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Synthesis and Characterization of CuO/NiO and CuO/Fe_3O_4 Nanocomposite for Super Capacitor Application

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***Abstract*:- A novel hydrothermal method has been utilized to synthesize copper oxide nanostructure that avoids any usage of surfactants. Wherein, CuO nanorods were synthesized in the temperature range between 400– 450◦C and resulting a greater reproducibility. The synthesized CuO nanostructures shows uniform surface morphology, high surface area and uniform pore size distribution. These nanostructures are aimed towards their contribution to the field of supercapacitor. Moreover, the report presented here also studies the enhanced properties of composites of copper oxide with nickel oxide and iron oxide composite as a supercapacitor. These nanomaterials/composites were morphologically analyzed scanning electron microscopy (SEM) respectively. The electrochemical properties of the synthesized nanomaterials and nanocomposites were analyzed using cyclic voltammetry (CV) and cyclic potentiometry (CP). Electrostatic impedance spectroscopy (EIS) was used to analyze the impedance of the synthesized nanomaterials and thermal degradation studies using thermogravimetric analysis (TG). The electrochemical investigations of the CuO/Fe_3O_4 and CuO/NiO composites results show the evident impact of surface properties on the pseudo capacitance execution. Accentuation is set on the synergistic impacts of the materials on the performance as super capacitors in terms of specific capacitance, energy density, power density, rate capability, and cyclic stability. This study demonstrates that CuO/NiO composite shows a enhanced properties than CuO/Fe_3O_4 and based on the low cost synthesis of CuO makes it a potential super capacitor material.**

Keywords - Pseudo capacitance, Super capacitor, cyclic stability, Electrochemical and Composite.

1. INTRODUCTION

Exhaustion of non-renewable energy sources and unfortunate outcomes from consuming them includes air contamination and expanding ozone-harming substances are the principle inspiration for the extraordinary research and endeavors toward the advancement of alternative energy storage device. [1] Pseudo capacitors have pulled in more consideration due to their longer life cycle and power densities compare to dielectric capacitors. [2] Three sorts of materials have been considered for pseudocapacitor application such as metal oxide with high specific capacitance, [3] carbon based materials used in electrochemical double layer capacitors (EDLC) [4] and application of conducting polymers due to their high charge density [5]. However, the major drawback is due to low cyclic life that is deficient for charge storage. Therefore, researchers have reported the usage of metal oxide such as RuO_2 [6], MnO_2 [7], Co_3O_4 [8], NiO [9], SnO_2[10], Fe_3O_4[11], and V_2O_5[12] and their improved capability towards charge storage. Moreover, form literature it is evident that RuO_2 has the highest specific capacitance of 1300 $F.g^{-1}$ for supercapacitor applications. However, for commercial application of RuO_2 as supercapacitor material would lead to the high cost of the supercapacitor and its harmful nature would eventually make it a non preferable material. On the other hand, the pure metal oxide shows a poor electrical conduction and low specific capacitance. The drawbacks of using pure metal oxide and avoiding the usage RuO_2 for the application of supercapacitor were overcome by the synthesis and application of mixed metal oxide nanocomposite. From reported studies it is evident that composites such as gold-iron oxide, [13] nickel oxide/graphene sheet/graphene ribbon, [14] iron oxide nanoparticles[15] exhibit high storage pseudocapacitor capability. Study by Shafi *et.al.* reports that graphene oxide-MnO_2 nanocomposite shows improved electrochemical behavior than the individual graphene and MnO_2.[16] Similarly, cobalt sulfide-graphene nanocomposite shows a high specific capacitance of 2423.3 $F.g^{-1}$.[17] Further, copper oxide nanoparticles were selected as they play an important role in catalysis and high-temperature superconductors. [18-20] Also, nickel oxide nanoparticles have been broadly contemplated for a long time due to their role in catalysis and semiconductor material. [21-24] The present study focuses on the synthesis and application of pseudocapactive copper oxide and copper oxide composite material for improved capacitance ability. Herein, the nanocomposites were synthesized via a simple hydrothermal method. The synthesized nanocomposites were thoroughly analyzed using SEM technique. Primarily electrochemical properties and pseudo capacitive capacitance behavior of bare CuO were studied and the effect of composites such as CuO/NiO and CuO/Fe_3O_4 on the capacitance ability was thoroughly examined.

