Supercapacitor properties of copper oxide/graphene oxide composites produced from a new Cu (II) complex containing hydrazone-hydrazide ligand

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Abstract: -

Well-defined copper oxide (CuO) nanoparticles were synthesized through the thermal breakdown of a Cu(II) complex at 400°C for three hours. The nanoparticles possess uniform forms of diverse sizes and were studied using SEM and TEM techniques. CuO nanoparticles are combined with graphene oxide (GO) to create a composite nanosystem, which was investigated for its application in supercapacitors. The specific capacity of the CuO-GO electrode is enhanced when spherical GO nanoparticles are tightly coiled on the surface of CuO nanoparticles, resulting in composites with an expanded surface area. The cyclic efficiencies of these electrodes after 2000 cycles were 88.3%, 95.5%, and 98.7%, respectively. Specifically, at 5 A g-1, CuO-GO exhibits a specific capacitance of 395 F g-1, significantly surpassing the values of GO (115 F g-1) and CuO (235 F g-1). This study presents a straight forward and reproducible method for synthesizing a CuO/GO nanocomposite for energy storage applications.

Keywords: Copper (II) complex; CuO/GO nano composite; electrochemical studies, supercapacitor.

1. INTRODUCTION

The demand for increasingly compact and powerful devices and electric cars is propelling advancements in high-density energy storage. [1,2]. Supercapacitors are a sort of electrochemical energy storage devices distinguished by their capacity to rapidly store substantial amounts of energy (high power density) and discharge it swiftly (fast charging/discharging). They possess an extended longevity (cycle life) and reliable performance [3,4]. Choosing the appropriate electrode material is vital for increasing the electrochemical behaviour of supercapacitors. The often utilized transition metal oxides and hydroxides include NiO, CoO, mixed oxide complexes, RuO_2, manganese oxide, among others, as well as carbonaceous materials such as carbon nano-onions, carbon nanotubes, graphene and activated carbon. Research on supercapacitors is investigating copper oxide

(CuO) because of its affordability and straightforward manufacture. Graphene oxide (GO), characterized by its extensive surface area and advantageous redox characteristics, presents itself as a possible candidate. Electrodeposition, an economical and uncomplicated method, is widely utilized for the fabrication of these supercapacitors. [15-20]

In the past decade, methodologies for synthesizing CuO nanoparticles have been investigated, including the sol-gel method [21], sonochemical approach [22], one-step room-temperature solid-state reaction technique [23], and electrochemical process [24]. Thermal decomposition is an innovative method in the midst of the several methods discovered for the production of stable monodisperse Cu and CuO nanoparticles, as well as for the co-implantation of oxygen ions and metals. The fabrication of coordination supra-molecules or polymer chains with coordination has recently become a potent and adaptable method for manufacturing metallo-polymers [27-28]. Coordination supramolecules are distinguished from conventional covalent polymers by their reliance on metal-ligand coordination bonding [29-30]. Supramolecular coordination complexes possess extensive potential applications in nanotechnology, as nanoscale materials frequently display fascinating size-dependent chemical and physical properties absent in their bulk counterparts.

Graphene Oxide (GO), an innovative material in the realm of renewable energy, possesses a substantial surface area and exhibits advantageous redox properties [31]. Besides water purification, these carbon nanostructures shown efficacy in other applications, including light-emitting diodes, fuel cells, sensors, batteries, nanoantennas, touch screens, liquid crystal displays and sound transducers [32]. This research presents the synthesis of new copper coordination complex with the formula $[(Cu(3,5\text{-dnb})_2(3\text{-pymc})_2(H_2O)_2]$, followed by calcination to yield CuO nanocrystals. A novel nanocomposite system has been developed by combining graphene with synthesized copper oxide, and its use for energy storage has been examined.

2. EXPERIMENTAL SECTION

Materials and Methods

3,5-Dinitrobenzoic acid and methyl carbazate (methyl hydrazinecarboxylate) were of analytical standard and procured from Sigma-Aldrich. Ethanol, phosphoric acid, H_2O_2, $KMnO_4$, and HCl were acquired from TCI Chemicals, each with a purity of 99%. NaOH, H_2SO_4, and graphite powder were procured from Avra Chemicals, with stated impurities of 99% and no additional purification conducted. All compounds were utilized in their unaltered state.

