOH +Na ₂ S+S) / Platinized FTO	A M 1.5	11.3	0.327	1.44	39	[18]
14	Chemical Bath deposition	CdSe (Titanium)/0.1M (NaOH +Na ₂ S+S)/Graphite	42	0.1	0.13	0.03	35	[19]
15	Electrodeposition	CdSe (Stainless Steel)/1M (NaOH +Na ₂ S+S)/Graphite	50	1.6	0.44	0.80	56	[20]
16	Electrodeposition	CdSe (SS or FTO or Titanium)/ 1M (NaOH +Na ₂ S+S)/ Graphite,	40	SS- 0.56 FTO-0.10 Ti- 0.85	0.31 0.30 0.35	0.123 0.0205 0.297	28 27 39	[21]

Conclusion

CdSe thin films have found to be synthesized by various deposition methods. An attempt has made to review performance of photoelectrochemical solar cell using CdSe photoanodes synthesized by different methods. We expect the planned overview can give a inclusive collection of key studies to steps forward in the field and look to the fore for further progress in the propose of superior photoelectrochemical solar cell of CdSe thin films in the future.

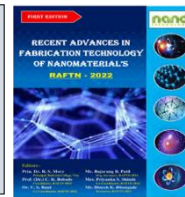
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**Recent Advances in Fabrication Technology of
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Supercapacitive performance of electrophoretically deposited grass like nanostructured Mn_3O_4 thin films

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KEYWORD

Mn_3O_4 nanomaterial,
Supercapacitor, cyclic
voltammetry.

ABSTRACT

The grass-like nanostructured Mn_3O_4 thin film has been deposited on a steel substrate by a simple electrophoretic deposition technique and further structural and morphological studies were done by XRD and SEM. The tetragonal crystal structure was observed with a crystallite size of ~ 130 nm. The SEM image shows grass like surface morphology with high porosity. The FT-IR and Raman study provides the compositional study of the Mn_3O_4 thin films. Cyclic voltammetry, galvanostatic discharge-charge tests, and electrochemical impedance spectroscopy were employed to study its super capacitive performance as an electrode material. The nanostructured Mn_3O_4 thin film has exhibited the maximum specific capacitance ($\sim 158 \text{ Fg}^{-1}$) and confirmed its ability to use as electrode material in supercapacitors.

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1. Introduction

The modernization led by recent electric and electronic devices and its key requisites can be accomplished by an electrochemical device known as a supercapacitor and it is the most suitable for practical applications as it is rechargeable. Batteries and fuel cells have low power density and high energy density than supercapacitors [1]. Electrochemical double-layer capacitors (EDLC) and pseudocapacitors are the two categories of supercapacitors reliant on the charge storage mechanism. In EDLC, the boundary between the electrode and the electrolyte stores the electric charge, while in the pseudocapacitor, the rapid redox reaction on the surface of the electrode is responsible for the charge storage. Due to high specific energy than EDLC, the pseudocapacitors are an exceptional contender for energy storage purposes [2].

High surface area, a variety of crystal structures such as MnO , Mn_3O_4 , Mn_2O_3 and MnO_2 and nanosized morphologies are the key aspects for the vast study of manganese oxides for the supercapacitor application. To boost the electrochemical performance, the morphology of the nanostructure plays a vital role. By tuning the size and morphology of the manganese oxide nanostructure, the growth of different nanocrystals can be controlled for enhanced electrochemical performance. Similar to MnO_2 , Mn_3O_4 has attracted researchers as an electrode material for supercapacitors due to its different merits like low cost, eco-friendly nature and large availability [3]. Also, it shows a pseudocapacitive nature with a very high theoretical specific capacitance of 1400 Fg^{-1} . It exhibits high electrochemical performance via spontaneous redox reactions between the Mn^{2+} and Mn^{3+} oxidation states during the charge-discharge process. Still, the Mn_3O_4 nanomaterial is not studied

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much for electrochemical applications in comparison with MnO_2 [4]. Many researchers have adopted various synthesis methods to prepare Mn_3O_4 -based electrode materials for supercapacitors, such as solvothermal [5], pulse electrodeposition [6], spray pyrolysis [7], hydrothermal [8], reflux [9], and chemical batch deposition [10]. A high value of specific capacitance (499 Fg^{-1}) has been reported for $\text{Mn}_3\text{O}_4/\text{CNT}$ (carbon nanotubes) nanocomposite synthesized by the chemical reflux method [11]. Recently, Shah and co-workers have prepared extraordinary spongy Mn_3O_4 nanoparticles via the hydrothermal method wherein a high specific capacitance value of 380 Fg^{-1} is reported, which is relatively higher than earlier synthesized Mn_3O_4 nanoparticles [12]. In addition, doping with different transition-metal ions, size-controlled synthesis of Mn_3O_4 octahedrons has been reported by Dong et al. and observed an improvement in the supercapacitive properties of Mn_3O_4 by doping transition metals signifying the synergistic effect of doping on the growth and electrochemical performance [13]. Diverse morphologies and their effects on the supercapacitive performance by achieving maximum capacitance value up to theoretical capacitance are the features that increased the interest in the synthesis of the Mn_3O_4 electrode material [14]. In this paper, the grass-like morphology of Mn_3O_4 nanostructure of controlled crystallite sizes prepared via electrophoretic deposition for supercapacitor application has been reported. The structural and morphological studies were carried out by XRD, FTIR, FT Raman and SEM. The cyclic voltametric, galvanostatic charge–discharge data and electrochemical impedance spectroscopy techniques were used to study the nanostructured Mn_3O_4 thin film as an electrode for the supercapacitor.

2. Experimental

2.1 Chemicals

Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine (HMTA), ammonium hydroxide (NH_4OH), and Na_2SO_4 were purchased from Thomas Becker and used as received. All solutions were prepared using double distilled water (DDW).

2.2 Preparation of Mn_3O_4 thin films

The Mn_3O_4 thin films were deposited electrophoretically on steel substrates at room temperature. Initially, 25 ml of MnSO_4 (0.05 M) solution and 20 ml of HMTA (0.05 M) solution was prepared with DDW and stirred for 30 min. After mixing the above solutions, 3 ml of NH_4OH (0.1 M) was added dropwise to form the whitish-brown precipitate with vigorous stirring for another 30 min. Afterward, the graphite and well-cleaned stainless-steel substrates were dipped and a constant potential of the value 1.1V was applied for 30 min to deposit uniform and well-adherent Mn_3O_4 thin film on a stainless-steel substrate.

2.3 Characterizations

The structural study of the prepared thin film was determined by X-ray diffraction (Bruker AXS DS Advance model) using $\text{Cu K}\alpha$ radiation. The FTIR (Bruker, Germany. ALPHA) spectrum was obtained in the range $400\text{--}4000 \text{ cm}^{-1}$. Raman spectrum was obtained using Micro Raman (Renishaw, INVIA0120-2). The surface morphology of the Mn_3O_4 thin film was observed by SEM (JEOL, JSM-IT200 model). The supercapacitive studies were conducted in a three-electrode system using a CHI660E electrochemical workstation with Mn_3O_4 thin film as the working electrode, Pt electrode as counter electrode and Standard Calomel Electrode (SCE) as a reference electrode in 1M Na_2SO_4 electrolyte.

3. Results and Discussion

3.1 Structural Characterizations

The XRD pattern consisting of clear and sharp diffraction peaks shown in Fig. 1 recognizes the tetragonal Mn_3O_4 nanostructure (hausmannite phase) of high crystallinity (I41/amd space group) (JCPDS Card No.00-001-1127). The Debye-Scherrer formula has been used to calculate the crystallite size. The average crystallite sizes were found to be 130 nm calculated from the diffraction peaks

(101,112, 103, 211, 004, 220,105, 321,224 and 314) [15]. It can be observed that the main peaks are (103,211,224) and the other peaks are of a smaller height which shows the preferred orientation and confirms its polycrystalline nature. The tetragonal unit cell has lattice parameters of the values, $a = b = 5.75 \text{ \AA}$ and $c = 9.42 \text{ \AA}$, which is consistent with earlier reports [16].

The information about chemical bonds in nanostructured Mn_3O_4 thin film can be obtained by FTIR study in the wavenumber range $400\text{--}4000 \text{ cm}^{-1}$ and is shown in Fig. 2. The absorption peak at 3398 cm^{-1} specifies the existence of a hydroxide group. The absorption peaks at 1525 and 1031 cm^{-1} are assigned to vibrations of O–H bending shared with Mn atoms [17]. The sharp absorption peaks that occurred at 815 , 673 , 564 and 515 cm^{-1} are related to the joint mode of vibrations of stretched bonds of Mn–O in tetrahedral and octahedral sites [18]. Due to an unstable Mn^{3+} ion, there are also stretched vibrations of MnO_6 octahedra observed.

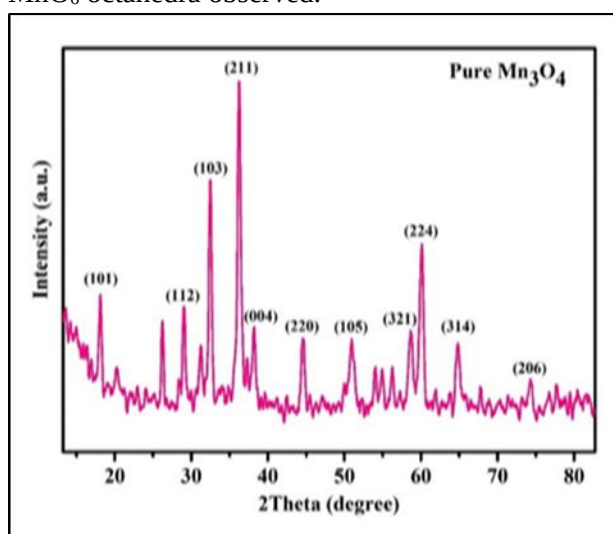


Fig. 1: XRD pattern of Mn_3O_4 thin film.

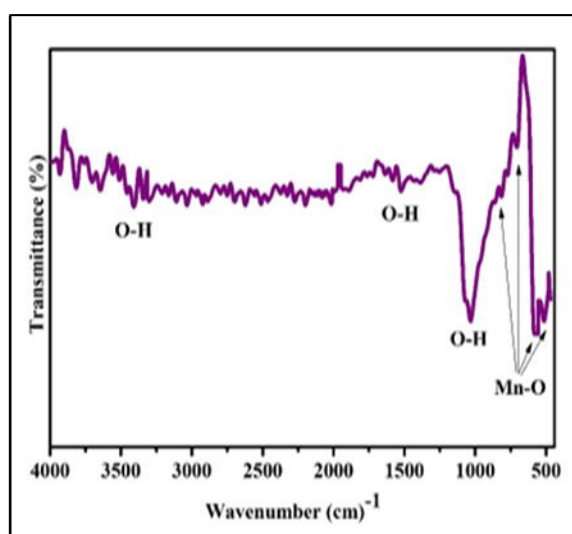


Fig. 2: FTIR spectrum of Mn_3O_4 thin film.

Fig. 3 represents the Raman spectra of electrodeposited nanostructured Mn_3O_4 thin film. The spectrum contains a peak at 616 cm^{-1} which is one of the characteristic peaks for all spinels. It represents the vibrations of stretched $\text{Mn}^{2+}\text{--O}$ bonds in the tetrahedral site. The peaks at 263 and 386 cm^{-1} are due to the $\text{Mn}^{3+}\text{--O}$ vibrations in Mn_3O_4 . The vibrations due to the distortion at octahedral sites are represented by a peak at 557 cm^{-1} [19].

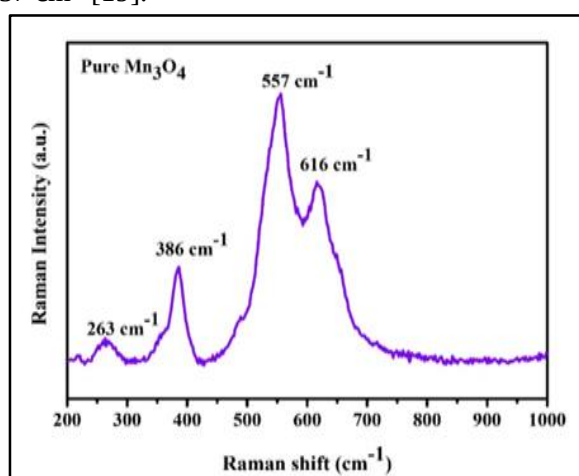


Fig. 3: Raman spectra of Mn_3O_4 thin film.