2. EXPERIMENTAL PROCEDURES:

2.1 *Materials: copper sulfate, NaOH*

2.2 *Synthesis of copper oxide (CuO)*

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.

2.3 Synthesis procedure for copper oxide -nickel oxide composite (CuO/NiO)

CuO-NiO nanocomposite was prepared by a similar procedure as reported by Albert O Juma *et. al* .[25] Wherein, 50 ml solution of 0.426 g of the cupric nitrate and 0.727 g of the nickel nitrate was prepared and thoroughly stirred at 50 °C 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 while continuously agitation and meanwhile maintaining the pH at ~7. After 5 min, the temperature was raised and maintained at 100 °C with continuous stirring for an additional 30 min. At high-pressure composite was obtained. The mixture was then allowed to cool down to room temperature. The precipitate was harvested by filtration and rinsed with milli Q water and then dried on a hot plate at 100 °C for hours. Finally, the powder was calcinated at 400 °C.

2.4 Synthesis procedure for copper oxide -iron oxide composite (CuO/Fe_3O_4)

CuO/Fe_3O_4 nanocomposites were synthesized by measuring 0.426 g of the cupric nitrate and 0.875 g of the iron chloride tetrahydrate and dissolving them in 50 ml milli Q water. The solution was thoroughly agitated at 50 °C for 30 min. And NaOH was added to the solution and stirred for 5 min. It was added dropwise to the mixed precursor solution while continuously stirring and maintaining the pH at ~7. After 5 min, the temperature was raised and maintained at 100 °C with continuous stirring for an additional 30 min. At high-pressure composite was obtained. The mixture was then allowed to cool down to room temperature. The precipitate was harvested by filtration and rinsed with milli Q water and then dried on a hot plate at 100 °C for 2 h. The powder was calcinated at 400 °C.

2.5 Characterization techniques

Scanning electron micrograph was obtained to understand the topographical morphology (texture), chemical composition, crystalline structure and orientation of materials.

2.6 Electrochemical Measurements

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. Integral (TGA) and derivative (DTG) thermogravimetric curves provide information about the material degradation and thermal stability.

3. RESULTS AND DISCUSSION

3.1 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 magnification of 30,000X. Moving to a nearby in magnification of 60,000X, it may be seen 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 electro active surface for Faradic reactions.

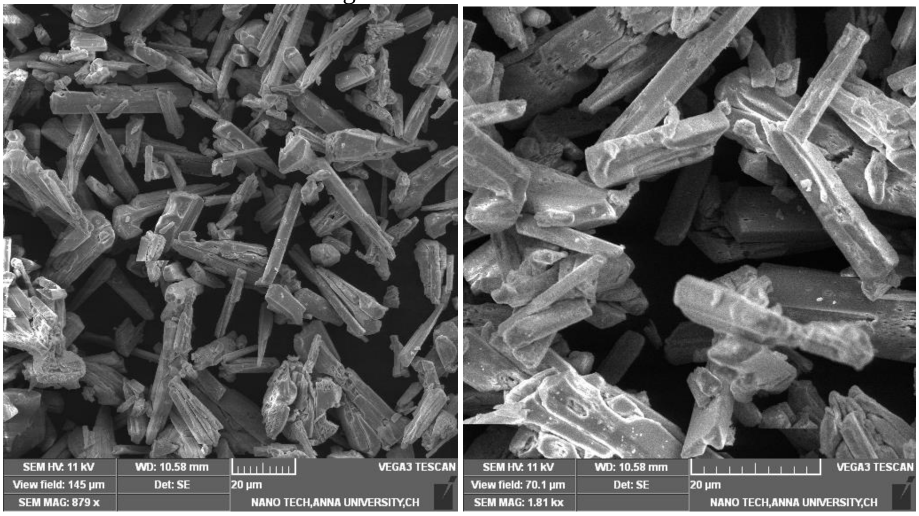

Figure 1. The SEM micrograph of CuO nanorods like structure at different magnifications

The morphology of the as synthesized materials was examined by SEM analysis. **Figure 2 (a)** and **(b)** shows the agglomerated spherical particles of CuO/NiO. **Figure 3 (a)** and **(b)** shows rods stacked with secondary particles of CuO/Fe_3O_4. This type of morphology contributes to the electrochemical properties for supercapacitors.