Synthesis of $[(Cu(3,5\text{-dnb})_2(3\text{-pymc})_2(H_2O)_2](1)$ & $[Cu_3(3,5\text{-dnb})_6(CH_3OH)_2]$

The production, characterisation, and crystallographic examinations of the title complexes have been documented in our prior research [33]. Figure 1 illustrates the chemical structure of the complex.

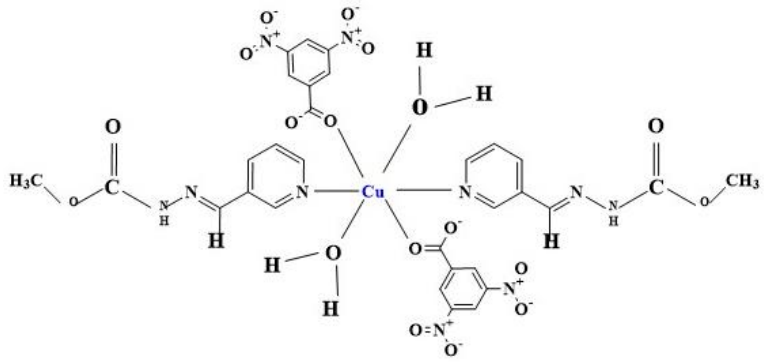

Figure 1. Chemical structure of Cu complex

2.4. Synthesis of Graphene Oxide (GO)

In a standard procedure, pure graphite powder was transformed into graphene oxide (GO) by a modified Hummers method. This technique entailed the amalgamation and agitation for many minutes of 27 milliliters of sulfuric acid and 3 milliliters of H_3PO_4 in a quantity ratio of 9:1. Afterwards, 225 mg of graphite was included into the fusion under agitation. Then, 1.32 g of $KMnO_4$ was incrementally introduced to the content. The reaction mixture became dark green in colour after 6 hours of strong agitation of the content. 0.675 ml of H_2O_2 was incrementally introduced and agitated for 10 minutes to eliminate the excess potassium permanganate. Subsequent to the exothermic process, permit it to cool. The graphene oxide produced was rinsed with 30 ml of deionized water and 10 ml of hydrochloric acid.

2.4. Electrochemical behaviour of CuO/GO composites

The working electrodes was fabricated by combining the active component (80 wt.%), polyvinylidene fluoride (10 wt.%), and carbon black (10 wt.%) in 1-Methyl-2-Pyrrolidone to create a uniform slurry, which was subsequently applied on nickel foam (1x3 cm^2) and dehydrated at 80 °C for 12 hours. The measurements were conducted in a aqueous 1M KOH through a three-electrode technique, utilizing a saturated calomel electrode (SCE) as the reference electrode and platinum electrode as the counter electrode. The electrochemical characteristics of the synthesized materials was assessed by means of electrochemical impedance spectroscopy (EIS), galvanostatic charge/discharge (GCD) measurements and cyclic voltammetry (CV), utilizing a CHI 660 E workstation.

3. Results and discussion

P-XRD Analysis

The P-XRD investigation, publicized in Fig. 2, validated the crystalline structure of the synthesized GO and CuO-GO nanocomposite. Diffraction peaks of GO nanosheets (Fig. 2b) are detected at 2θ = 28.48°, 30.37°, 32.37°, 42.13°, and 50.44°, corresponding to the (100),

(002), (101), (102), and (110) planes. They pertain to the attributes of the Hexagonal phase of GO (JCPDS01-076-2378). The (110) reflection peak of the multilayer GO nearly vanished. The diffraction peak was suggested to be imperceptible upon the exfoliation of GO. The PXRD pattern of CuO-GO composites reveals peaks at 2 θ = 32.41°, 35.13°, 39.13°, 53.88°, and 66.22°, corresponding to the (110), (002), (200), (112), (202), and (022) planes, respectively. The pattern signifies that the CuO is in monoclinic phase (JCPDS 00-002-1041). The carbonyl group of carboxylic acids and ketones on GO exhibited significant coupling with Cu ion, thereby forming a layer-on-layer network.

