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Synthesis and Correlation of CuO and ZnO Doped CuO Nanostructures as Potential Supercapacitors

Nirmala Nithya R.[1] *, Mubeen G.[2], Koushi Kumar U.[1] and Sai Nandhini R.[1]
[1] Vel Tech Rangarajan Dr. Sagunthala R&D Institute of Science and Technology, Chennai, India.
[2] Centre for Nanoscience and Nanotechnology, Anna University, Chennai, India.

***Abstract*:- Facile and simple hydrothermal method has been used to synthesis copper oxide (CuO) nanostructures and ZnO doped CuO nanostructures. The effect of temperature on the structural, morphological and electrochemical properties of the CuO has been studied and reported. The whole report relies on the non usage of structure directing agents /surfactants for the synthesis of nanostructure. With a controlled pH ambiance during the reaction, nanorods CuO structures were synthesized at a temperature of 400–450◦C with greater reproducibility. These CuO nanostructures show incredible surface properties like uniform surface morphology, high surface area and uniform pore size distribution of CuO tests. Further, with the addition of nickel oxide and iron oxide composite materials, their properties can be upgraded. The physicochemical analysis (X-ray diffractometer (XRD) which gives the phase structure of the material, Scanning Electron Microscopy (SEM)) and electrochemical studies (Cyclic voltammetry analysis (CV), Cyclic potentiometry analysis (CP), electrostatic impedance spectroscopy (EIS)) revels their capacity of categorizing them into materials for supercapacitors. The electrochemical investigations of the CuO/ZnO composites tests show the evident impact of surface properties on the pseudocapacitance execution.**

Keywords:- Pseudocapacitance, Supercapacitor, Electrochemical, nanorods and Composite.

INTRODUCTION

Nanomaterials have played an important role in revolutionizing various files due to their size dependency properties. These revolutions include their application into the field of energy. In recent years supercapacitors have been recognized as important material in the field of transportable electronics which could replace conventional batteries and capacitors[1,11]. Transitional metal oxide have played an important role towards contribution to the field of energy[8,10,13]. Among them copper oxide has played significant role because of their efficiency[6,9]. The parameters that has to be considered while fabricating supercapacitors includes electrical conductivity, structural flexibility, band gap and charge carrier mobility[4,7,14]. Also doping enhances the property as a supercapacitor by increasing the charge carriers in them.

The performance of supercapacitors can be enhanced by improving the properties and nature of the electrode. Composite electrodes that include zinc oxide, ruthenium oxide, manganese oxide etc. improve the performance of the supercapacitor. Amongst the different types of dopant zinc oxide have been widely studied separately and as a composite material for application in storage field. The reason for the wide study of zinc oxide is due to the ease in controlling the morphology of the end nanoparticles. ZnO nanoparticles can be synthesized using different synthesis methods include sol–gel technique[2] , mechanical milling[3], hydrothermal processing[15] , sonochemical or microwave-assisted synthesis[5], and direct precipitation[12] .

In this study we report the synthesis and physicochemical characterization of CuO nanorods via hydrothermal method and CuO-ZnO nanocomposite towards the application of supercapacitor. The synthesized nanorods and nanocomposite were characterized using XRD, SEM and their electrochemical studies were performed to determine their efficiency.

MATERIAL AND METHODS

Synthesis of CuO nanorods:
In the synthesis of CuO nanorods, copper sulfate ($CuSO_4$) was added to milli Q water and sodium hydroxide (NaOH) was added to this prepared solution. The addition causes visible precipitation in the solution. Further, the solution was then transferred to a 100 mL teflon-liner autoclave, which was sealed and heated to 105°C for 24 hour. After the autoclave was cooled to room temperature, the resulting precipitate was sonicated for 2 hours with an interval of 30 min. Then the precipitates were collected by centrifugation. The collected samples were thoroughly washed times with milli Q water and ethanol respectively, and dried in vacuum for 48 hours. The dried sample was then calcinated at 400 °C for 5 hr. Finally, the black coloured powder of CuO was obtained.