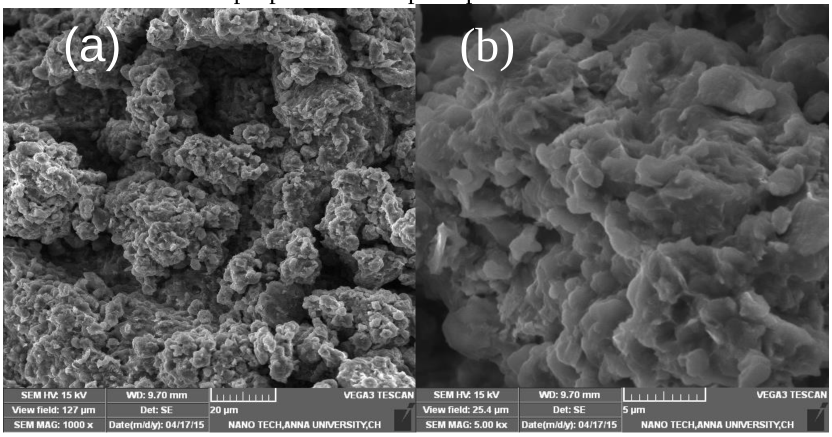

Figure 2. Represents the (a) and (b) SEM micrographs of CuO/NiO nanocomposite

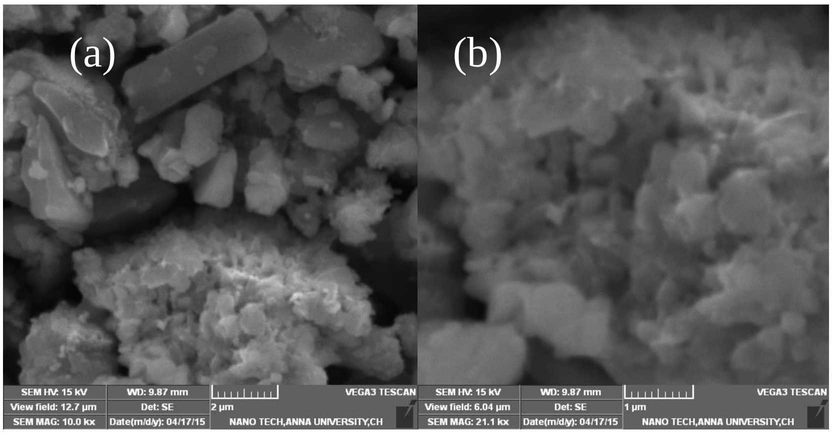

Figure 3. Represents the (a) and (b) SEM micrographs of CuO/Fe_3O_4 nanocomposite

3.2 *Cyclic voltammetry analysis*

The cyclic voltammetry analysis of copper oxide at the scan rates of 10, 20, 50 and 100 mV/s as shown in **figure 4**. 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. The copper oxide CV curve shapes reveal that the capacitance characteristic mainly results from the pseudo capacitive capacitance behavior, caused by the fast and reversible faradic redox reactions of electro active materials.[27] The redox peaks are obtained from different scan rates in 1M KOH electrolyte, which corresponds to the conversion between different copper oxidation states.