The surface morphology of the as-synthesized Mn_3O_4 nanostructure was studied using SEM as shown in Fig. 4. It shows a well-shaped grass-like nanostructure having an average crystallite size equal

to 100-150 nm which agrees well with the result obtained by Debye-Scherrer formula. It is seen that the Mn_3O_4 nanostructured film surface is spongy and well-covered with smooth, regular-shaped grains of sharp needles or grass which are interconnected with each other. These grains form bunches with some bands of overgrowth. Such overgrowth of the grains of sharp needles or grass could occur due to nucleation and coalescence phenomenon. Such surface increases the surface area which is beneficial for supercapacitor application [3]. The sharp needle or grass-like nanostructured crystal growth is possible due to the use of surfactant during the synthesis that convinces the strain for the growth.

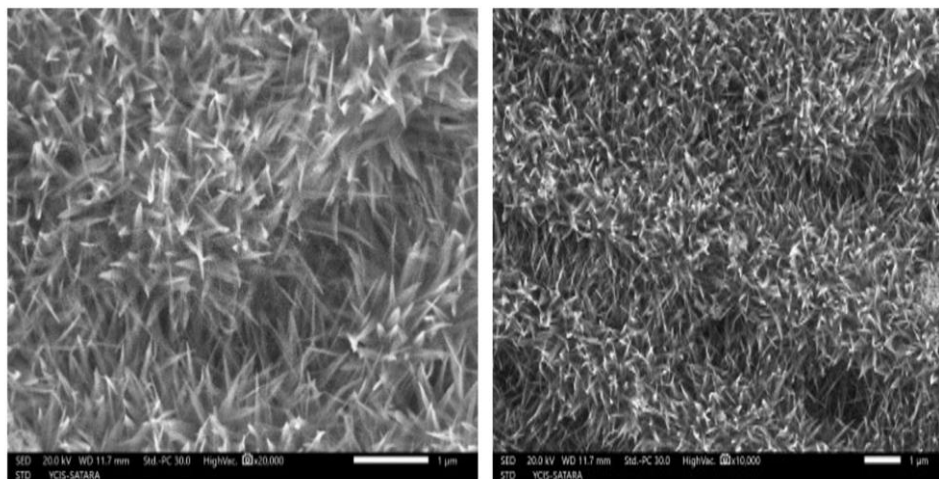


Fig. 4: SEM images of Mn_3O_4 thin film at different magnifications.

3.2 Supercapacitive study Mn_3O_4 thin films

To investigate electrochemical or supercapacitive performance, the capacitive behavior of nanostructured Mn_3O_4 electrode using a three-electrode arrangement with saturated 1M Na_2SO_4 as the aqueous electrolyte has been studied by cyclic voltammetry (CV) and galvanostatic charge–discharge techniques. Fig. 5 shows the cyclic voltammetry (CV) curves of the Mn_3O_4 nanostructured thin film at sweep rates of 10, 20, 50 and 100mV/s between the potential range 0 and 1 V. These curves confirm the predictable pseudocapacitive behavior. Fig. 6 explains the variation of specific capacitance calculated from cyclic voltammetry curves with respect to scan rate. At a low scan rate, the Mn_3O_4 nanostructured material has a high value of capacitance and it decreases as the scan rate increases due to inactive sites of its structure at a higher scan rate. The galvanostatic charge–discharge measurements were executed for further supercapacitive study of the electrode material of Mn_3O_4 nanostructure in aqueous 1M Na_2SO_4 electrolyte in the potential range 0 and 0.80 V at current densities of 1 and 2 Ag^{-1} , as shown in Fig. 7. This study also specifies the pseudocapacitive behavior along with the double layer capacitive nature in smaller extent, because of the variable insertion–deinsertion of (Na^+) ion from the electrolyte to Mn_3O_4 nanostructure [20]. The higher value of specific capacitance ($C_s = 158 \text{ Fg}^{-1}$ at current density 1 Ag^{-1}) is due to the ionic diffusion from the electrolyte by entering almost all of the existing pores of the electrode. However, at high current density, the active interaction between the ions and the nanostructured electrode significantly decreases, which results in a value of capacitance reduction [21].

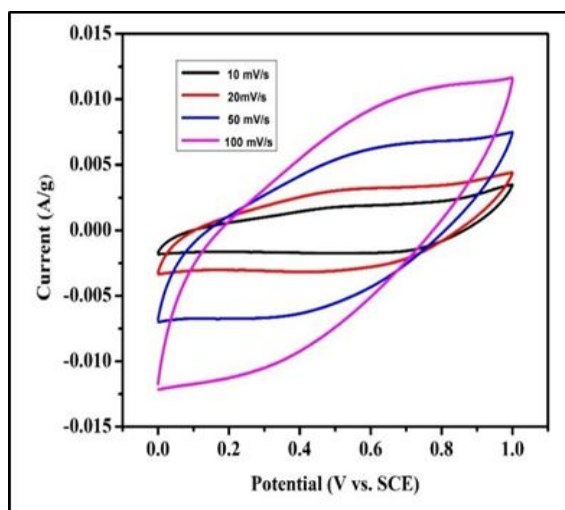


Fig. 5: CV curves of Mn_3O_4 thin film,

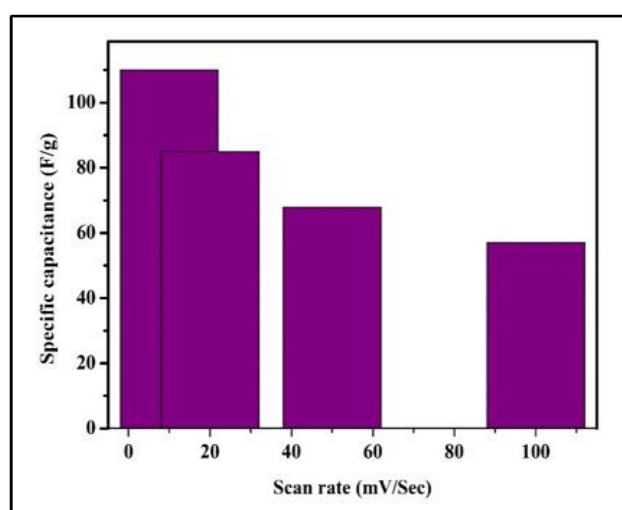


Fig. 6: Variation of specific capacitance with scan rate.

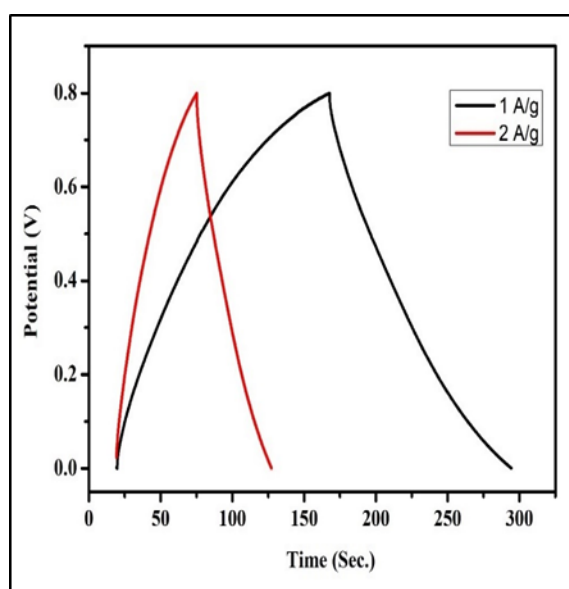


Fig. 7: Galvanostatic charge-discharge curves of Mn_3O_4 thin film.

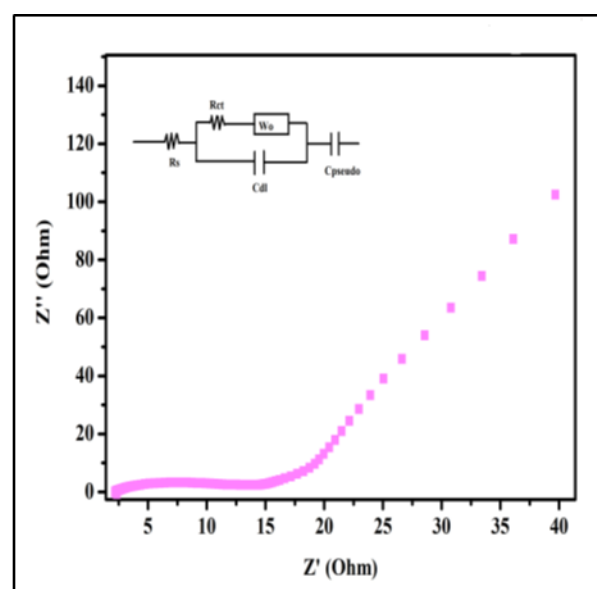


Fig. 8: Nyquist plot of Mn_3O_4 thin film electrode with an equivalent circuit.

By EIS study, the Nyquist plot is plotted, as shown in Fig. 9 contains a semi-circle at higher values of the high-frequency range. After a semi-circle, a straight line at high frequency signifies the ionic diffusion and charge transfer resistance. Here the intercept at the real axis provides the value electrolyte resistance (R_s) equal to 2.3Ω , and the diameter of the semicircle gives the charge transfer resistance (R_{ct}) at the interface of electrode/electrolyte equal to $25 \Omega\text{cm}^2$. The Warburg resistance (W_s) is the resistance due to ionic diffusion, calculated from the slope of the straight line in the low-frequency region is found to be 2.81Ω [22]. Thus, the EIS study provides valuable information about supercapacitive performance by the considerable diffusion of charges across the interface of the electrolyte and electrode interface available for redox reactions.

4. Conclusion

Highly porous grass-like nanostructured Mn_3O_4 thin films were successfully deposited by a simple electrophoretic deposition technique. The tetragonal crystal structure was observed by XRD study with

a crystallite size of ~ 130 nm. FTIR, Raman and SEM studies have provided information about composition and surface morphology. By electrochemical studies, it was observed that the nanostructured Mn_3O_4 electrode shows a maximum specific capacitance equal to 158 F/g at 1 A/g, which also approves the porous nanostructure on the surface of the electrode. This study explores the nanostructured Mn_3O_4 as an electrode material for supercapacitor and further efforts are required for enhancement in the performance.

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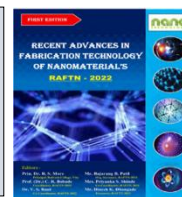
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Recent Advances in Fabrication Technology of Nanomaterials

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Overview of Ni-MoO₄ Thin Films: Structure, Classification and Applications

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1. Introduction

Supercapacitors (SCs) are electrochemical energy storage devices that store and release energy by reversible adsorption and desorption of ions at the interfaces between electrode materials and electrolyte. It is also called as ultracapacitors. A supercapacitor is made up of two metal electrode plates separated by a thin and porous insulator usually made from carbon, paper or plastic that has been soaked in an electrolyte [1]. Supercapacitors differ from conventional capacitors due to their fast charge-discharge rates, longer life cycle, high power, and high energy density. Supercapacitors have gained a lot of attention due to their unique features like high power, long cycle life and environment-friendly nature. They act as a link for energy-power difference between a traditional capacitor (having high power) and fuel cells/batteries (having high energy storage) [2].

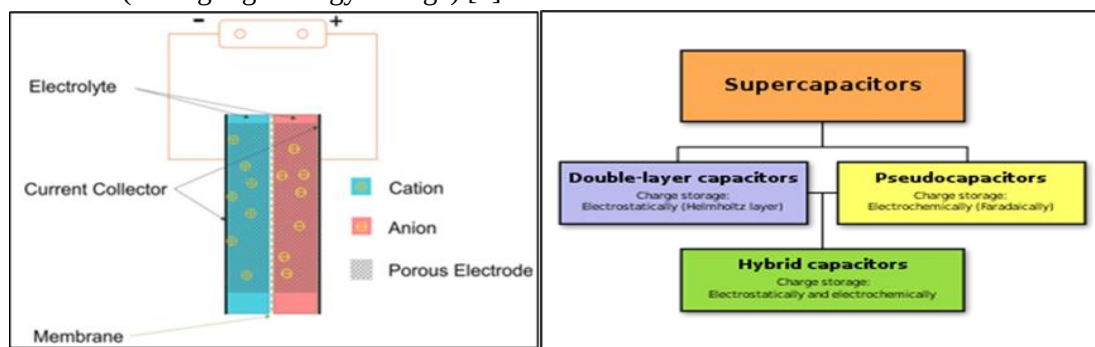


Fig.1: Schematic illustration of a supercapacitor [4], **Fig.2:** A diagram that shows a hierarchical classification of supercapacitors and capacitors of related types [8].

The metal oxides/hydroxides and conductive polymers are widely used as pseudocapacitive materials. The series of metal oxides/hydroxides such as RuO₂, MnO₂, NiO/Ni(OH)₂, Co₃O₄/Co(OH)₂, Fe₂O₃/Fe₃O₄, Cu₂O/CuO, V₂O₅, SnO₂, NiMoO₄ are used as electrode materials for supercapacitors. On the other hand, polyaniline, poly-pyrrole, and polythiophene are well-known conductive polymers for supercapacitor electrode [3].