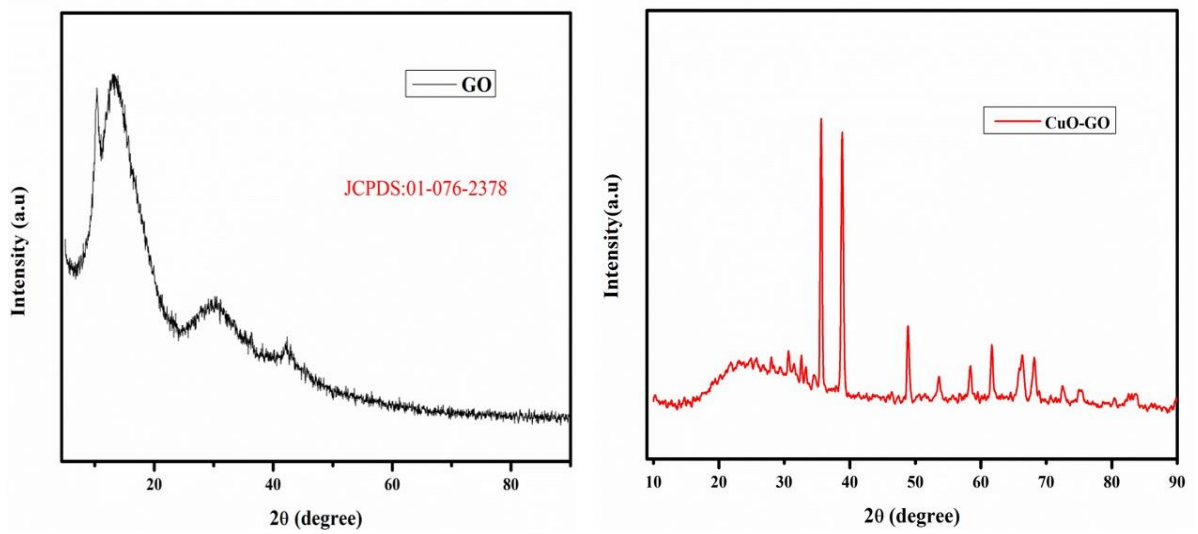

Figure 2. The XRD patterns of (IV-b) GO, and (IV-c) GO-CuO nanocomposite.

SEM image of CuO-GO

The nanocomposite SEM was obtained in powder form, and images were recorded on carbon tape. Figure 3(a) and (b) presents the SEM images, clearly illustrating that the morphology of the intercalated nanocomposite particles is indeed at the nanoscale, although the irregular form resulting from particle aggregation in the solution during synthesis.

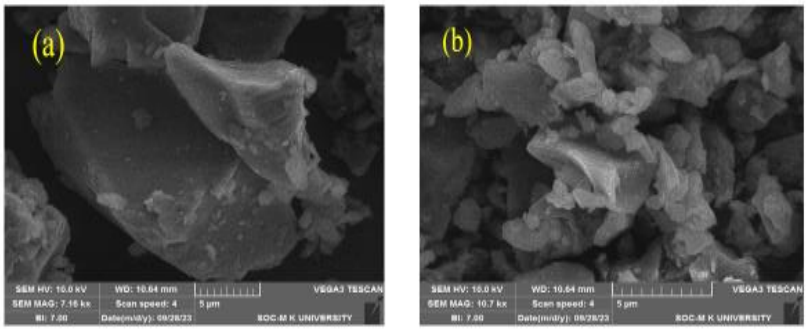

Figure 3. a-b) FE-SEM images of CuO-GO composite particles

HR-TEM image of GO &CuO nanoparticle

The prior study unequivocally demonstrated that hydrazine hydrate is the most potent reducing agent in the chemical reduction of graphene oxide. TEM analyses revealed that the treatment of GO with hydrazine hydrate yielded high-quality, ultrathin graphene sheets. Substantial, dense, multilayered agglomerates of GO were found naturally flat on the surface of the carbon sheet (Fig. 4(a)).[34] The TEM image of GO in Fig. 4b indicates that the GO sheet is irregular, and the folded GO sheet demonstrates a lamellar structure and significant flexibility. Consequently, we can ascertain that graphene oxide with a single layer and a two-dimensional nanoscale was successfully synthesized [35].