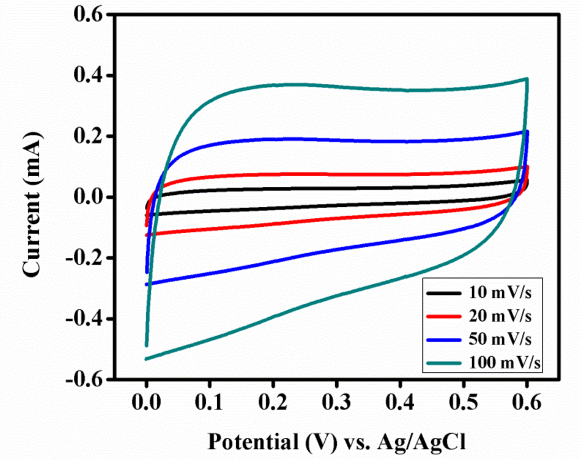

Figure 4. Cyclic voltametric curves of CuO nanorods with different sweep rates.

The electrochemical properties of electro-active materials were analyzed by Cyclic Voltammetry for supercapacitor. The electro-active materials were analyzed in 1molar KOH electrolyte solution with the potential range between -0.6 to +0.6 V. **Figure 5** shows the CV curves of CuO/NiO and CuO/Fe_3O_4 composites. **Figure 5 (a)** and **(b)** shows CV curve of CuO/NiO and CuO/ Fe_3O_4 at different scan rates varying from 25, 50, 75 and 100mV/s. It was observed that CuO/NiO and CuO/ Fe_3O_4 composites nearly rectangle like structure.

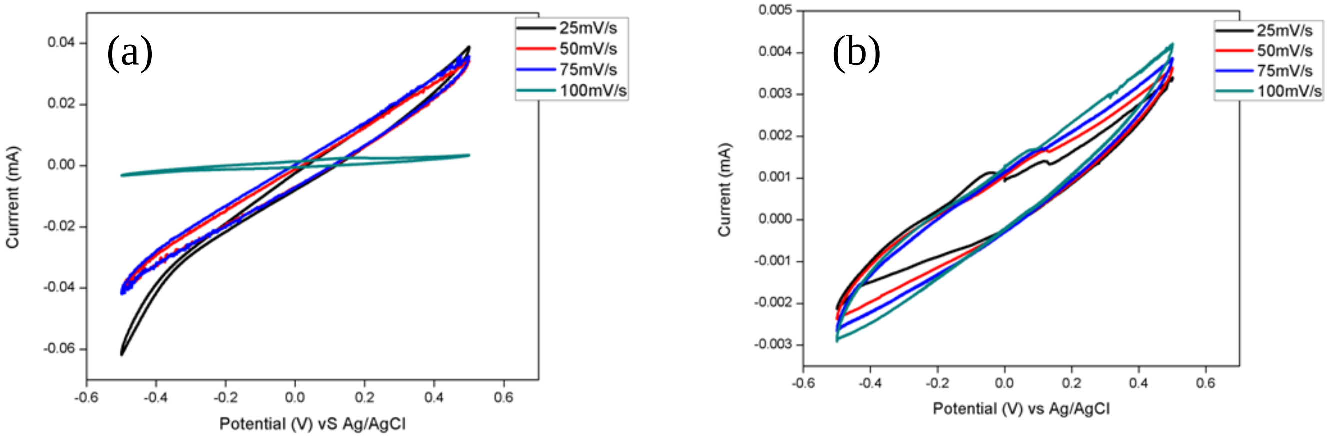

Figure 5. Represents the (a) represents the cyclic voltagram of CuO/NiO and (b) represents the cyclic voltagram of CuO/Fe_3O_4

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 the 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.

Further, the capacitance 'C' was calculated equation (1);

$$C = \frac{I}{dV/dt} \quad \text{-------------------------------------}(1)$$

Where 'I' is the average current in amperes and dV/dt is the scan rate in mVs^{-1}. The specific capacitance (380 Fg^{-1}) of the electrode is obtained by dividing the capacitance by the mass of the electrode material given by equation (2).

$$\text{Specific Capacitance value} = \frac{1}{2mv(V_a - V_b)s}\int_{V_a}^{V_b} I\,V\,dv \quad \text{----------------------------------}(2)$$

Figure 6 and 7 represents the specific capacitance value at different scanning rates with different molar concentration of CuO and CuO/NiO and CuO/ Fe_3O_4 respectively in 1M KOH electrolyte.