1.2. Types of supercapacitors

Supercapacitors are classified into three types [5]:

1. Electrostatic double-layer capacitors
2. Pseudo-capacitors
3. Hybrid capacitors

1. Electrostatic double layer capacitors

These types of capacitors include two electrodes, a separator, and an electrolyte. The electrolyte is the mixture that constitutes positive and negative ions dissolved in water. The two electrodes are separated by a separator. These supercapacitors use carbon electrodes or derivatives with much higher electrostatic double-layer capacitance. The separation of charge in electrostatic double-layer capacitors is less than in a conventional capacitor; it ranges from 0.3–0.8 nm [6].

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2. Pseudo capacitors

Pseudo capacitors are also referred to as electrochemical pseudo-capacitors. These capacitors make use of metal oxide or conducting polymer electrodes with a high amount of electrochemical pseudo-capacitance. These types of components store electrical energy by electron charge transfer between electrode and electrolyte. This can be done by a reduction-oxidation reaction commonly known as a redox reaction [7].

3. Hybrid capacitors

The hybrid capacitors are developed by using the techniques of double-layer capacitors and pseudo-capacitors. In these components, electrodes with different characteristics are used. One electrode with the capacity to display electrostatic capacitance, and the other electrode with electrochemical capacitance [8]. Examples of hybrid capacitors: the lithium-ion capacitor.

1.3. Introduction of Molybdenum Trioxide (MoO_3)

Molybdenum trioxide describes a family of inorganic compounds with the formula $\text{MoO}_3(\text{H}_2\text{O})_n$ where $n = 0, 1, 2$. These compounds are produced on the largest scale of any molybdenum compound. The anhydrous oxide is a precursor to molybdenum metal, an important alloying agent. It is also an important industrial catalyst. It is a yellow solid, although impure samples can appear blue or green. Molybdenum trioxide occurs as the rare mineral molybdite. The molybdenum trioxide is used in coatings, nanowires, nanofibers, plastics, and textiles. In specific alloy and catalyst application. Before 2000, nanomaterials based on molybdenum compounds, such as MoS_2 , MoSi_2 , MoSe_2 , etc., had been investigated extensively. It is only during the last few years that MoO_x nanowires have attracted any attention in the literature [9].

Krishnakumar and Menon [10] synthesized of molybdenum trioxide thin film by physical vapour deposition. They studied electrical and optical properties and reported that activation energy of conductivity for MoO_3 thin film varied with thickness of the film. In 2000, Zach et al. used the electrode position method to prepare MoO_x nanowires ranging from 20 nm to 1.3 μm in diameter for the first time. In the same year, carbon nanotubes were used as a template to synthesize $\alpha\text{-MoO}_3$ nanowires with a diameter of 5 – 15 nm. After that, various strategies were developed to design and rationally synthesize MoO_x nanowires with predictable control the key structural, chemical, and physical properties [11].

1.3. Introduction of Nickel Molybdate (NiMoO_4)

Nickel molybdate is a light green, crystalline powder, slightly soluble in water until the addition of Ammonium Hydroxide which significantly increases the solubility. It is a high purity compound. The chemical formula of nickel molybdate is NiMoO_4 . Supercapacitors based on the nanomaterial electrodes exhibit great potential as power sources for advanced electronic devices. The development of clean and environmentally-friendly energy source is a key to fundamentally solve environmental pollution caused by human activities an outstanding example of clean energy storage device is the supercapacitor, which has become a core component in various technologies, such as portable electronic devices, electronic hybrid vehicles, and medical equipment [12].

A crucial factor for the commercialization of supercapacitors is the development of environmentally-friendly electrodes that can be fabricated at low cost, provide high energy/power densities and have excellent stability. Carbon materials, polymer-based materials, and transition metal oxides have been widely studied for their application as supercapacitor electrodes. Carbon materials have small specific capacities, and polymer-based materials have demonstrated insufficient electrochemical stability. Transition metal oxides are promising electrode materials because of their high-capacity, long-cycle-life performance and environmental friendliness. Harish. S. Chavan et al. [13] synthesized NiMoO_4 compound thin films were fabricated on stainless steel substrates using a SILAR technique. They prepared by the precursor solutions were using 0.1M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.1M $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$. The pH of the Ni-containing bath was adjusted to 12.2 by adding an ammonia solution dropwise. The Mo-

containing bath was maintained at 65 °C. They studied the NiMoO₄ film was fabricated by successively dipping a stainless-steel substrate in each bath.

2. Historical development

In 1950s General Electric Engineers started experimenting components using porous carbon electrodes for fuel cells and rechargeable batteries. In 1957 H. Becker developed a “low voltage electrolytic capacitor with porous carbon electrodes”. In 1966 researchers at standard oil of Ohio (SOHIO) developed another version of the component as electrical energy storage apparatus. Even in 1970, the electrochemical capacitor patented by Donald L. Boos was registered as an electrolytic capacitor with activated carbon electrodes. SOHIO did not commercialize their invention, licensing the technology to NEC (Nippon Electric Company), who finally marketed the results as "supercapacitors" in 1978. Between 1975 and 1980 Brian Evans Conway conducted extensive fundamental and development work on ruthenium oxide electrochemical capacitors.

The first supercapacitor with low internal resistance was developed in 1982 for military applications through the Pinnacle Research Institute (PRI), and were marketed under the brand name "PRI Ultracapacitor". In 1992, Maxwell Laboratories (later Maxwell Technologies) took over this development [14]. In 1999 he defined the term "supercapacitor" to make reference to the increase in observed capacitance by surface redox reactions with faradaic charge transfer between electrodes and ions. Recent developments include lithium-ion capacitors. These hybrid capacitors were pioneered by Fujitsu's FDK in 2007. The use of NiMoO₄ dates to the mid-20th century, where early research on this material was primarily focused on assessing its catalytic activity in oxidative hydrogenation reactions. However, the production of NiMoO₄ on the nanoscale has spurred renewed attention in the last few years due to the increased interest in employing this material for electrochemical storage application. The different methods have been utilized to produce nanostructured NiMoO₄, including sol-gel [15], hydrothermal [16], sono-chemical [17], microwave-assisted solvothermal [18], co-precipitation [19], electrochemical deposition [20], laser ablation [21], and mechanochemical [22] synthesis. Despite the availability of numerous synthesis techniques, fundamental studies on the synthesis, characterization, and properties of nanometric NiMoO₄, have been limited to date.

Also, the synthesis of multi-component, nanostructured metal oxide like NiMoO₄ has been associated in traditional methods with several limitations, such as long synthesis time, phase separation, and irregular particle size. Further, most of the currently used chemical methods generate toxic chemical waste, leading to environmental hazards and non-biodegradable products, while physical methods necessitate massive energy requirements. Approaches based on the use of ‘biological/green’ chemicals to synthesize metal-oxide nanostructures have emerged as more viable options in the realm of “green chemistry” [23]. The solution combustion synthesis (SCS) method is well established and popular due to its simplicity, low cost, established performance, and energy saving aspects. The method is based on the concepts used in propellant chemistry where a fuel (reducing agent) and an oxidant (e.g., metal cation precursor), under adequate experimental conditions, give rise to an intense exothermic, self-propagating redox reaction, resulting in the production of oxide nano powders.[24]

In addition to its simplicity, low cost, and versatility, the main aspect that makes SCS an attractive method is that a highly crystalline material could be obtained in a relatively short duration, owing to the rapid release of energy during the combustion step. This often eliminates the need for a long and energy-intensive calcination step. The proper selection of the experimental conditions in the solution combustion approach is essential. In particular, the fuel type greatly influences the physicochemical properties of the desired products [25].

Hence, we decide the best material for supercapacitor is NiMoO₄ by successive ionic layer adsorption reaction (SILAR). This material is eco-friendly and low cost.

2.1. Structure of NiMoO₄

NiMoO₄ is zeta iron carbide-derived structured and crystallizes in the monoclinic P2/c space group. Mo⁶⁺ is bonded to six O²⁻ atoms to form distorted MoO₆ octahedra that share corners with eight equivalent NiO₆ octahedra and edges with two equivalent MoO₆ octahedra. The corner-sharing octahedral tilt angles range from 47–56°. [26]

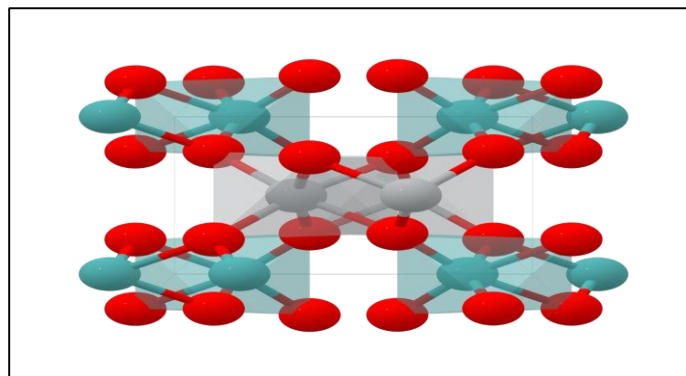


Fig. 3 Structure of Nickel Molybdate [26]

There are spread of Mo–O bond distances ranging from 1.82–2.16 Å. Ni²⁺ is bonded to six O²⁻ atoms to form NiO₆ octahedra that share corners with eight equivalent MoO₆ octahedra and edges with two equivalent NiO₆ octahedra. The corner-sharing octahedral tilt angles range from 47–56°. There are four shorter (2.07 Å) and two longer (2.12 Å) Ni–O bond lengths. There are two inequivalent O²⁻ sites. In the first O²⁻ site, O²⁻ is bonded in a distorted trigonal planar geometry to two equivalent Mo⁶⁺ and one Ni²⁺ atom. In the second O²⁻ site, O²⁻ is bonded in a 3-coordinate geometry to one Mo⁶⁺ and two equivalent Ni²⁺ atoms [27]

3. Literature review

Kandalkar, et al. [28] synthesized cobalt oxide thin film electrode by adopting simple and inexpensive chemical deposition and characterized for structural and morphological studies. They studied that the super-capacitive properties of cobalt oxide electrode in aqueous KOH electrolyte solution, specific capacitance and stability. They also showed maximum capacitance. Patil, et al. [29] synthesized nanostructured nickel hydroxide thin film by chemical bath deposition technique. They studied its structural, surface morphological and electrochemical properties. They also reported that the solution is saturated then film formation is observed. Salunkhe and lokhande [30] synthesized nickel Oxide thin film for supercapacitor application by chemical bath deposition process from aqueous solution. They also studied phase changed from β -Ni(OH)₂ to NiO and reported that porous thin film investigated by CBD method are promising candidate for supercapacitor applications.

Also detailed synthesis and characterization of Ni-MoO₄ thin films synthesized by SILAR technique for supercapacitor applications summarized in the following table.

Sr. No.	Materials	Methods	Preparation Conditions	Specific Capacitance	Energy density	Ref. No.
1	Graphene Carbon nanotubes	Chemical vapour deposition	500 1000 °C	178 Fg ⁻¹	6 Whkg ⁻¹	[3]
2	(MoO ₃) nanowires	Electro-deposition	500 °C for 48 hrs.	68 Fg ⁻¹	76.80 Whkg ⁻¹	[11]

3	(NiMoO ₄)	SILAR	100 ⁰ C for 2 hrs	1180 Fg ⁻¹	119 Whkg ⁻¹	[13]
4	(NiMoO ₄) nanoparticles	Sol-gel	650 °C for 2 hrs.	1123 Fg ⁻¹	32.40 Whkg ⁻¹	[15]
5	(Ni(OH) ₂)	Hydro thermal	120 °C for 4 hrs.	2653.2 Fg ⁻¹	32.7 Whkg ⁻¹	[16]
6	(MnO ₂ /RGO) nanohybrid	sonochemical	45 °C for 2 hrs.	375 Fg ⁻¹	1 Whkg ⁻¹	[17]
7 7	(CuO) nanostructure	Microwave-assisted solvothermal	60 °C for 8 hrs.	612 Fg ⁻¹	27.27 Whkg ⁻¹	[18]
8	NiMoO ₄ NPs/rGO nanocomposite	Co-Precipitation	350 °C for 2 hrs.	900 Fg ⁻¹	32.40 Whkg ⁻¹	[19]
9	(MnO ₂) nanorod arrays	Electrochemical deposition	70 °C	660.7 Fg ⁻¹	308 Whkg ⁻¹	[20]
10	Iron Oxide (Fe ₃ O ₄) nanoparticles	Laser ablation	200-500°C for 5 hrs.	834 Fg ⁻¹	15.84 Whkg ⁻¹	[21]
11	Cobalt Oxide (Co ₂ O ₃)	CBD	65 ⁰ C for 4 hrs	118 Fg ⁻¹	5.8 Whkg ⁻¹	[28]
12	β-Ni(OH) ₂	CBD	60 °C	398 Fg ⁻¹	74.2 Whkg ⁻¹	[29]
13	Nickel oxide (NiO)	CBD	350C for 2 hrs	167 Fg ⁻¹	23 Whkg ⁻¹	[30]

