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DEVELOPMENT OF CuO/rGO NANOWIRE ELECTRODES FOR HYBRID ELECTROCHEMICAL SUPERCAPACITOR

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The development of high-performance and cost-effective electrode materials is crucial in advancing supercapacitor technology. For supercapacitors, nanostructured Cu oxides are promising materials due to their high theoretical capacitance, low cost, and non-toxicity. One major drawback to the practical applications of CuO lies in the poor electrical conductivity and cyclic stability of the material, despite its theoretically high specific capacitance. Here in, the CuO nanowire composite electrode coated with reduced graphene oxide (rGO) was prepared via a simple and scalable three-step method by anodization of a copper coated titanium substrate to grow copper hydroxide ($Cu(OH)_2$) nanowires, dip coating with a graphene oxide (GO) dispersion, and thermal treatment of the electrode at 400 ^oC in a single step. The annealing converted $Cu(OH)_2$ to CuO, and GO to rGO. X-ray diffraction (XRD) analysis confirmed the successful formation of phase-pure CuO, with prominent peaks observed. The SEM analysis confirmed the formation of a uniform CuO nanowire structure on Ti substrate. The electrochemical study revealed a synergistic charge storage mechanism, combining the electrical double layer capacitance of rGO with pseudocapacitance from CuO redox reactions. At a scan rate of 5 mVs^{-1} in CV, the rGO/CuO composite electrode gave the highest specific capacitance of 78.45 Fg^{-1} and current density of 0.25 Ag^{-1} in Galvanostatic Charge Discharge (GCD); the composite electrode exhibited a maximum specific capacitance of 83 Fg^{-1}. In addition, the electrode also showed excellent cyclic stability, after 1000 charge–discharge cycles at 5 Ag^{-1} current density, it retained more than 95% of its original capacitance. The observed enhancement in performance is due to high conductive pathways and the large surface area of the rGO network. In contrast, the CuO nanowires can deliver a significant amount of pseudocapacitance. The results suggest that the rGO/CuO composite prepared by this low-cost and effective method can be successfully implemented as an electrode material for the fabrication of high-performance hybrid supercapacitors.

Keywords: supercapacitor, CuO nanowire, rGO, composite electrode, specific capacitance, cyclic stability

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INTRODUCTION

Energy storage devices are important for various applications, from portable electronics to large-scale grid management. Supercapacitors came as significant energy storage devices, gaining a unique position between traditional capacitors and batteries (Abdou Ahmed Abdou Elsehsah et al., 2024). Improving the performance of supercapacitors has driven extensive research into advanced materials for electrodes. Graphene-enhanced metal oxides are a promising candidate in this field (Li et al., 2015). Incorporating reduced graphene oxide (rGO) into the cupric oxide (CuO) based electrode addresses the poor electrical conduction associated with CuO. The highly conductive rGO network from the composite acts as an efficient pathway for electron transport that significantly improves the overall conductivity of the electrode (Jiang et al., 2012). The rGO nanosheets also form a supporting matrix for CuO nanoparticles and prevent them from aggregating, leading to the good distribution of the active material (Bierwirth et al., 2015). This, together with the high surface area of the rGO, creates a larger electrochemically active surface area for increased interaction between the electrode and the electrolyte (Kötz & Carlen, 2000). Furthermore, CuO serves as the composite because it has a higher energy storage mechanism due to pseudocapacitive redox reactions involving copper ions (Aljaafari et al., 2019). This pseudocapacitive mechanism enhances the overall energy density of supercapacitors that solely rely on the electrical double-layer capacitance of rGO (Pech et al., 2010). This paper reports on the fabrication of CuO and CuO/rGO nanowires via low-cost anodization, annealing, and dip coating methods for hybrid supercapacitor electrode preparation.

METHODOLOGY

Cu-coated Ti plates were utilized as the current collectors. Titanium substrates were polished using sandpaper (Grit size 2000), rinsed with detergent, followed by distilled water, and cleaned using HCl and dried. Cu was electrodeposited with an Autolab PGSTAT302N with a three-electrode configuration. The substrate to be coated was employed as the working electrode, whilst a carbon rod served as the counter, and the potential of -0.7 V vs Ag/AgCl for 10 minutes in 0.01 M copper (II) acetate and 0.1 M sodium acetate at 60 °C (Mezine et al., 2018). After deposition electrodes were washed with distilled water and dried.

The CuO-coated Ti electrode was synthesized via an anodization followed by a thermal reduction method. The Ti/Cu electrode was anodized in 3 M sodium hydroxide (NaOH) solution using galvanostat mode in Auto lab PGSTAT302N with a two-electrode configuration. The current density was 10 mA/cm² and the anodizing time was 180 seconds for the formation of Cu $(OH)_2$ nanowires (Hyam et al., 2012). The resultant was rinsed and dried for 10 minutes at 80 ˚C before the thermal reduction process. The Ti/Cu$(OH)_2$ electrodes are subjected to a heat treatment for 4 minutes at 400 ˚C to facilitate the thermal reduction of Cu$(OH)_2$ into CuO nanowires. The fabricated Ti/CuO nanowire electrode serves as the cathode of the supercapacitor.