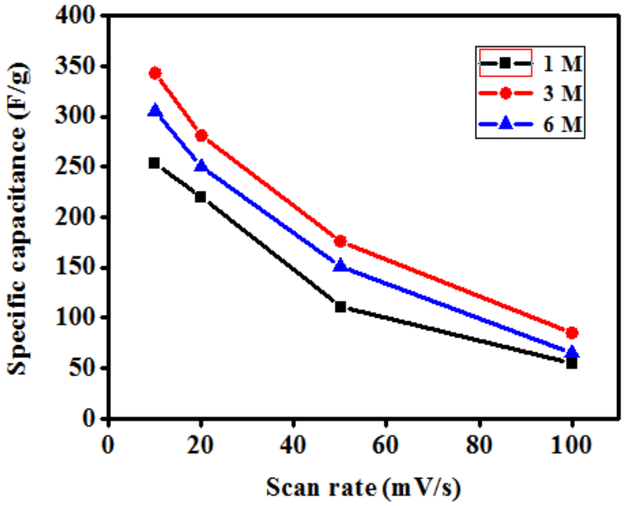

Figure 6. Specific capacitance value at different scanning rates with different molar concentration CV curve of CuO in 1M KOH electrolyte

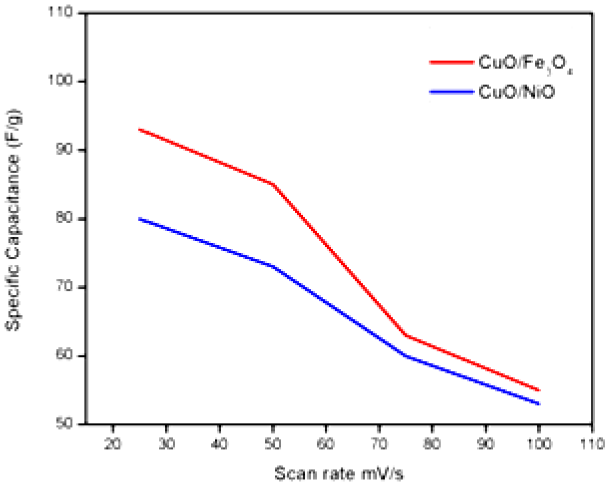

Figure 7. Specific capacitance value at different scanning rates with different molar concentration CV curve of CuO/NiO and CuO/ Fe_3O_4 in 1M KOH electrolyte

3.3 *Cyclic potentiometry analysis (CP)*

The electrochemical properties of electro-active materials were analyzed by Cyclic Potentiometry for supercapacitor. The electro-active materials were analyzed in 1molar KOH electrolyte solution with the potential range between -0.2 to +0.5 V. All figures show linear and symmetric structures.

Figure 8 (a) and **(b)** represents the CP curve of CuO/NiO and of CuO/Fe_3O_4 at different current densities varying from 1A, 2A, 3A, 4A and 5A respectively.