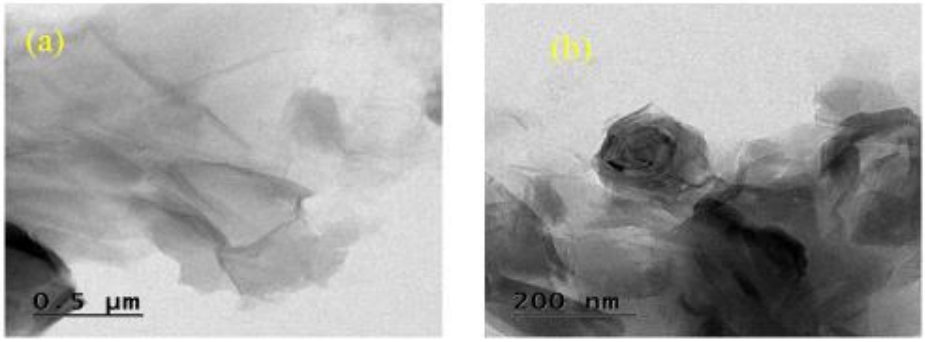

Figure 4 TEM images of CuO-GO composite particles

Electrochemical analysis

The example cyclic voltammetry (CV) responses for GO, CuO, and the CuO-GO nanocomposite, obtained at scan rates of 10, 20, 30, 50, 70, and 100 mV s^{-1} within the potential range of 0.0 V to 0.7 V, are demonstrated in Figure 5(a-c). It is essential to observe that both the current density and the region beneath the cyclic voltammetry curve increase with the scan rate [36]. The potential limits were established betwixt 0.7 and 0 V, amid the scan rate varying starting 10 to 100 mV/s. The redox peaks are clearly discernible in all cyclic voltammetry responses, deviating from the rectangular behavior indicative of the electric double layer capacitance method. The peak separation enlarges with a rising scan rate, transitioning from a lower to a higher rate, for instance, from 10 to 100 mV s-1, attributable to the ion exchange method. The constancy of the form parameters of the cyclic voltammetry responses at elevated scan rates signifies the remarkable durability of CuO-GO electrodes [37]. The area delineated by the unit-based CuO, GO, and GO/CuO curves. The specific capacitance data of the CuO-GO coated Ni foam are significantly higher than those of the individual compounds of the bare GO and CuO coated electrodes. The specific capacity of the CuO-GO electrode is enhanced when spherical GO nanoparticles are tightly wrapped around the surface of CuO nanoparticles, resulting in composites with an increased surface area.[38-39].

The following CV equation is utilised to compute the specific capacitance (F g^{-1}) of the deposited metal-oxides-electrodes.[40].

$$Csp = \frac{A}{2mkV(v2-v1)} \qquad (1)$$

Where (m) is the quantity of the active material (g), (A) is the applied area, (k) is the scan rate, and (V) is the discharge potential window (v2-v1) rangs specific capacitance (csp).