4. Applications

Ever since the discovery of supercapacitor have been playing an increasingly important role in techniques and applications. There are many applications of supercapacitor are as follow

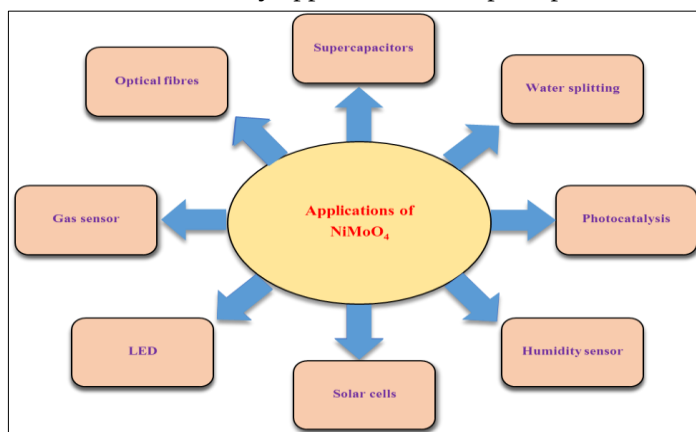


Fig.4 The various applications of NiMoO₄

1.5.1 Gas-sensor

The gas-sensor performance of Co_3O_4 strongly depends on its microstructure. Among the reported nanostructures, porous Co_3O_4 nanostructures shows better performance in energy storage and gas-sensor due to their fast electron transport and large active interfacial sites owing to the large surface areas. To meet the requirement, many methods have been applied in the synthesis of porous Co_3O_4 nanostructures [31]. Zang, et al. [32] synthesized 1T/2H- MoS_2 /graphene fishnet tube by solvothermal process and they studied electrochemical and electrical measurement. They reported that all gas sensing experiments were carried out at room temperature and at atmospheric pressure. Junyeong Yun, et al. [33] synthesized NO_2 gas sensor by chemical vapour deposition (CVD) process. They reported that NO_2 gas based on patterned graphene. They also studied electrical resistance and chemical sensitivity of gas sensor.

1.5.2 Photocatalyst

Semiconductor photocatalysis offers a green and energy-saving technology for the degradation of carcinogenic dyes in environmental and waste water treatment. Among eco-friendly photocatalytic materials ceramic Oxide (CeO_2), a direct band gap semiconductor material has fascinated significant interest of researchers due to its wide band gap (~ 3.2) and considered has a potential material for photocatalyst, fuel cells, three-way catalyst, sensors, water treatment, solar cell, etc [34]. Liqi Bai, et al. [35] synthesized the role of transition metal oxides in g- C_3N_4 -based heterojunction for photocatalysis and supercapacitors. They reported that excellent performance of transition metal oxides. They also studied the heterostructure designs, supercapacitor applications and photocatalytic applications. Govindhasamy Murugadoss, et al. [36] synthesized the selective metal ions doped CeO_2 nanoparticles for excellent photocatalytic activity under sunlight and supercapacitor application by one step chemical precipitation process. They showed that excellent catalyst for dye degradation at room temperature and smaller optical band gap. They studied physical and chemical properties of Ag doped CeO_2 .

1.5.3 Water splitting

Water electrolysis is a fast and efficient produce for storing intermittent solar and wind energy in the form of chemical fuels, namely hydrogen and oxygen. Among the different energy carriers, H_2 has attracted a great deal of attention due to its lightweight environmentally safe oxidation product H_2O and high energy densities. In spite of their catalytic activities towards HER and OER, their scarcity, high-cost and operation at a high cell voltage. Direct solar-to-hydrogen conversion by light driven water splitting has to been considered as a promising route to convert and store solar energy into chemical fuels [37]. Chunyang Zhang, et al. [38] synthesized nanostructured CoFe_2O_4 by electro-deposition method. They studies performance of electrode for energy generation and storage system and they reported that the stability of electrodes after 10,000 cycles showed capacitance retention 80 %.

1.5.4 Solar cell

The development of modern electronics requires the use of flexible devices for both energy conversion and storage. For instance, excitonic solar cell such as polymer and dye-sensitized solar cell that can be coated on flexible substrate are widely studies to offer the electrical properties of conventional rigid silicon wafer-based technologies. Electrochemical supercapacitors have been made into a flexible-films to expands the application scope, such as various portable electronic facilities [39]. Rajaram Mane, et al. [40] synthesized tin oxide thin film by electrochemical deposition method for dye-sensitized solar cell and electrochemical supercapacitor applications. They studied demonstrated synthesis, structural, hydrophilicity and morphological properties. They also reported that interfacial and specific capacitance of supercapacitors. Vanita Raut, et al. [41] synthesized indium doped CdSe thin film using aqueous bath by potentio-static electrodeposition method. They studied thin films possess n-type conductivity, photo-conversion efficiency and fill Factor. They also reported that optical absorption showed that indium doping causes decreased band gap energy between (2.02 - 1.67) eV. They showed structural and morphological properties.

1.5.5 Supercapacitors

A supercapacitor is a pulse current system used to meet high current and specific power ($10,000\text{Wkg}^{-1}$) requirement for duration of less than 1min. Consequently, supercapacitors can be used alone or in combination with another energy storage option i.e., batteries to offer improved power efficiency and enhanced cycle life for applications such as hybrid vehicles, cranes, trains etc. until the 1990, the demand for supercapacitor technology was low outside the field and aims to increase the electrical performance of electrode materials [42]. Rahul Salunkhe, et al. [43] synthesized nickel cobaltite (NiCo_2O_4) film containing nanorods and nanoflakes by chemical bath deposition method. They studied electrochemical properties and specific capacitance of supercapacitor. They also measured BET surface area and absorption or adsorption nitrogen isotherms.

1.5.6 Optical Fibers

Sheng-Hui Liao, et al. [44] synthesized NiMoO_4 nanofibers by electrospinning method in the first time. They reported that this work should provided a new pathway for the design of advanced glucose catalyst for nonenzymatic sensor. They also studied possible electrocatalytic mechanism of nanoparticles for the glucose oxidation. Emanuele Mura, et al. [45] synthesized phosphate glasses for optical fibers characterization in the present work. They studied thermo-mechanical properties and optical properties. They also studied fabrication of passive optical fiber for amplifier and laser applications. They reported that the inner surface quality of the tubes manufactured by the rotating casting.

1.5.7 Light emitting diode

Xuyong Yang, et al. [46] synthesized red phosphors for white LED by a convenient solid-state method. They studied the improvement of the intensity of the red emission has been achieved by adding an alkali chloride to phosphor sample. They also reported that the influence of the sintering temperature on the luminescence properties of the phosphors. Feng Hong, et al. [47] synthesized red phosphors for white-warm LED by co-precipitation method at room temperature. They studied crystal structure, morphology, composition, and optical properties of red phosphors. They also studied the optimized mechanism of an ionic surfactants. They reported that the phosphors can absorbed blue light at 468 nm and emitted a narrow red-light emissions peak at 635 nm.

1.5.8 Humidity sensor

R. S. Andre, et al. [48] CaZrO_3 stoichiometric and non-stoichiometric (CaO and ZrO_2 excess) powder synthesized by a chemical method which is based on polymeric precursors. They studied that the humidity sensing properties were evaluated by using an inductance, capacitance, and resistance analyser. They also reported that the result demonstrated the great potential of CZO samples for use in the development of new humidity sensor. Zhuyi Wang et al. [49] synthesized of porous TiO_2 for a high-performance humidity sensor by sol-gel method. They reported that this sensor exhibited high sensitivity and linear response in the wide relative humidity range (11%-95%). They showed that the complex impedance spectra show the conduction process depends on the RH range and the microstructure of the sensing materials.

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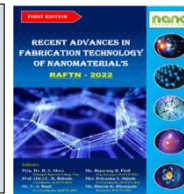
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**Recent Advances in Fabrication Technology of
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Mixed Spinel Ferrites – An overview on synthesis methods and structural properties

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KEYWORDS

Magnetism,
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Mixed spinel ferrites,
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ABSTRACT

The research in the field of ferrites has attracted attention due to its immense potential applications in various fields. Out of different types of ferrites spinel ferrites has been shown great interest due to its versatile structural, morphological, electrical and magnetic properties. The mixed spinel ferrite is class of spinel ferrite which is widely investigated. According to the requirement, the features of the mixed spinel ferrites can be modified by varying the composition and method of preparation. These materials can be produced by using different methods by controlling the experimental parameters. Structural properties show strong dependence on the preparation methods. Here an overview of mixed spinel ferrites is discussed regarding to its various synthesis methods and structural properties.

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1. Introduction

In the ancient world people noticed that Loadstone which is a naturally magnetized piece of the mineral magnetite that can attract iron. Magnetism is associated with the kind of magnetic moments and their mutual interactions. Magnetite (Fe_3O_4) is naturally occurring spinel ferrite. Depending on the presence of magnetic domains materials are classified as follows,

- 1) Diamagnetism: Diamagnetism is the property of a material to oppose magnetic field that applied to it therefore to be repelled by a magnetic field. In a diamagnetic material there are no unpaired electrons.
- 2) Paramagnetism: In this type of magnetism, materials have unpaired electrons. These materials have permanent dipole moments and which are randomly oriented in the absence of the external magnetic field. When an external magnetic field is applied the magnetic moments will tend themselves in the same direction as applied field.
- 3) Ferromagnetism: The material which have ferromagnetism property show hysteresis behavior with coercive and retentive properties. Materials that retain permanent magnetization in the absence of external magnetic field are known as hard magnets. It possesses the curie temperature i.e. point above which it loses its ferromagnetic property.
- 4) Antiferromagnetism: Materials having atomic magnetic moments of equal magnitude that arranged in an antiparallel fashion display shows antiferromagnetism.
- 5) Ferrimagnetism: Ferrimagnetism is exhibited by ferrites and magnetic garnets. Magnetization in the ferrimagnets retains in the absence of field.
- 6) Superparamagnetism: This property found in magnetic material at nanoscale level which having negligible coercivity and retentivity value.

2. Ferrites:

Ferrite is a class of magnetic materials having tremendous applications in various fields [1, 2]. Recently, the researcher has been shown great interest in the field of ferrites due to their versatile structural, electric as well as magnetic properties [3]. Ferrite contains iron oxide as their major component. Depending upon the coercive field ferrites are classified as

1] Hard ferrites - The class of ferrite that have high coercive field.

2] Soft ferrites - The class of ferrite that have low coercive field.

The physical properties like electrical and magnetic properties of ferrites depend on structure of ferrites [4]. Depending upon the structure ferrites are classified as spinel ferrites, garnet ferrites, ortho-ferrites and hexa-ferrites. Out of which spinel ferrites show good structural, morphological, electric and magnetic properties [5].

3. Spinel Ferrites

Spinel ferrite is a very attractive class of the ferrite. Due to their remarkable properties spinel ferrites are widely investigated in the recent years [6, 7]. The general formula of the spinel ferrite is represented as the MFe_2O_4 . Where, M is divalent metal ions. In spinel ferrite the metal ion are within the interstitial positions of four fold and six fold oxygen coordination. The magnetic ion surrounded by four oxygen ions at the vertices of a tetrahedron is called tetrahedral site or A-site and in another type the magnetic ion is surrounded by six oxygen ions at vertices of an octahedron is called as octahedral site or B-site. The distribution of divalent and trivalent metal ions among the tetrahedral and octahedral site results in classification of spinel ferrites in to three types which are shown in the fig. 1.

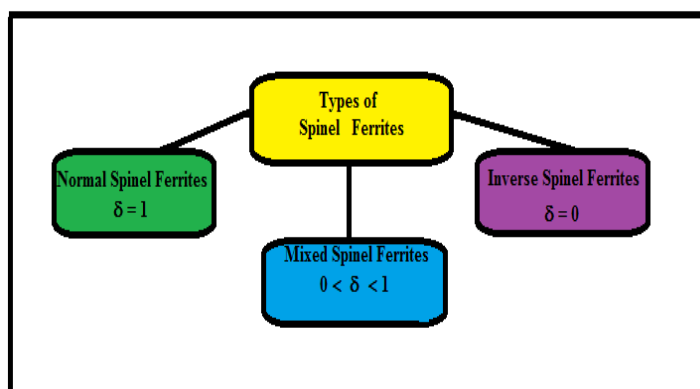


Fig.1 Types of Spinel Ferrites

- 1) **Normal Spinel Ferrites** – In this type of spinel ferrites all divalent metal ions present at tetrahedral site (A – site) and all trivalent metal ions present at octahedral site (B- site). eg. $ZnFe_2O_4$
- 2) **Inverse Spinel Ferrites** – In this type of spinel ferrites all divalent metal ions present at the octahedral site (B- site) and all trivalent metal ions equally distributed over tetrahedral and octahedral site. eg. $NiFe_2O_4$
- 3) **Mixed Spinel Ferrites** – In this type of spinel ferrites divalent metal ions and trivalent metal ions are distributed on both tetrahedral and octahedral sites randomly. eg. $MnFe_2O_4$

4. Mixed Spinel ferrites

Till date more attention and importance is given to the mixed spinel ferrites due their enhanced structural, electrical and magnetic properties [8]. Mixed spinel ferrites have vast applications such as gas sensor [9], biomedical application [10], microwave application [11], antimicrobial activity [12] etc. Fig. 2 highlights some important properties of mixed spinel ferrites. Modification in the structural, electrical and magnetic properties due to change in the composition and method of preparation have been investigated by several researchers [13, 14].