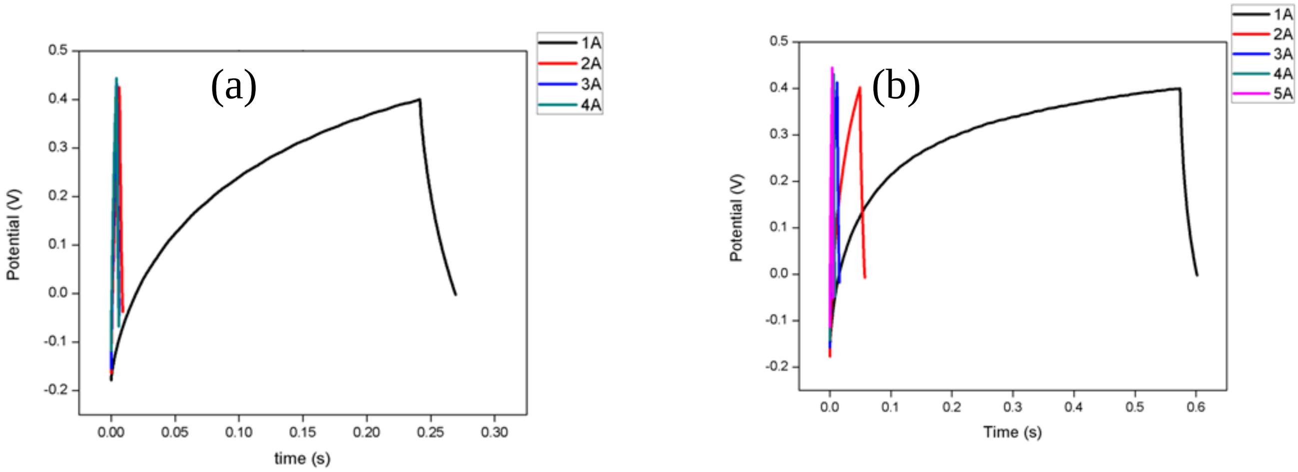

Figure 8. Represents the (a) cyclic potentiometry of CuO/NiO and (b) cyclic potentiometry of CuO/Fe_3O_4

3.4 *Electrostatic Impedance Spectroscopy (EIS)*

The electrochemical impedance spectroscopy properties of electro-active materials were analyzed for supercapacitor. The electro-active materials were analyzed in 1molar KOH electrolyte solution with the frequency range of 1mh to 1Mh. The **figure 9 (a)** and **(b)** corresponds to the CuO/NiO and CuO/Fe_3O_4 composites. From the overall **figure 9** which shows the absence of semi-circle in the higher frequency range and the presence of linear curve was observed in lower frequency regions respectively.

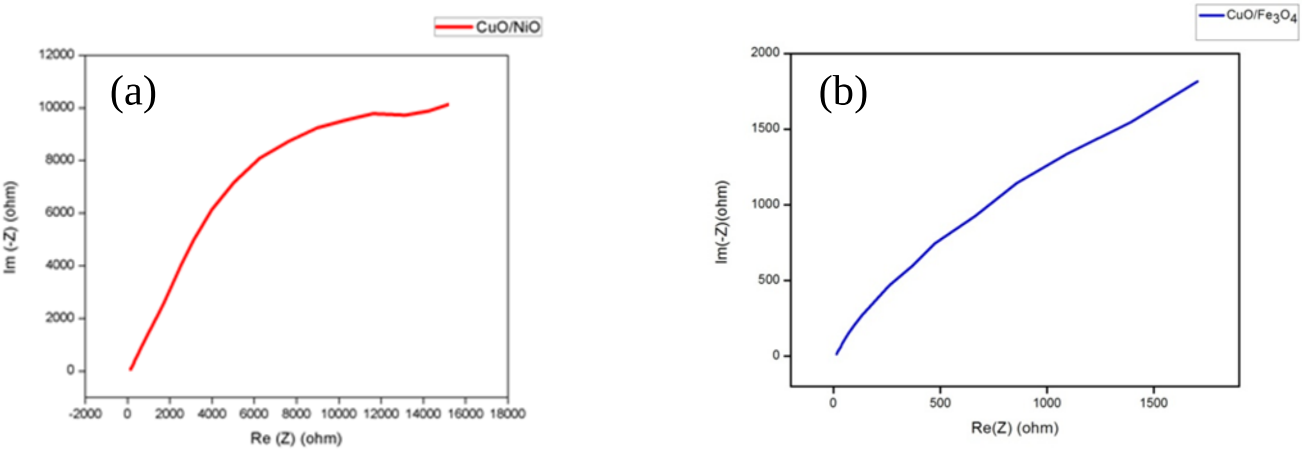

Figure 9. Represents the (a) electrochemical impedance spectra of CuO/ NiO and (b) electrochemical impedance spectra of CuO/ Fe_3O_4