Synthesis of CuO-ZnO composite:
CuO-ZnO composite was synthesized via hydrothermal method. Wherein, 30 ml solution of 0.5 g of the cupric nitrate and 0.6 g of the zinc chloride was prepared and thoroughly stirred for 30 min on a magnetic stirrer. And NaOH solution was prepared separately by dissolving 2 g of NaOH in milli Q water and stirred for 5 min. NaOH was added dropwise to the mixed precursor solution on continuous agitation. After 5 min, the temperature was raised and maintained at 80 °C with continuous stirring for 24 hours. The mixture was then allowed to cool down to

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room temperature. The precipitate was harvested by filtration and rinsed with milli Q water and then dried on a hot plate at 80 °C for 12 hours.

Characterization techniques:

The crystal structure of the synthesized CuO and CuO-ZnO composite was determined using X ray diffractogram (**XRD**). It was performed using Philips' X-ray diffractometer with Nickel filtered Cu Kα radiation (1.54 Å). The 2θ values were set in the range 5°-80º with a scanning speed of 5º per min.

Topographical, morphological studies and chemical composition of the synthesized samples were studied using Scanning electron microscope (**SEM**).

Chemical structure of the nanomaterials was carried out using Fourier Transform Infrared Spectroscopy (FT-IR) in the range between 4000-400 cm^{-1}.

Electrochemical experiments were investigated by electrochemical work station. The three-electrode cell consisted of platinum wire as a counter electrode, Ag/AgCl as a reference electrode and Glassy Carbon as working electrode. Cyclic Voltammetry (CV) were measured using 6M aqueous KOH solution as the electrolyte. Cyclic Potentiometry (CP) was analyzed in 1M KOH electrolyte solution with the potential range between -0.2 to +0.5 V. The electro-active materials were analyzed by Electrochemical Impedance Spectroscopy (EIS) in 1M KOH electrolyte solution with the frequency range of 1mh to 1Mh.

Thermal degradation studies were carried out using **TGA/DTA.** Integral (TGA) and derivative (DTG) thermogravimetric curves provide information about the material degradation and thermal stability.

RESULTS AND DISCUSSION

Structural analysis:

Figure 1 shows the X ray difractrogram of the CuO sample. The XRD pattern of the calcinated sample can be well indexed as the mono-clinic copper oxide (CuO) phase with lattice parameters of a = 4.668, b = 3.323, and c = 5.122 (JCPDS card, no. 05-0661). Using Scherrer formula copper oxide crystallite size was found to be ~14 nm. Additionally, no impurities can be seen in the peaks such as $Cu(OH)_2$ or Cu_2O were detected.

The figure 2. shows the X ray diffractogram of CuO/ZnO. The XRD patterns of the annealed samples were well indexed with the JCPDS numbers given as CuO/ZnO – 05-0661 with monoclinic structure. Moreover, no characteristic peaks were assigned to impurities for the same.

Morphological studies:

The topographical morphology of synthesized CuO was investigated using SEM. It is evident from the figure 3 that the CuO sample is of rod-shaped nanoparticles with uniform morphology in a lower magnification (30,000X). Moving to a nearby in higher magnification (60,000X), it is evident that these nanoparticles are certainly isolated with clear limits. Numerous pores structure can be seen between neighboring copper oxide nanoparticles and its reality enables the electrolyte particles to enter into the inner region of the electrode and contact a larger electroactive surface for Faradaic reactions. The morphology of the CuO, as synthesized nanocomposite materials were examined by SEM analysis. Figure 4 (a) and (b) represents the SEM micrographs of CuO/ZnO depicting sphere like structures. This type of morphology contributes to the electrochemical properties for supercapacitors.

FT-IR Spectroscopy of CuO:

The vibrational spectra of CuO is represented in the figure 5. The spectra at 3362 cm^{-1} indicates the presence of hydroxide group. The absorption peaks around at 1624 cm^{-1} and 1107 cm^{-1} may be attributed to O–H bending vibrations combined with copper atoms. The two broad absorption bands at 600 and 520 cm^{-1} are associated with Cu–O stretching modes. Thus, the FTIR result suggests the presence of Cu–O bonds and some constitutional water incorporated in the copper oxide structure. Thus, the formation of copper oxide compound is confirmed from FTIR study.