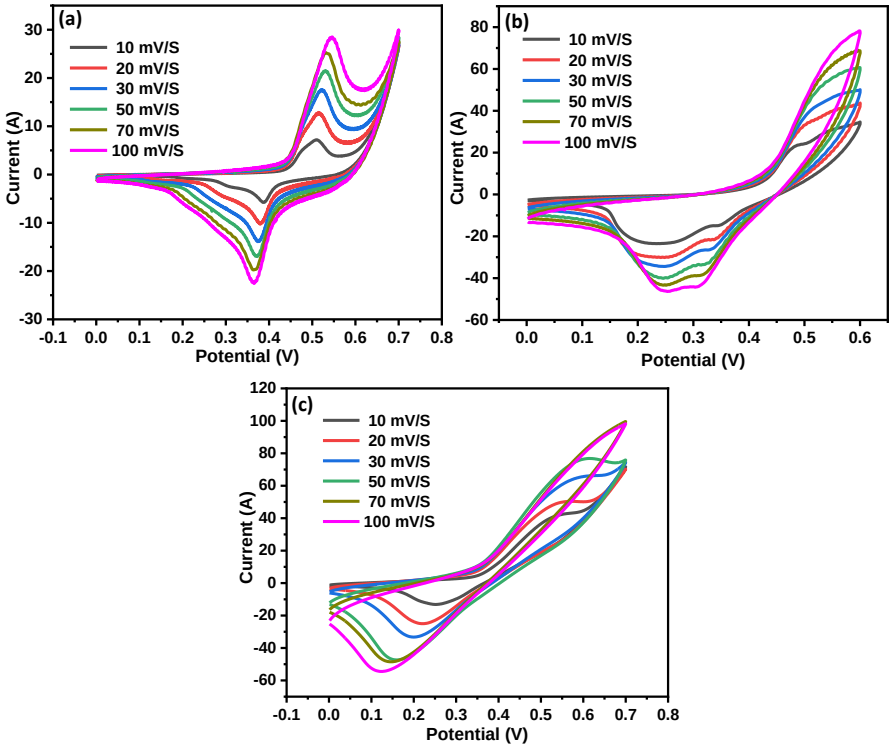

Figure 5. CV curve of a) GO, b) CuO, and c) CuO-GO nanocomposites.

Figure 6(a-c) illustrates the GCD responses of GO, Copper oxide and CuO-GO throughout various current density ranges from 5 to 10 A g⁻¹. The curves have subtly curved, approximately triangular shapes, signifying robust electrochemical reversibility and advantageous capacitive characteristics. GCD profiles demonstrated nonlinear charging and discharging behaviors, affirming the occurrence of Faradaic processes at the electrode interface. Equation 2 was employed to get particular capacitance data derived from the GCD responses [41].

$$\mathrm{C}sp = \frac{I\Delta t}{m\Delta V} \qquad (2)$$

where m denotes the quantity of the active material (g), V represents the discharge potential range (V), Δt indicates the discharge duration (s) and I signifies the applied current (A). As ion transport in the CuO-GO system slows at elevated current densities, a rise in current density clearly leads to a prompt reduction in specific capacitance (Cp). This is a characteristic tendency seen by all electrochemical capacitors. There is sufficient time for electrolyte ions to access the electrode surface and subsequently exit at reduced current densities. Specifically, at 5 A g-1, CuO-GO exhibits a specific capacitance of 395 F g-1, significantly surpassing the value of graphene oxide at 115 F g-1 and CuO at 235 F g-1.

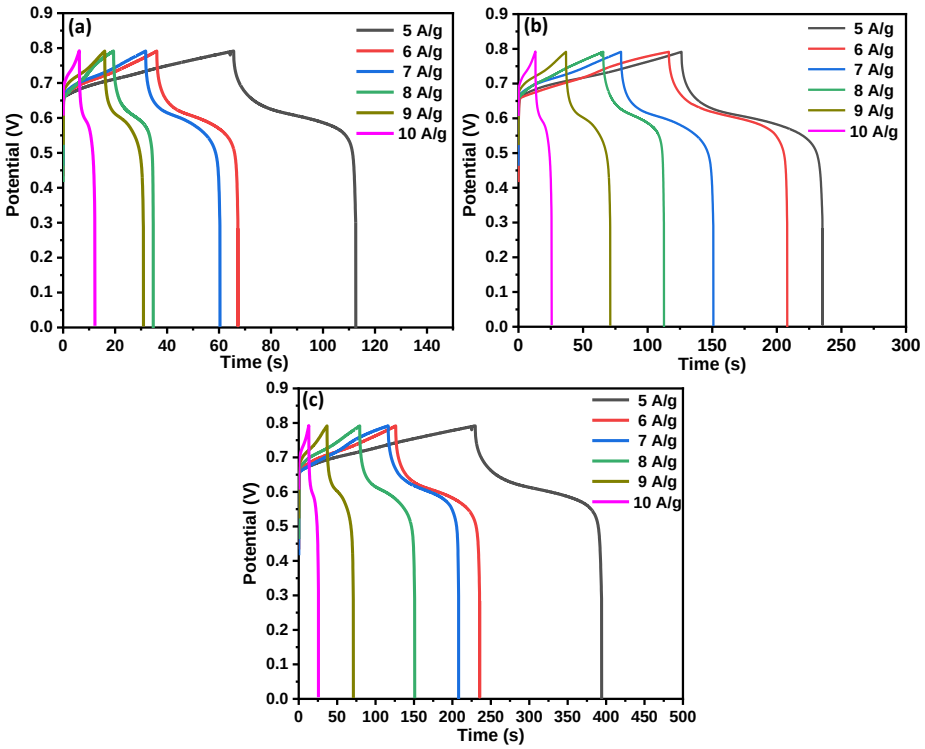

Figure 6.GCD curve of a) GO, b) CuO, and c) CuO-GO nanocomposites.