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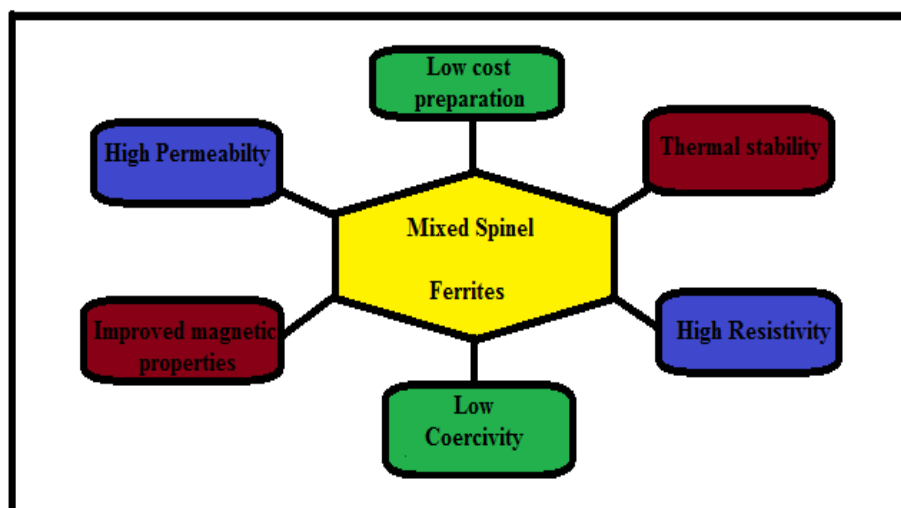


Fig. 2 Properties of mixed spinel ferrites

5. Methods of synthesis of mixed spinel ferrites

Mixed spinel ferrites can be synthesized by various methods. Method of preparation plays vital role for controlling the properties of the spinel ferrites [15]. Researchers have been used different methods to synthesis of mixed spinel ferrites. Out of which standard ceramic method [16], sol – gel autocombustion method [17], co – precipitation method [18] are widely used to synthesis the mixed spinel ferrites.

- 1) **Standard ceramic method** – Ceramic method is used to synthesis ferrites by many researchers [19, 20]. It involves the four steps a) Mixing of high purity divalent metal oxides and ferric oxide in the required proportion. b) Presintering and calcination. c) Converting the presintered material in to powder. d) Final sintering to get required product .This method possess some advantages like A] It is widely accepted commercial method. B] It is possible to maintain stoichiometry of the final product. Few drawbacks of this method are A] It is time consuming method B] This method yields particles of comparatively large course [20].
- 2) **Sol – gel autocombustion method** – This is the chemical method to synthesis the ferrite nanoparticles. This method involves the two main phases such as sol and gel i.e. the synthesized material must transits from two phases i.e. sol and gel [21]. Several merits of this method are A] It easy and cheap chemical method of synthesis. B] Operating temperature is low. C] Not time consuming method. Large scale production not possible is main disadvantage of this method [22].
- 3) **Co – precipitation method** – It is simple bottom – up approach method of synthesis of mixed spinel ferrites. It involves the simultaneous occurrence of nucleation, growth, coarsening and or agglomeration [23]. Some advantages of this method are A] It is possible to carried out this process in a small laboratory. B] It is possible to obtain small particle size. Several disadvantages of this method are A] Possibility of contamination. B] Not work well if reactants have very different precipitation rates [24]. According to the requirement, the properties of the mixed spinel ferrites may be modified by changing the composition and method of synthesis. These materials can be produced by using various methods by controlling the experimental parameters.

6. Literature review on structural properties of mixed spinel ferrites

Several researchers studied that the structural properties shows strong dependence on the methods of preparation and also observed that cationic distribution plays vital role for controlling the structural, electrical and magnetic properties [33,34]. Muddassar Naeem et al. [35] prepared mixed spinel ferrite

$\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) by co-precipitation method. They obtained the crystallite size within the range 10-13 nm. They also observed that extra peak for the sample with $x = 0.75$ and $x = 1$ which is the cause of the impurity. Furthermore the lattice constant increases with increase in Mg – concentration due to the larger ionic radii of the Mg than Ni. Md. Mahbubul Haque et al. [36].

Table 1. The summary of some mixed spinel ferrites regarding to its method of preparation and analysis performed.

Method of Synthesis	Material	Analysis Performed	Ref. No.
Ceramic method	Mg – Zn Ferrites	Physical and Magnetic Properties	25
Sol-gel autocombustion method	Ni – Cu – Zn Ferrites	Structural and Magnetic Properties	26
Co-precipitation method	Zn – Nd Ferrites	Structural and Electrical Properties	27
Sol-gel autocombustion method	Ni – Cd Ferrites	Temperature Dependent Electrical Properties	28
Co-precipitation method	Mn - Co Ferrites	Structural and Magnetic Properties	29
Ceramic method	Ni – Zn Ferrites	Structural and Morphological Properties	30
Sol-gel autocombustion method	Li – Mn Ferrites	Structural and Morphological Properties	31
Co – precipitation Method	Co - Cu - Al Ferrites	Structural, Morphological and Magnetic Properties	32

Investigated Ni-Mg mixed spinel ferrite by using the conventional ceramic method having the composition $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ [0.0, 0.2, 0.4, 0.6, 0.8 and 1.0]. They noticed that lattice constant increases with the Mg content that can be explained on the basis of Vegard's law. They also observed that bulk density is lower than the X – ray density due to the existence of pores developed during the synthesis or sintering process. E. Ranjith Kumar et al. [37] studied the manganese substituted copper ferrite nanoparticles. They used sol – gel autocombustion technique for synthesis of nanoparticles. They observed that lattice constant and crystallite size increases with annealing temperature. The crystallite size of synthesized materials is in the range 9 nm– 45 nm. P. Chavan et al. [38] used the solid state reaction method to synthesis $\text{Ni}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0 - 0.5$). They found that lattice constant lies in range $8.332 \text{ \AA} - 8.375 \text{ \AA}$ and crystallite size ranges from $0.930 \mu\text{m} - 1.04 \mu\text{m}$. Both lattice constant and crystallite size shows increasing trend with increasing Ni content. M. M. Mallapur et al. [39] investigated $\text{Ni}_{0.7-x}\text{Zn}_{0.3}\text{Co}_x\text{Fe}_2\text{O}_4$ with $x = 0.0 - 0.3$. They have used combustion method to synthesis nanocrystalline magnetic nanoparticles. They determined the average crystallite size from XRD data using Debye - Scherer's formula and found that crystallite size lies in the range of 20 – 30 nm. They obtained particle size from TEM micrographs which is $\sim 10\text{nm}$. K. Maaz et al. [40] studied nickel doped cobalt ferrite which is synthesized by co-precipitation method. They obtained crystallite size in the range 18 – 28 $\pm 4\text{nm}$. From energy dispersive spectroscopy they confirmed the presence of Co, Ni, Fe and oxygen in the synthesized samples.

7. Conclusions

Mixed spinel ferrites are novel materials that hold great potentials for various applications due to their unique structural, electrical and magnetic properties. Synthesis of mixed spinel ferrites is achieved by different methods each having advantages and some limitations. Modification in the structural properties is observed due to change in the method of synthesis. As the method of synthesis plays vital

role to modify the structural parameters researchers are interested in mixed spinel ferrites by changing their composition and method of preparation. Due to numerous favorable properties such as structural, electrical and magnetic researchers are interested in mixed spinel ferrites that show immense potential applications in various fields.

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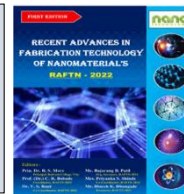
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Co-precipitation Synthesis and Characterization of Pure BaTiO₃ Perovskite Nanospheres for Electrocatalysis

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KEYWORDS

Barium Titanate;
 Electrocatalyst;
 FE-SEM;
 Nanosphere;
 Oxygen Evolution Reaction;
 Tafel plot.

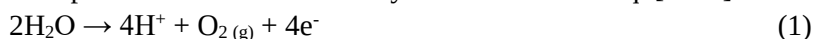
ABSTRACT

Pure Barium Titanate (BaTiO₃) (BTO) nanospheres were synthesized using the simple onestep Co-precipitation method. The prepared BTO samples were annealed at 950°C. The BTO samples with variations of concentration of ingredients BaCl₂ and TiCl₃ have been further characterized by various physico-chemical techniques like XRD, FT-IR, FE-SEM, and EDS. The nanosized BTO samples exhibit spherical morphology. The electrocatalytic activity study showed an overpotential of 0.446 V at a current density of 10 mA cm⁻² and Tafel slope of 107 mV dec⁻¹ in 1 M NaOH solution. So prepared BTO samples catalyse OER efficiently finding its applications for catalysis.

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1. Introduction

Modern society has greatly benefited from the most cutting-edge technologies since the first and second industrial revolutions. But these systems rely on exhaustible carbon-based fuels like gas, coal, and oil. Due to the increasing demand for energy, the constant depletion of nonrenewable energy sources, and their effects on the environment, the focus of scientific research has switched to the progress of renewable energy resources [1–3]. Right now, fossil fuels supply 80% of that energy. As we know, the stock of fossil fuels under the earth's crust is limited and will be exhausted soon. Because of their origins, fossil fuels have high carbon content, hence burning them releases carbon dioxide (CO₂) in the atmosphere which causes the greenhouse effect [4,5]. Due to this, it is widely agreed that fossil fuels cannot be the major energy supplier. This motivated intense research into the pursuit and utilization of clean and sustainable alternative energy sources [6]. The two half-reactions in total water splitting are the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). OER typically takes place at the anode and has complex kinetics since it needs to oxidise two water molecules with four electrons, then remove four protons to create a relatively weak O-O bond Eq. [7–10].



The structural and morphological changes in BTO can enhance catalytic efficiency in OER reaction could be achieved by Co-precipitation. The present study describes the synthesis and electrocatalytic performance of BTO thin films. The impact of structural and morphological characteristics of BTO thin film was examined. To describe the ECSA (electrochemical active surface area) and Tafel plot will be plotted, the relevant OER activities also evaluated using linear sweep voltammetry (LSV) and EIS (electrochemical impedance spectroscopy) in 1 M NaOH electrolyte solution

2. Experimental Section

2.1. Chemicals

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All analytical grade materials have been used for the experiment. The chemical includes Barium (II) Chloride [$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$], Titanium (III) trichloride [TiCl_3] and potassium hydroxide (KOH) which have been obtained from Thomas Baker India pvt Ltd. (Mumbai) and used as it is without further purification.

2.2. Synthesis of BTO nano-spher

Barium titanate was synthesized using the co-precipitation method. In the first beaker 2.4428 ml of Titanium (III) trichloride (TiCl_3) was slowly added to 50 ml of distilled water at room temperature under continuous stirring, this is homogeneous solution. In the second beaker, 1.8971 g of Barium (II) chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) was dissolved in 50 ml distilled water under continuous stirring. After 20min both aqueous solutions were mixed with continuous stirring under room temperature then 3 M NaOH solution was added into the solution to maintain the PH 13 at constant stirring.

2.3. Characterizations

Morphology of BTO thin film was characterized by FE-SEM (field emission scanning electron microscopy, Mira-3, Tescan Pvt. Brno-Czech Republic), X-ray diffraction (XRD), (Bruker D2 phaser tabletop model) with a $\text{Cu K}\alpha$ radiation ($1.5405\text{\AA}$) was used to investigate the crystal phase of barium titanate. LSV (Linear sweep voltammetry), CV (Cyclic voltammetry), and EIS (electrochemical impedance spectroscopy) measurements were conducted on an electrochemical workstation (CHI660e, CH Instruments) using a three-electrode configuration. The elemental analysis of samples was studied with EDS (energy-dispersive X-ray spectroscopy, Oxford Instrumentations), inbuilt with FE-SEM. All the electrochemical tests were carried out at room temperature.