Cyclic voltammetry analysis (CV):

The cyclic voltammetry analysis of CuO at the scan rates of 10, 20, 50 and 100 mV/s as shown in figure 6 (a). In the present study, the aqueous electrolyte KOH was tested for copper oxide. The aqueous electrolyte of 1M concentration was prepared in freshly prepared de-ionized water (2D water). Typical C–V curves shows for different sweep rates in 1M KOH electrolyte at the potential range between 0.6 to -0.6V. From CV curves, ideal rectangular shape of the typical electric double-layer capacitance was observed. Figure 6 (b) represents the CV curves of CuO/ZnO composites at different scan rates varying from 25, 50, 75 and 100mV/s. From figure 6 (b) we observed nearly rectangle like structure. When the applied scan rate increases, the area of the CV curve increases which indicates that I α V. The specific capacitance of the material is high when applied scan rate is low. Because of the electrolytes ions interact with the inner site of the electro active material ions. When specific capacitance is low, scan rate is high. Because of the electrolytes ions interact with the outer site of the electro active material ions.

The electrochemical properties of electro-active materials were analyzed by chrono potentiometry for supercapacitor. The electro-active materials were analyzed in 1M KOH electrolyte solution with the potential range between -0.2 to +0.5 V. All figures show linear and symmetric structures. Figure shows cp curve of CuO/ZnO at different current densities varying from 1, 2,3,4,5 Amp respectively.

The electrochemical impedance spectroscopy properties of electro-active materials were analyzed by EIS for supercapacitor. The electro-active materials were analyzed in 1molar KOH electrolyte solution with the frequency range of 1mh to 1Mh. The figure 8 corresponds to the CuO/ZnO composites. The overall study of figure 8 shows the absence of semi-circle in the higher frequency range

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and the presence of linear curve in lower frequency regions respectively.

Differential thermal analysis (DTA) / thermogravimetric analysis (TG):

TG-DTA Curve of CuO/ZnO as represented in figure 9. Removal of nitrate takes place with the formation of CuO/ZnO. The dramatic mass loss initiated at about 250˚C can be attributed to decomposition of CuO/ZnO and mass loss from 200 to 400˚C is about 7.85%. The mass loss at above 400˚C can be attributed to phase formation of Cu_2O/ZnO and the mass loss from 700 to 1000˚C is about 10.03% with complete decomposition of residue composite at about 1000˚C. The endothermic peak was observed at about 250˚C which corresponds to decomposition of CuO/ZnO group.