The graphene oxide was synthesized via the improved Hummers method (Marcano et al., 2010). A stable dispersion of GO was prepared by ultrasonication of GO sheets for about 20 min. The Ti/Cu$(OH)_2$ electrode was dipped in the prepared GO solution for 10 minutes. After dip coating, the electrode was annealed at 400 ˚C for 4 minutes. This thermal treatment simultaneously facilitates the Ti/CuO/rGO electrode, which serves as the anode (Sengupta et al., 2018). Electrode materials of the supercapacitor were characterized using SEM, XRD. Electrochemical measurements were obtained using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) plots, and a cyclic stability test using 1000 GCDs at the current density of 5 Ag^{-1} using an Auto lab PGSTAT302N workstation. Retention of capacitance was analyzed using the calculation of the capacitance once every 100 cycles.

RESULTS AND DISCUSSION

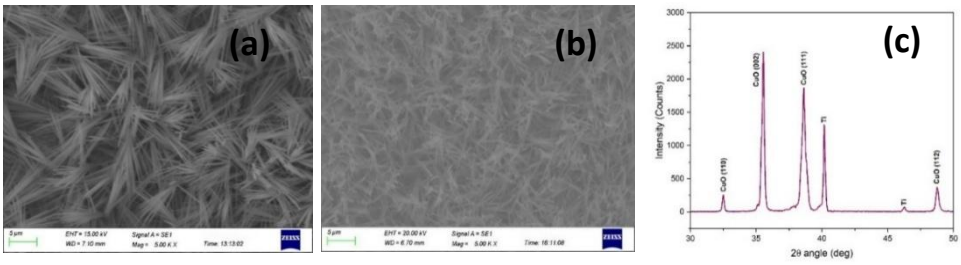

Figure 46: (a) SEM image of Cu$(OH)_2$ Nanowires, (b) SEM of CuO Nanowires, (c) XRD of CuO-coated titanium electrode.

This section details the morphological and electrochemical characterization of the synthesized CuO electrodes. To investigate the morphology of the synthesized materials, Scanning Electron Microscopy (SEM) was employed. The SEM images in Figure 1 (b) confirm the successful synthesis of CuO nanowires through an annealing route, resulting in a morphology that is expected to be beneficial for its application as a supercapacitor electrode material. The structure of the synthesized CuO nanowire electrode was studied using XRD, and the pattern is illustrated in Figure 1(c). The XRD pattern displays diffraction peaks characteristic of CuO, with the major intensity peaks related to CuO, respectively (Jhansi et al., 2016). The absence of foreign phases also confirms the complete conversion of Cu$(OH)_2$ to pure CuO during annealing. These well-formed nanowires are expected to enhance pseudocapacitive behavior by

providing numerous active sites for redox reactions and clear pathways for electron transfer.

The electrochemical properties of electrodes fabricated with CuO and CuO/rGO were analyzed using Cyclic Voltammetry (CV) and Galvanostatic Charge Discharge (GCD), which have all been determined in 1.5 M, 3 M, and 4.5 M NaOH electrolytes using Auto lab PGSTAT302N potentiostat/galvanostat.

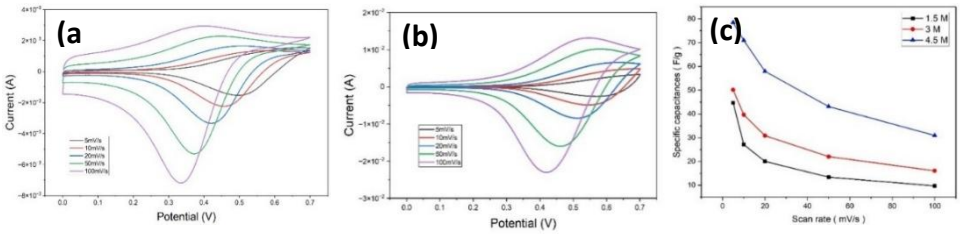

Figure 47: CV curves of rGO/CuO electrode at (a) & (b) 1.5 & 4.5 M NaOH electrolytes at different scan rates (c) rGO/CuO electrodes' specific capacitance for different scan rates and NaOH concentrations

In a three-electrode system, Cyclic Voltammetry (CV) measurements were conducted to study the charge storage properties of the rGO/CuO electrode. Figure 2 (a) shows the CV curves obtained at scan rates ranging from 5 mVs^{-1} to 100 mVs^{-1} within the potential window of 0 V to 0.7 V. The CV curves exhibit a quasi-rectangular shape with clear redox peaks, which deviate from the perfect rectangular signature of a pure Electric double-layer capacitor (EDLC), as shown in Figure 2 (a). This defined shape confirms that the charge storage mechanism is a hybrid combination of EDLC and pseudo capacitor due to the high surface area of reduced rGO and Faradaic pseudocapacitance from CuO redox reactions in the alkaline electrolyte.