2.4. Preparation of electrode and Electrochemical measurements

Prior to deposition, a stainless-steel substrate ($2 \times 5\text{ cm}$) was polished using various polishing papers. The substrate was first washed with 1 M H_2SO_4 and then applied to ultrasonic treatment to remove the greasy surface. The working electrode has been prepared BTO sample, using the mass proportionate ratio of 80:10:10, carbon black and polyvinylidene difluoride polymer binder are combined. A $1\text{ cm} \times 1\text{ cm}$ section of SS was coated with a slurry of N methyl pyrrolidinone (NMP) and dried overnight at 800°C in a vacuum. Electrochemical experiments were performed using a CHI-608E instrument connected to a standard three-electrode setup. The as-prepared sample were used directly as the working electrode ($1\text{ cm} \times 1\text{ cm}$) while pt wire and the saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively in 1 M NaOH as the electrolyte. Nernst equation (Eqⁿ. 2) was used to convert the measured potential from the SCE scale to the reversible hydrogen electrode (RHE) scale as $\text{ERHE} = \text{ESCE} + 0.059 \times \text{pH} + \text{E}^0\text{ SCE}$ (2) Where ERHE is converted potential vs RHE, ESCE is the experimentally measured potential vs reference electrode (SCE) and $\text{E}^0\text{ SCE}$ is standard redox potential of SCE at 298 K ($0.244\text{ V} \pm 0.002\text{ V}$). By using the Tafel equation to fit a linear section of the Tafel plot, the Tafel slope was calculated [8,11].

$$\eta = b \log j + a \quad (3)$$

3. Results and Discussion

3.1. XRD

For the structural analysis of the sample, XRD was recorded in the 2θ range of $10-90^\circ$. Fig. 1 shows the XRD pattern of the BTO sample. The XRD pattern of the sample revealed the formation of BTO, with a tetragonal crystal structure [JCPDS card no. #892475]. The diffraction peaks at angles (2θ) of 22.2° , 31.5° , 38.9° , 45.2° , 50.8° , 56.1° , 65.9° , and 75.0° are assigned to the (100), (110), (111), (200), (210), (211), (220) and (310) planes of the BTO crystal lattice, with Lattice parameters $a=b=c=4.03\text{ \AA}$. The crystallite size (D) of the sample are estimated from Scherer's formula [12].

$$D = 0.9\lambda / \beta \cos\theta \quad (4)$$

Where all the symbols have usual meaning.

The calculated crystallite size for BTO is 20 nm.

3.2. FT-IR

FT-IR spectra of the synthesized BTO material, fig. 2 the FT-IR spectra of BTO material in the range of 4000-400 cm^{-1} . The peaks look as if in the range of 400-800 cm^{-1} is an M-O bond. The peaks at 560 cm^{-1} are given to Ti-O stretching modes. The individual peaks at 1446 cm^{-1} may be dispensed to stretching vibrations of a carbon-oxygen bond. The individual band at 1645 cm^{-1} specifies the bending / stretching mode of C-O. The specific broadband seems at 3450 cm^{-1} assigned to the stretching mode of the O-H bond. From the FT-IR analysis, the formation of BTO material is confirmed by the existence of the Ba-Ti-O bond [13].

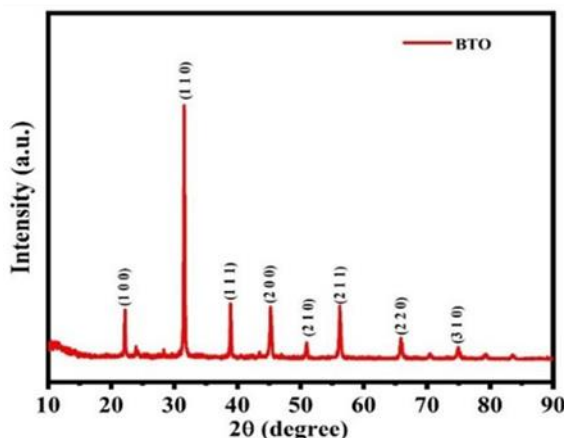


Fig. 1 XRD pattern of the BTO sample

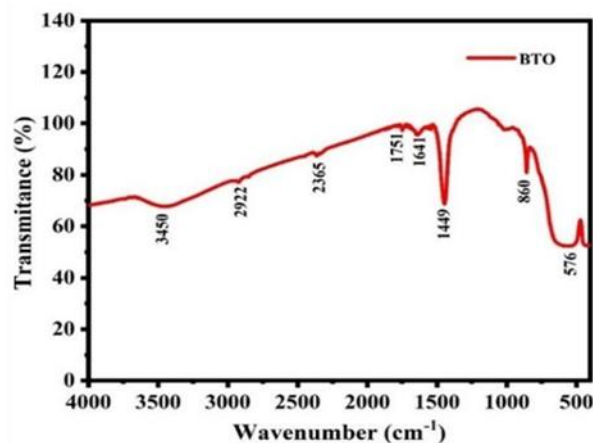


Fig. 2 FT-IR of the BTO sample

3.3. FE-SEM and EDS

The FE-SEM image of BTO sample is shown in fig. 3(A). It is found that the surface morphology of BTO shows clear nano spherical is observed. It is observed that the diameter of nanospheres increases with an increase in the particle size of material due to the interconnected nanospheres. In the study of chemical stoichiometry quantitative analysis technique EDS was used. Fig. 3(B) shows the recorded EDS spectrum on a selected area of the BTO sample by the coprecipitation method exhibited elemental peaks only for barium (Ba), titanium (Ti), and Oxygen (O) substantiating the presence of the important elements in the as-synthesized BTO as shown in table 1 compositional analysis of BTO. The present sample study shows that the prepared BTO consists of O, Ba, and Ti. These results indicated confirmed the formation of BTO nanosphere.

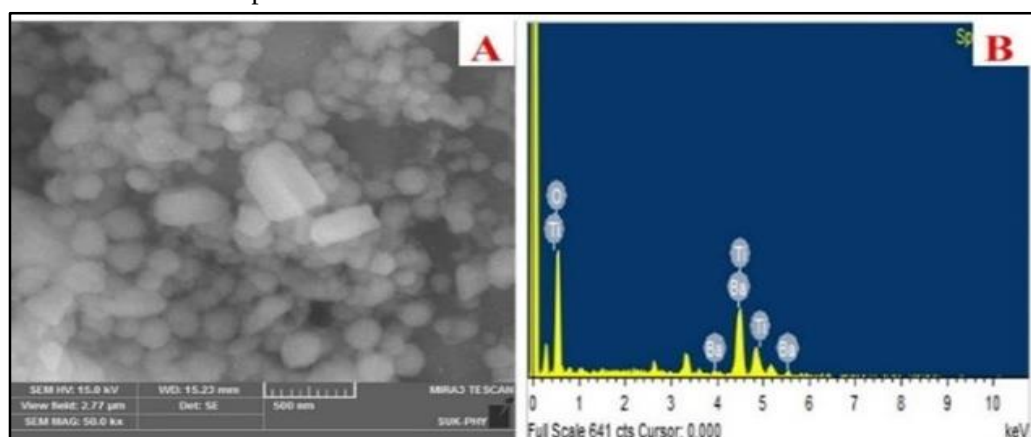


Fig. 3. A) The FE-SEM and

B) EDS spectra of the BTO sample

Table: 1 Compositional analysis from EDS of BTO sample

Sr.no.	sample	Weight%		
		Oxygen	Barium	Titanium

1	BTO	52.26	28.46	19.27
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4. Electrochemical measurement

BTO sample, analyses by LSV and CV route. Therefore, the catalytic activity of substrate is studied, additionally, using a common three-electrode setup, we assessed their OER activity by LSV. Fig. 4(A) shows the LSV curves for OER at a scan rate of 10 mV s^{-1} in electrolyte solution using 1 M NaOH . The polarization curve of BTO sample has a distinct oxidative peak at 0.446 V versus RHE, it reached the overpotential of 446 mV at the current density of 10 mA cm^{-2} . At the same time, the current density of BTO sample shows an obvious increase in the potential range of 0 to 0.7 V . The electrocatalytic activity of the prepared perovskite BTO toward OER has been examined by using Tafel linear polarization measurements. Fig 4(B) Tafel curve verified in the potential region of Oxygen evolution for the platinum electrode. The BTO sample exhibited an overpotential of 446 mV at a current density of the 10 mA cm^{-2} and Tafel slope of 107 mV dec^{-1} . Sr.no. sample Weight% Oxygen Barium Titanium 1 BTO 52.26 28.46 19.27

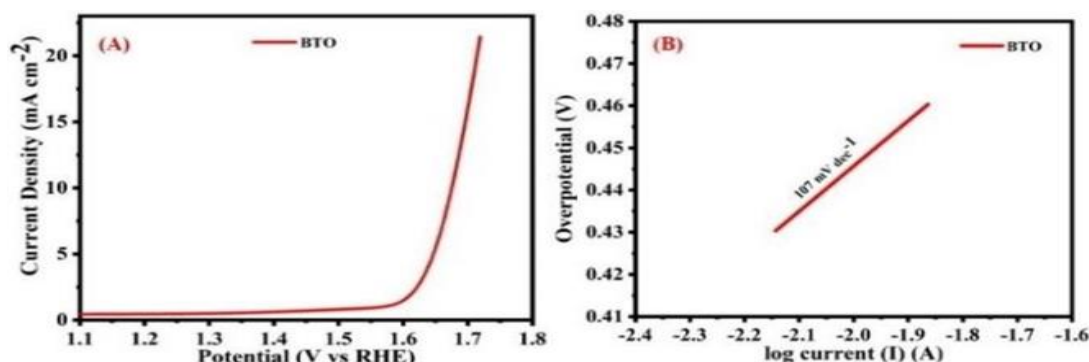


Fig. 4 (A) LSV and

(B) Tafel plot of the BTO sample.

Cyclic voltammetry (CV) is a powerful analytical technique to study electrochemical reactions, which is presented in fig. 5(A). In the solution of NaOH cyclic voltammetric study is performed by using the standard three-electrode system such as stainless steel (SS) substrate as cathode, platinum electrode as anode and SCE as the reference electrode. The voltammetric curves are scanned in the potential range of 0.00 to 0.45 V vs SCE. Fig. 5(A) shows the typical cyclic voltammograms recorded for BTO sample substrate electrode in an aqueous solution mixture at different scan rate at room temperature an enlarged view of the CV curve. The electrochemical impedance spectroscopy (EIS) measurement can be processed at the electrode-electrolyte interface can be better understood. Fig. 6 illustrations representative Nyquist plots designed for BTO sample from 10 Hz to 100 KHz by the amplitude of 10 mV . Illustrations of representative Nyquist plot for all the samples with the current collector (CC) and 1 M NaOH as an electrolyte. The inset shows the equivalent circuit electrodes fig. 6 for EIS. The equivalent circuit is made up of two resistances one R_s is solution resistance and another R_{ct} is charge transfer resistance. It is seen that the R_s value of BTO thin film in NaOH is $2.61 \Omega \text{ cm}^{-2}$, respectively. Also, R_{ct} value of the BTO sample is $78.41 \Omega \text{ cm}^{-2}$.

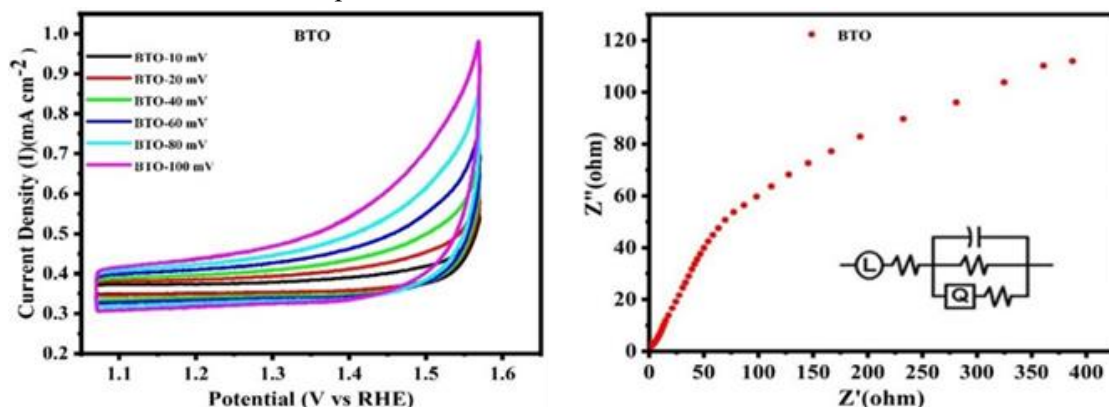


Fig. 5 CV of the BTO sample.**Fig. 6** EIS of the BTO sample and the equivalent circuit model

5. Conclusions

The BTO nanospheres was synthesized by a simple Co-precipitation method. The structural properties of XRD shows BTO has a tetragonal crystal structure. FE-SEM image shows BTO has a nano spherical morphology. EDS is confirmed that product contains only oxygen, barium and titanium having atomic weight 52.26, 28.46 and 19.17% respectively. The of BTO sample for the OER exhibited an overpotential of 446 mV at a current density of the 10 mA cm⁻² and tafel slope of 107 mV dec⁻¹. The electrochemical impedance spectroscopy measured the Rs value of BTO thin film in NaOH are 2.61 Ω cm⁻², respectively. Also, Rct value of BTO thin film is 78.41 Ω cm⁻².