3.5 Differential thermal analysis (DTA) / thermogravimetric analysis (TG) of CuO/NiO, CuO/Fe_3O_4

TG-DTA plot of CuO/NiO is shown as in **figure 10 (a)**. Removal of nitrate takes place with the formation of CuO/NiO. The dramatic mass loss initiated at about 220˚C can be attributed to the decomposition of CuO/NiO and mass loss from 200 to 400˚C is about 8.8 %. The mass loss at above 400˚C can be attributed to phase formation of Cu_2O/NiO and the mass loss from 400 to 800˚C is about 20.3 % with the complete decomposition of residue composite at about 800˚C. The endothermic peak was observed at about 250°C, 600°C and 800°C which correspond to the decomposition of CuO/NiO group.

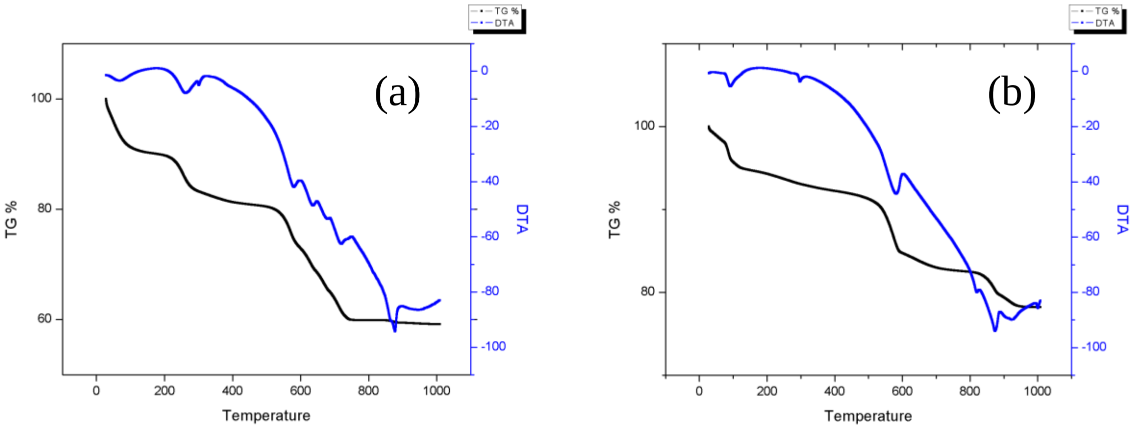

Figure 10. Represents the (a) TG/DTA of CuO/NiO and (b) TG/DTA of CuO/Fe_3O_4

TG-DTA curve of CuO/Fe_3O_4 nanocomposite is as shown in **figure10 (b)**. Removal of nitrate takes place with the formation of CuO/Fe_3O_4. The dramatic mass loss initiated at about 220˚C can be attributed to the decomposition of CuO/$Fe_3O_4$and mass loss from 200 to 400˚C is about 9.4 %. The mass loss at above 400˚C can be attributed to phase formation of Cu_2O/Fe_3O_4 and the mass loss from 400 to 1000˚C is about 4.2 % with the complete decomposition of residue composite at about 1000˚C. The endothermic peak was observed at about 250˚C which corresponds to the decomposition of CuO/ Fe_3O_4 group.

4. CONCLUSION

Herein this work represents the synthesis of CuO nanocomposite towards the enhancement of capacitance for supercapacitor application. Where in hydrothermal method was employed for the synthesis of CuO/ NiO and CuO/ Fe_3O_4. The synthesized CuO nanorods were confirmed via XRD and SEM. Further, CuO/ NiO and CuO/Fe_3O_4 were analyzed and studied their electrochemical properties and pseudo capacitive capacitance behavior at different sweep rates. This material shows the specific capacitance value of 380 F/g at 5 mV/s. CuO composites showed enhanced results. With the CuO nanocomposite results of XRD, SEM, electrochemical properties and TG/DTA data. From the studies conducted it is concluded that CuO/NiO has highest capacitance than CuO/Fe_3O_4. The study results open a new window towards using these nanocomposite materials for supercapacitor application and can be explored further to get a detailed insight.

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