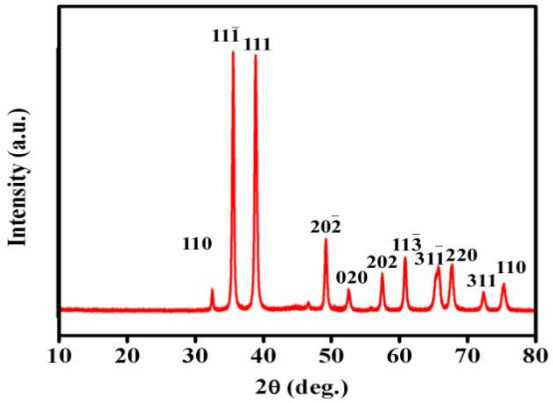

Fig. 1: X ray diffractogram of CuO nanomaterials

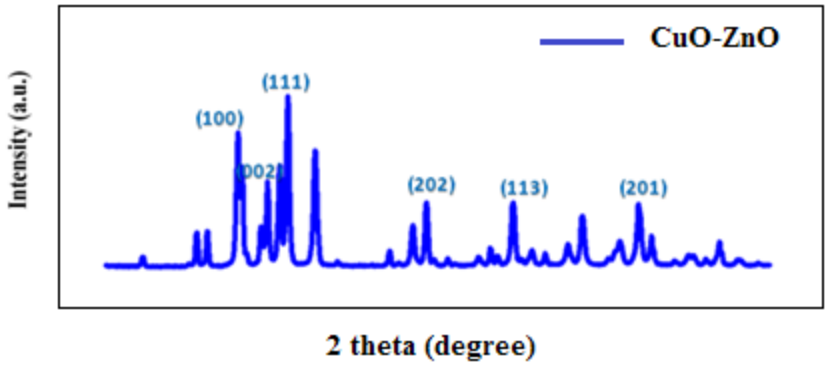

Fig. 2: X ray diffractogram of CuO-ZnO composite

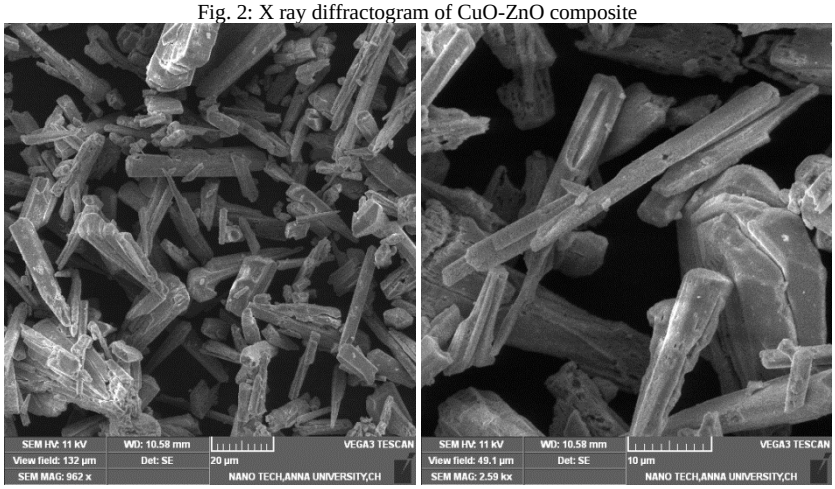

Fig. 3: The SEM micrograph of CuO nanorods like structure at different magnifications

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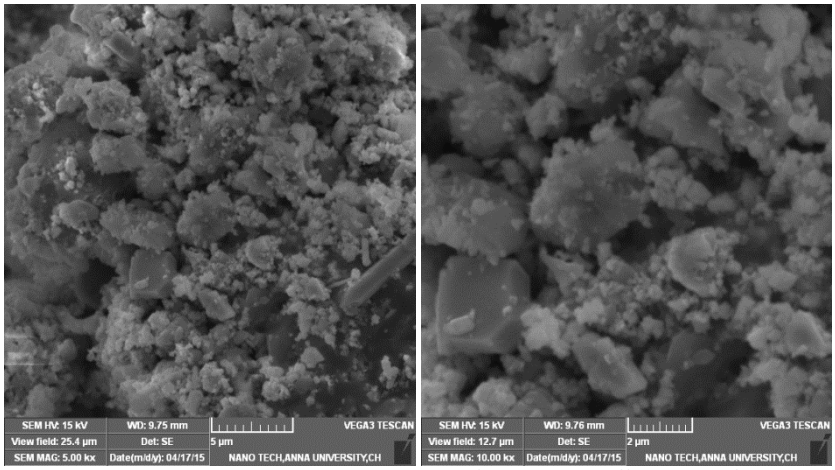

Fig. 4: (a) and (b) represents the SEM micrograph of CuO-ZnO at different magnifications