Electrochemical impedance analysis (EIS)

Furthermore, EIS assessments were conducted to estimate the conductive properties of the GO, CuO, and CuO-GO nanocomposites. Figure 7a illustrates the Nyquist plot of GO, CuO nanoparticles and CuO-GO composite electrodes. The kinetics of charge transport in electroactive materials were investigated using EIS across a frequency range of 0.01 Hz to 100 kHz. The pertinent Nyquist plot and equivalent circuit employed to model the experimental data for all CuO-GO electrodes are presented. The corresponding series resistance at the electrolyte/electrode interface decreases as the oxygen concentration of the CuO-GO film rises, indicates the suitability of CuO-GO electrode for supercapacitor utility. The parameters RΩ, CPE-T, and CPE-P were derived from impedance plots utilizing the equivalent circuit [42]. The charts were fitted utilizing equivalent circuit fitting [43].

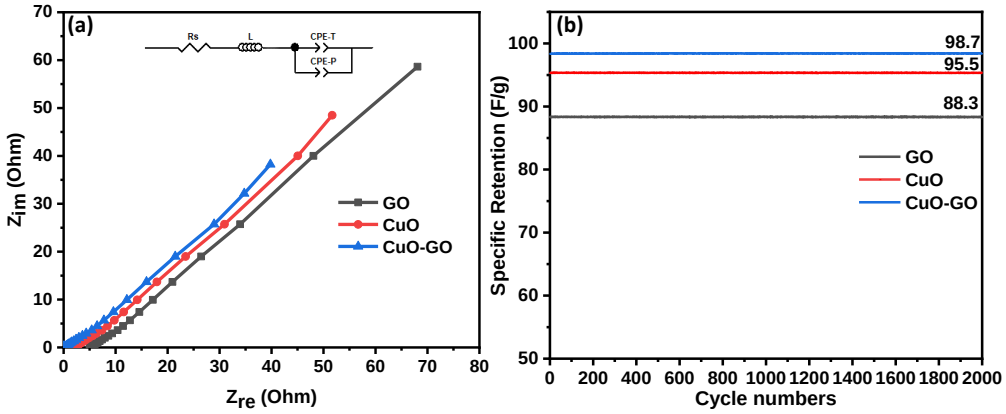

Figure 7. (a) EIS spectrum, and (b) Capacitance retention for 2000 cycles.

The cyclic stability of GO, CuO, and CuO-GO electrodes was assessed during 2000 cycles at a current density of 5 A.g-1. Figure 7b illustrates that the cyclic efficiencies of these electrodes after 2000 cycles were 88.3%, 95.5%, and 98.7%, respectively. The results highlight the enhanced cyclic stability of CuO-GO relative to the other samples, as indicated by electrochemical analyses.

CONCLUSION

We synthesized CuO using a coordination complex as a precursor and blended it with graphene oxide to serve as an electrode for supercapacitor utility. The specific capacity of the CuO-GO electrode is enhanced when spherical GO nanoparticles are tightly coiled on the surface of CuO nanoparticles, resulting in composites having improved surface area. The cyclic stability of GO, CuO, and CuO-GO electrodes was assessed to have a current density of 5 A.g-1 during 2000 cycles. After 2000 cycles, the cyclic efficiencies of these electrodes were 88.3%, 95.5%, and 98.7%, respectively. Specifically, at 5 A g-1, CuO-GO exhibits a specific capacitance of 395 F g-1, significantly surpassing the valye of graphene oxide (115 F g-1) and CuO (235 F g-1). This study presents an efficient and reproducible method for fabricating a CuO-GO nanocomposite layer and the promising results reveals the suitability of this composite towards supercapacitor applications.

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