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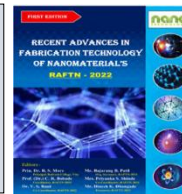
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Recent Advances in Electrospun Composite Nanofibers for Energy Storage in high performance Supercapacitors

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KEYWORDS

Electrospinning,
Supercapacitor,
1D Nanofibers,
Energy storage.

ABSTRACT

The development of electrochemical energy storage has been spurred by the ongoing need for sustainable and clean energy as well as the depletion of fossil fuels. Nanomaterials are characterized by their particle size measured in nanoscale Supercapacitors (SCs) are efficient electrochemical energy storage devices with a wide range of uses. The performance of these devices is based on the makeup and arrangement of the electrodes. Effective supercapacitive materials are those made of carbon-based compounds and transition metal oxides. Electrospinning has been utilised to create planned one-dimensional structure with specific components for cutting-edge energy storage devices since it is a practical and affordable technique. The ability to produce and electro spin inorganic materials, particularly metal oxides, to improve conducting and ceramic characteristics, is extremely advantageous for energy storage. In this work, an overview of the recent progress and applications of hybrid supercapacitors that utilize activated carbon derived nanofibers, along with transitional metal oxides, as electrode materials is presented. This article also summarizes the performance of SCs electrospinning 1D nanofibers for energy storage in supercapacitor.

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1. Introduction

The issue of energy has emerged as one of the most pressing global issues. Demand for renewable and sustainable energy storage technologies is heightened by the depletion of fossil fuel supplies, the growth of the world's population, and pollution from mining and hydrocarbon use [1]. To achieve highly efficient utilization of energy storage by using multiple renewable energy sources for storage and employing nanomaterials, it is crucial to create high-performance supercapacitor. Nanomaterials are substances with nanoscale dimensions in which surface or interface characteristics predominate over bulk characteristics [2]. Due to their high surface-to-volume ratio and short ion and electron transit lengths, which result in improved intercalation kinetics, nanomaterials and their composites are regarded as optimal candidates to enhance the electrochemical activity of electrode materials [3]. Supercapacitors receive a lot of attention because of their superior qualities compared to batteries, including quick charging and discharging, high power density, exceptional cycle stability, and minimal maintenance costs. Since H. I. Becker of General Electric Company received a patent for them in 1957, supercapacitors have been the most widely used kind of energy storage. The patent made the first mention of porous carbon's capacity to store charge in an aqueous electrolyte. The energy storage of porous carbon supercapacitors took place at the interface between the electrode and the electrolyte, as confirmed in the 1960s by the Standard Oil Company of Ohio (SOHIO) and in 1970, they created the first supercapacitor for commercial use utilizing porous carbon as the electrode material [4]. The creation of 1D nanostructures has been researched using a variety of techniques, including solvothermal or hydrothermal synthesis, self-assembly, solution growth, chemical vapor deposition, template-directed

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methods and electrospinning. The benefits of using electrospinning include ease of handling, low solution consumption, controlled fiber diameter, ease of processing, cost effectiveness, simplicity and reproducibility in fibre processing, and scientific developments (scale up process). "Electrostatic interactions" is the key tenet of this method. In more detail, the high voltage power supply is connected to the needle where the peristaltic pump pushes the solution from. A single droplet that is discharged from the needle's tip will be caught in a collector counter electrode. It is conceivable that electrostatic interactions cause the generation of fibres [5]. By combining NFs with hybrid materials like transition metal oxides (TMOs) and conducting polymers (CPs), carbons which undergo higher capacitance than NFs alone, significant efforts have been devoted to achieving high specific capacitance and an electrochemical improvement of supercapacitors. This is a comprehensive review on TMO/CP/Carbon based fibres and their utilisation in the advancement of supercapacitor application.

2. Supercapacitors

Supercapacitors also known as ECs or ultracapacitors have attracted significant attention in energy sustainability due to their excellent electrochemical performance, that is, high specific capacitance, rapid charge/discharge rate, high specific power and long cycle life (>10⁵ times), which is incomparable to those of other energy storage devices [6]. A full-cell supercapacitor typically needs two electrodes, an electrolyte, and a separator to be put together. A full-cell supercapacitor can have an asymmetric or symmetric design. A separator (filter paper, glassy paper, cellulose, or polyacrylonitrile membrane) that has strong ion permeability qualities for ion transit is used to separate two electrodes. Supercapacitors are classified into electrical double-layer capacitors (EDLCs), pseudo capacitors (PCs) and hybrid capacitors (HCs).

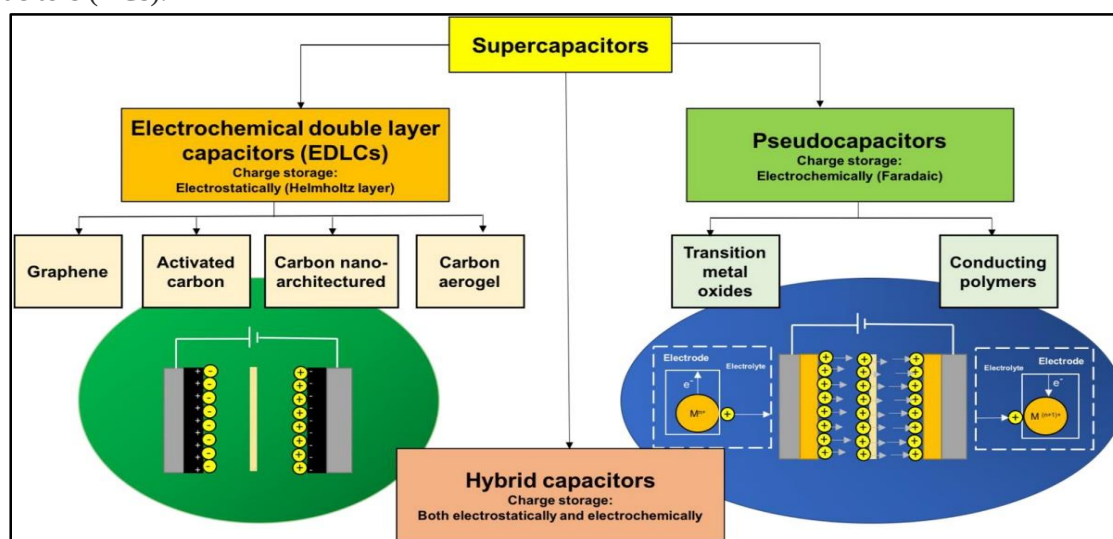


Figure 1: Classification of supercapacitors [6].

3. Electrospun supercapacitor electrode materials

There are several ways to synthesize nanofibers, including hydrothermal synthesis, chemical vapour deposition (CVD), plasma-induced synthesis, wet spinning, dry spinning, solution blow spinning, gel spinning, centrifugal jet spinning, and electrospinning (ES). However, certain processes are rather time-consuming, expensive, and complicated, which can restrict the repeatability of the NFs as they are made. Therefore, it is important to create a quick and easy method for creating NFs. Because of its simplicity, ability to produce customizable properties (such as diameter, shape, and composition), and ability to be scaled up for industrial production, the ES approach has gained widespread use [7].

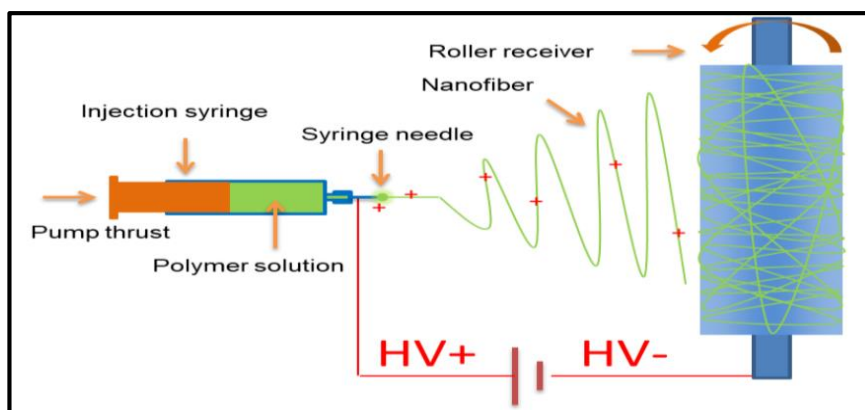


Figure 2: Schematic diagram of electrospinning

Different morphologies of electrospinning nanofibers

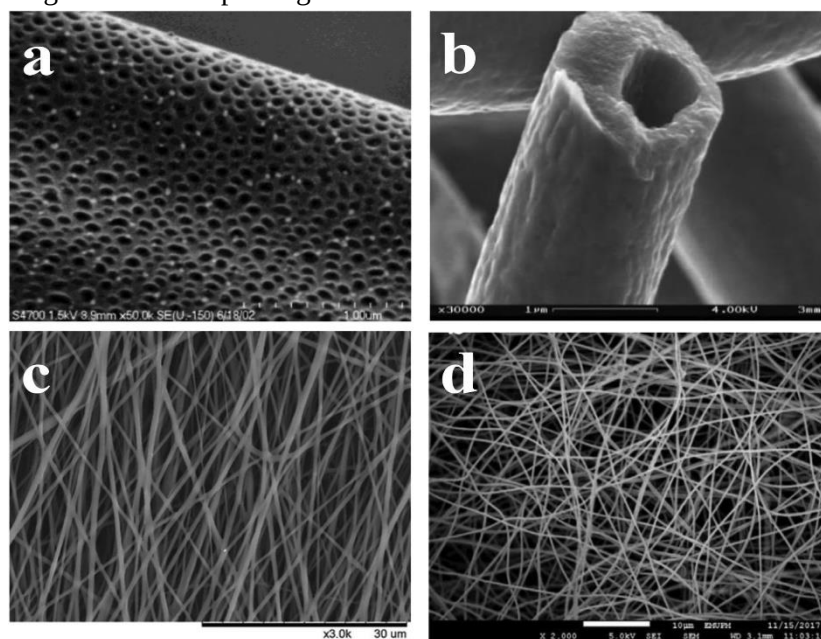


Figure 2: (a) a hierarchical porous fibre (b) a core/shell fibre, (c) an aligned fibre and (d) a randomly oriented fibre [6].

a. Electrospun Metal oxide/Carbon nanofibers/Conducting polymers for supercapacitor.

Carbon nanofibers fibers (CNFs) are carbonaceous materials having a diameter in the micrometer range (often 5–10 μm) and a fibrous morphology. Carbon fibers are defined by the International Union of Pure and Applied Chemistry (IUPAC) as filaments, lines, or reels with a carbon content of more than 92% and a high specific surface area characteristic (a term used to describe a crystal structure in which the basal planes have shifted out of alignment). The two-step process of stabilizing and carbonizing polyacrylonitrile (PAN) nanofibers using catalytic and electrospinning processes is now the standard approach for producing carbon nanofibers. Precursor is the term for the basic ingredient required to create CNFs. Many different synthetic and natural precursors, including PAN, polyphenol, viscose rayon, cellulose phosphate phenolic and pitch-based fibers, etc., are used in the synthesis of CNFs [16].

Abdullah M. Al-Enizi and his fellows synthesized polyacrylonitrile (PAN) with a polyaniline and graphene sol-gel mixture produced uniform, smooth fibres with an average diameter of 0.3 μm . Electrospinning graphene sheets and PAN with PANI, CNFs were created, and these materials were further loaded with $\text{Ni}(\text{OH})_2$ nanoparticles by pyrolyzing a Ni nitrate solution. Electrospun fibres were stabilized for 2 h at 200 $^{\circ}\text{C}$ and then carbonized at 800 $^{\circ}\text{C}$ for 5 h. Cyclic voltammetry and electrochemical

impedance spectroscopy were used to examine how the calcination temperatures affected the electrochemical characteristics. The specific capacitance (SC) was found to be highest (738 F g^{-1}) at a calcination temperature of 400°C [8]. Mohamed Ramadan developed a facile one-step synthesis method of binder-free $\text{MnO}@C$ nanofibers as electrodes for supercapacitor applications.