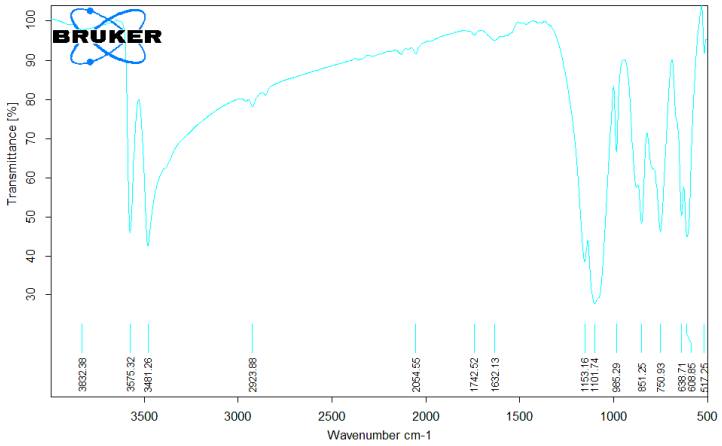

Fig. 5: FTIR spectra of CuO nanorods

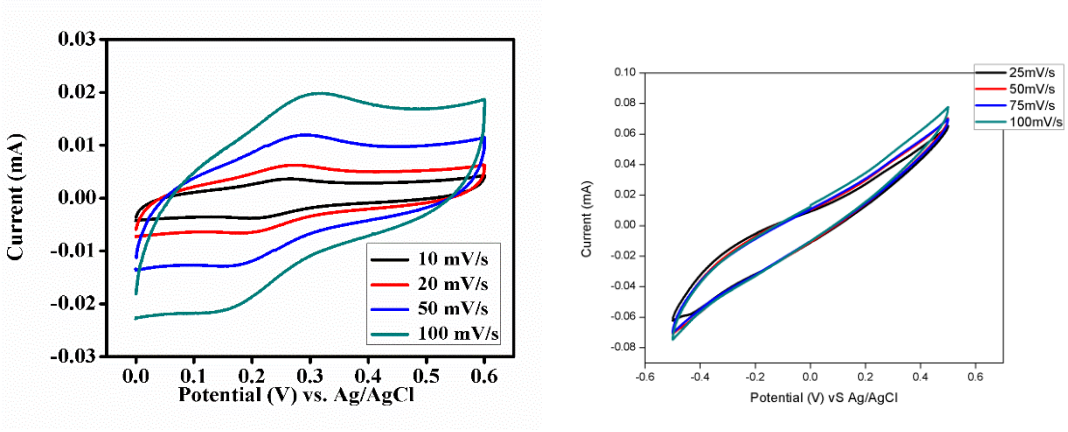

Fig. 6: Cyclic voltametric curves of (a) CuO nanorods with different sweep rates and (b) CuO-ZnO composite with different sweep rates

International Journal of Engineering Research & Technology (IJERT)
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Vol. 8 Issue 08, August-2019

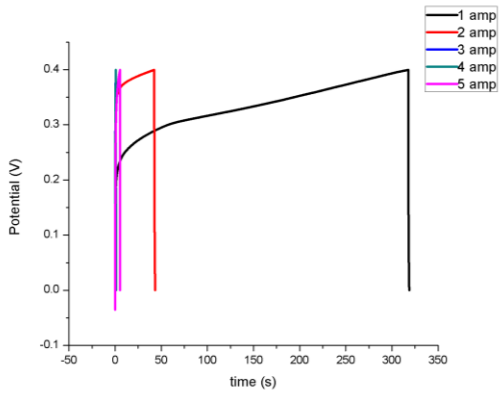

Fig. 7: Represents the (a) cyclic potentiometry of CuO-ZnO

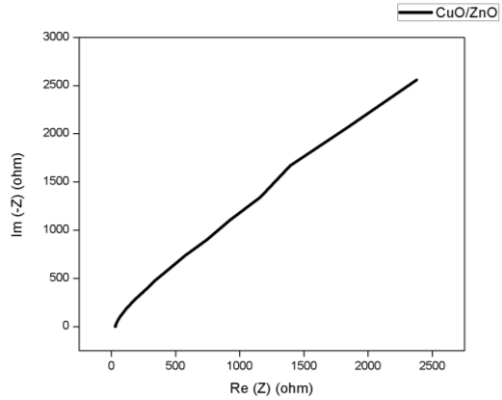

Fig. 8: Represents the electrochemical impedance spectra of CuO/ZnO

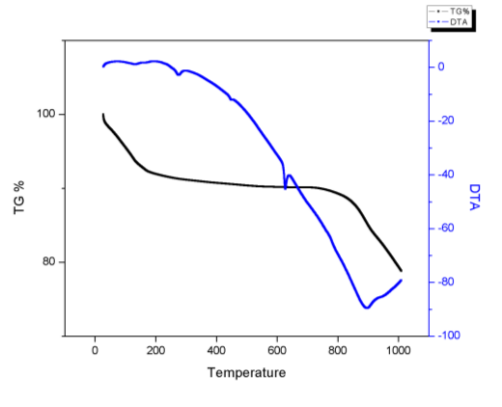

Fig. 9: Represents the TG/DTA of CuO/ZnO

CONCLUSION

Herein this work represents the synthesis of CuO and CuO-ZnO nanocomposite towards the supercapacitor application. The synthesis was carried out using hydrothermal technique with using any structure driving agents. The synthesized CuO nanorods and CuO-ZnO composite were studied via XRD and SEM. Further, CuO-ZnO composite were analyzed and studied for their electrochemical properties and pseudocapacitive capacitance behavior at different sweep rates. This CuO-ZnO composite shows the specific capacitance value higher than that of bare CuO nanorods. The enhancement in the electrochemical properties for the CuO-ZnO composite could be attributed to the increase of charge carriers in the composite by means of ZnO. The study provides a preliminary confirmation of CuO-ZnO to be a potential supercapacitor material and can be further explored.

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