As the scan rate increases, the specific capacitance decreases for all NaOH concentrations. In 4.5 M NaOH, the specific capacitance drops from 78.45 Fg^{-1} at 5 mVs^{-1} to 30.93 Fg^{-1} at 100 mVs^{-1}. This occurs because at lower scan rates, ions have more time to diffuse into the electrode's inner pores and engage in the slower Faradaic redox reactions of CuO, leading to higher charge storage. It is also clear that specific capacitance increases with higher NaOH concentrations at any given scan rate. For instance, at 10 mVs^{-1}, the specific capacitance increases from 27.12 Fg^{-1} in 1.5 M NaOH to 70.94 Fg^{-1} in 4.5 M NaOH. The specific capacitance of CV is calculated using Equation (1).

$$C = \frac{\int i\, dV}{2m.\Delta V.S} \qquad (1)$$

Where, $\int i\, dV$ is the integrated area of the CV curve, S, ΔV, and m are the scan rate, potential range, and mass of a single working electrode (Luan et al., 2019).

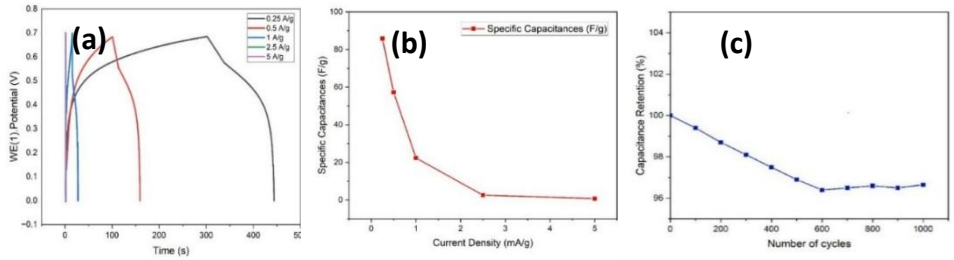

Figure 48: (a) GCD curve of rGO/CuO electrodes in 1.5 M NaOH concentration (b) Change of Specific capacitance with different current densities. (c) Capacitance retentions within 1000 galvanostatic charge tests at the current density of 5 Ag^{-1}

To further evaluate, GCD measurements were performed using anode as CuO/rGO and cathode as CuO at different current densities, from 0.25 Ag^{-1} to 5 Ag^{-1}, in a 1.5 M NaOH electrolyte. Thus, enabling further assessment of the rGO/CuO electrodes' capacitive behavior and charge storage kinetics, the GCD profiles within a potential window of 0 to 0.7 V are shown in **Figure 3 (a)**.

GCD measurements were performed at current densities from 0.25 Ag^{-1} to 5 Ag^{-1} in a 1.5 M NaOH electrolyte. It reaches maximum specific capacitance as 83 Fg^{-1} at current density of 0.25 Ag^{-1}. The discharge curves are not perfectly linear, which indicates a hybrid contribution from Faradaic redox reactions, confirming the pseudocapacitive behavior of CuO alongside the EDLC behavior of rGO. A distinct potential drop is visible at the beginning of the discharge curve, which is caused by the internal resistance of the system. As expected, the specific capacitance decreases as the current density increases from 0.25 Ag^{-1} to 5 Ag^{-1}.The specific capacitance of GCD is calculated using Equation (2).

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

Where I (A) is the discharge current for the applied time duration Δt (s), ΔV (V) is the potential window, and m is the weight of CuO (Senthilkumar et al., 2015).

The cyclic stability is a critical parameter for evaluating the practical applicability of supercapacitor electrodes. The cyclic stability of the rGO/CuO composite electrode was tested using GCD cycles of 1000 repetitions at 5 Ag^{-1} current density in 3 M NaOH solution. Figure 3(c) shows the capacitance retention of the rGO/CuO electrode versus the number of cycles. As shown in Figure 3(c), the rGO/CuO electrode exhibits excellent cyclic stability behavior. After 600 successive charge-discharge processes, the electrode was stabilized at more than 95% of its original capacitance.

CONCLUSIONS

In this study, a composite electrode of rGO-coated CuO nanowires was synthesized for supercapacitors using a simple and inexpensive method that combines anodization, dip-coating, and a single thermal treatment step. Morphological investigation using Scanning Electron Microscopy (SEM) confirmed that the CuO has developed a uniform nanowire morphology, which was successfully coated by rGO nanosheets. Electrochemical characterization revealed a hybrid mechanism of pseudo and EDLC charge storage in the rGO/CuO-based electrodes, as evidenced by the quasi-rectangular CV curves with clear redox peaks. The XRD analysis has provided some evidence for the CuO nanowires, where characteristic diffractions corresponding to CuO are observed, hence confirming the nanowire nature and phase purity.

The composite electrode has demonstrated the best performance in an electrolyte of 4.5 M NaOH, having its highest specific capacitance of 78.45 Fg^{-1} at a scanning rate of 5 mVs^{-1}. This capacitance was much higher than observed at lower concentration electrolytes, indicating the influence of electrolyte concentration on charge storage. Moreover, the electrode exhibited excellent cyclic stability upon long-term cycling, retaining more than 95% of its initial capacitance after 1000 charge-discharge cycles at a current density of 5 Ag^{-1}.

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