The electrospun $\text{MnO}@C$ electrodes have an exceptional cycle performance and a high specific capacitance of 578 F g^{-1} at 1 Ag^{-1} in $1 \text{ M Na}_2\text{SO}_4$. An asymmetric supercapacitor with a negative electrode made of activated carbon and a positive electrode made of $\text{MnO}@C$ exhibits an ultrahigh energy density of 35.5 Wh/kg and a power density of 1000 W/kg . Superior columbic efficiency, cycle life, and capacity retention are all displayed by the equipment [9]. Sheng-Chi Lin and his co-members synthesized Carbon nanofibers modified with carboxyl groups (CNF-COOH) possessing good wettability and high porosity are homogeneously deposited with amorphous manganese dioxide (amorphous MnO_2) by potentiodynamic deposition for asymmetric super-capacitors (ASCs). The composite of $\text{CNF-COOH}@MnO_2$ -20 shows a high specific capacitance of 415 F g^{-1} at 5 mVs^{-1} . The capacitance retention of this composite is 94% in a 10,000-cycle test [10]. Mohammad Ali Mohammadi and his teammates fabricated electrode material for supercapacitors, by electrospinning carbon nanofibers (ECNF) that have been thermally treated and infused with metal nanoparticles. The metal/ECNF samples feature a porous structure with a high specific surface area and fibrous shape, as well as scattered metal nanoparticles. The incorporation of Cu into ECNF resulted in the highest specific capacitance. The specific capacitance of the Cu/ECNF sample was 332 F g^{-1} while it was 4 F g^{-1} for the ECNF sample. At the scan rate of 5 mVs^{-1} . In account of its low cost and ease of manufacture, Cu/ECNF can be regarded as a suitable option for supercapacitor electrodes [11]. Chao Liu and his co-workers fabricated a kind of N-doped hierarchal carbon fiber web by electrospinning hollow mesoporous carbon spheres (HMCSs) into fibrous structure. The as-synthesized carbon fiberweb with innovative mulberry-like morphology, henceforth referred to as MC-FW, has properties that are widely wanted for supercapacitor electrode materials, including micro/meso/macroporous porosity, large surface area, high conductivity, and multi-level structure. MC-FW shows high capacitance (298.6 F g^{-1}), favourable capacitance retention (71.0%) and long cycle life (97.3% capacitance retention after 5000 cycles). Notably, the capacitance of 298.6 F g^{-1} for MC-FW is higher than the capacitance reported so far for many hollow carbon spheres and carbon fibers, which may contribute to the synergistic effect between the merits of HMCS (e.g. micro/meso/ macroporous hierarchal structure, large surface area, high pore volume) and advantages of 1D carbon fiber (e.g. large aspect ratio and high conductivity). It is believed that this distinctive carbon fiber web may show promising prospects as advanced energy storage materials and catalyst [12]. Amorphous and crystal TiO_2 composite carbon nanofibers were prepared via one-step electrospinning. The three composite electrodes' morphology, structure, and electrochemical performances are characterized of $\text{TiO}_2@\text{CNFs}$, $\text{OCTi}@\text{CNFs}$, and $\text{HybTi}@\text{CNFs}$. Kexin Tang and his co-workers assembled symmetric supercapacitor demonstrated good capacitance of $\text{HybTi}@\text{CNFs}$ (280.3 F g^{-1}) and great stability (97.5 %) after 4000 cycles [13]. $\text{ZnFe}_2\text{O}_4/\text{carbon}$ (ZFO/C) nanofibers were prepared by electrospinning method with subsequent stabilization treatment, high temperature carbonization, and extra induced annealing for high performance supercapacitor electrode. The extra induced annealing is introduced, successfully producing ZFO/C nanofibers without any other phases. The optimized ZFO/C exhibits a remarkable specific capacitance of 237 F g^{-1} at the current density of 1 Ag^{-1} . Even at the current density of 10 Ag^{-1} , 88.2% of capacity is retained [14]. Pichitchai Butnoi prepared Flexible lignin-based composite nanofibers which includes iron oxide nanoparticles ($\text{L-CNFs}@ \text{Fe}_3\text{O}_4$ nanofibers) in one-step via electrospinning. The $\text{L-CNFs}@ \text{Fe}_3\text{O}_4$ nanostructured composite showed highest specific capacity of 216 F g^{-1} at a current density of 0.1 A g^{-1} , high energy density of 43 Wh kg^{-1} at power density of 242 W kg^{-1} and high capacitance retention of 96.7% after 1000cycle at current density of 1 Ag^{-1} [15].

Table 1: Electrospinning metal oxide/Carbon nanofibers/ Conducting polymers for supercapacitor.

Electrode material	Electrospinning Solution Precursor/polymer/Solvent	Applied Voltage kV	Flow rate	Morphology	Specific capacitance Fg^{-1}	Current density $\text{Ag}^{-1}/\text{mAcm}^{-2}$	Electrolyte	Scan rate mVs^{-1}	Cycle	Ref
Nickel oxide/carbon nanofibers	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /PAN and PANI/DMF	20 kV	0.5 ml^{-1}	Nanofibers	738 Fg^{-1}	-	6M KOH	50 mVs^{-1}	-	[8]
MnO@C nanofibers	MnCl_2 /PVP/Ethanol	15 kV	0.6 ml^{-1}	Nanofibers	578 Fg^{-1}	1 Ag^{-1}	1M Na_2SO_4	5 mVs^{-1}	127% increase after 3000	[9]
CNF@COOHMnO ₂	MnO_2 /PAN/DMF	12 kV	-	Nanofibers	415 Fg^{-1}	-	1M H_2SO_4	5 mVs^{-1}	94% after 10000	[10]
Cu/ECNF	$\text{Cu}(\text{acac})_2$ /PAN/DMF	11.5 kV	0.5 ml^{-1}	Nanofibers	332 Fg^{-1}	-	-	5 mVs^{-1}	-	[11]
N-doped hierarchal carbon fiber web	HMCSSs/PAN/DMF	10-11 kV	$5 \mu\text{l min}^{-1}$	Fiber web	298.6 Fg^{-1}	1 Ag^{-1}	1M H_2SO_4	-	97.3% after 5000	[12]
HybTi@CNFs	TOA/PAN and PVP/DMF	12.5 kV	1 ml^{-1}	Nanofibers	280 Fg^{-1}	1 Ag^{-1}	6M KOH	-	97.5% after 4000	[13]
ZFO/C nanofibers	ZnFe_2O_4 /PAN/DMF	15 kV	0.01 ml^{-1}	Nanofibers	237 Fg^{-1}	1 Ag^{-1}	2M KOH	-	93.1% after 10000	[14]
L-CNFs@Fe ₃ O ₄ nanofibers	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /Lignin and PEO/DMF	10-12 kV	0.2 ml^{-1}	Nanofibers	216 Fg^{-1}	0.1 Ag^{-1}	1M Na_2SO_4	-	97% after 1000	[15]

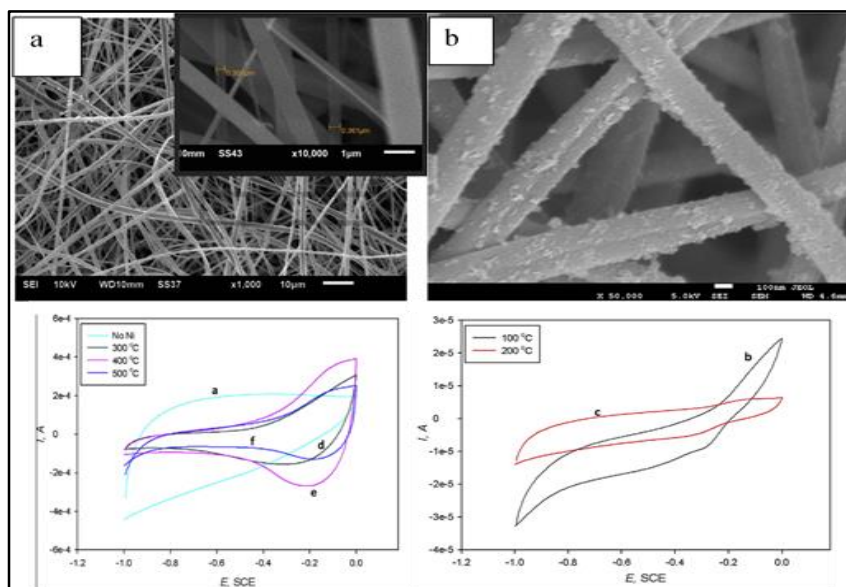


Figure 3: a) SEM micrographs of the PAN/PANI/graphene composite electrospun fibers before fixation and carbonization b) SEM micrographs of the CNF loaded with Ni hydroxide calcined at 400°C. CVs for the (a) bare CNF support and CNFs loaded with Ni hydroxide calcined at temperatures of (b) 100, (C) 200, (d) 300, 400 and (f) 500°C. The CVs were collected in a 6 M KOH aqueous solution at 25°C at a scan rate of 50 mVs⁻¹ [8].

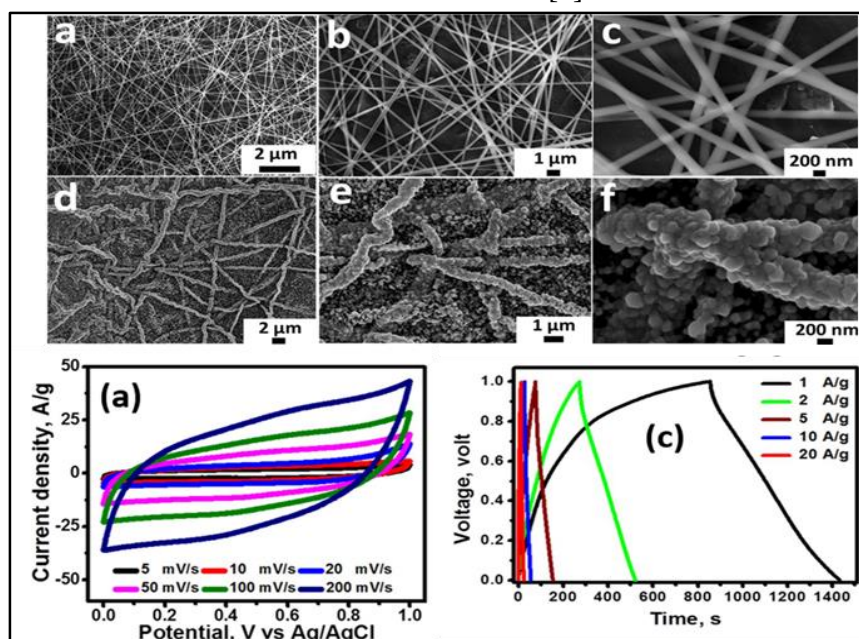


Figure 4: (a–c) As-spun NFs, (d–f) MnO@C collected on graphite substrate at 650 °C for 4 h, (a) CV curves of MnO@C at different scan rates, (c) constant current charge/discharge curves at different current densities from 1 to 20 A/g⁻¹ [9].

4. Conclusion

This overview of electrospinning synthesis of metal oxide/carbon/conducting polymer nanofibers, followed by stabilisation and carbonization, enables clearly preparing quite large areas of nanofibers, mats at affordable prices. The morphology, pore size, and surface area of the fibres should all be taken into account as the design and ideal conditions for creating fibres with better properties still present a significant difficulty. In this review, recent progress in metal oxide/carbon nanofibers/conducting polymers-based fibres have been pointed out and reviewed.

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ABOUT COLLEGE

Balwant College is one of the biggest and well known multi-faculty college in the jurisdiction of Shivaji University, Kolhapur, Maharashtra. It was established in 1963 at the behest of Late Shri. Yashwantrao Chavan Saheb, supported generously by local community. Today, college offers 40 different academic programmes through 16 UG and 11 PG Departments. Students are benefitted with the large number of support services and inter-disciplinary activities. The college is accredited with 'A' grade by NAAC in 3rd Cycle. The college strives continuously to achieve excellence in all the spheres of academic activities. College is funded by UGC, DST-FIST and RUSA in and ISO 9001:2015 certified.

ABOUT DEPARTMENT

The department of Physics was established in the year 1979. The UG courses offered in the department are B.Sc. I to B.Sc. III under CBCS Pattern of Shivaji University, Kolhapur. The Department also offers Master of Science (specialization:-Solid State Physics) from academic year 2021-22. In addition to regular courses, the department also runs a Career Oriented Course entitled "Information & Computer Technology" which was initially funded by UGC. This course is of six months duration and now run by college on its own funds. The department has well equipped laboratories at UG & PG level and advanced scientific equipment's are made available through funding sanctioned by UGC, DST - FIST and RUSA from time to time.

ABOUT BOOK

The proceeding book of national conference entitled "Recent Advances in Fabrication Technology of Nanomaterial-2022" organized by Department of Physics, Balwant College, Vita aimed to provide an opportunity to Students, Faculty teachers, Research scholars, Scientists, Industrial persons from Science and Technology disciplines to present their innovative research work in this book and which will be beneficial for the nation. Conference proceeding also provide an opportunity to authors in material science to publish their ideas, projects and research as a book chapter in this book. It will enlighten the participants about new emerging trends in material science and recent development in nanomaterial and nanotechnology.

