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Enhancement of the energy storage properties of supercapacitors using graphene nanosheets dispersed with macro-structured porous copper oxide

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ABSTRACT

Graphene nanosheets (GN) dispersed with macroporous copper oxide (macroCuO) was investigated as an electrode material for supercapacitors. A facile and cost-effective synthesis approach was used to prepare macro-structured porous copper oxide monoliths via modified Sol–Gel route. 1, 3, 5-trimethylbenzene was used as an organic structural directing agent to enhance the pore size, pore volume, pore density and surface area of the resulting CuO hybrid templated with Pluronic P-123. GN/macroCuO nanocomposite was prepared by ultrasonication of the GN and macroCuO. The macroCuO and GN/macroCuO nanocomposite were characterized using various surface analytical techniques. Electrochemical performance of the composite electrode was investigated using cyclic voltammetry and chronopotentiometry. GN/macroCuO/GCE showed pseudocapacitance behaviour due to the Faradaic type of capacitance involving redox process between Cu (0) and Cu (II) of porous copper oxide network. Electrochemical measurements revealed the maximum specific capacitance, energy density and power density of 417 $F\,g^{-1}$, 58 $Wh\,kg^{-1}$ and 17.85 $kW\,kg^{-1}$, respectively for the supercapacitor based on GN/macroCuO nanocomposite electrode at a current density of 0.9 $A\,g^{-1}$. The fabricated supercapacitor device exhibited excellent cycle life with 91.4% of the initial specific capacitance retained after 1000 cycles. The results suggest that the hybrid composite is a promising supercapacitor electrode material.

1. Introduction

Energy storage, an intermediate step to the versatile, clean, and efficient use of energy, has received worldwide concern and increasing research interest [1]. Among the various power source devices, supercapacitors (SCs), also known as electrochemical capacitors, have attracted considerable attention over the past decade due to their high power densities, fast charging/discharging rate, and long cycle life compared to secondary batteries and fuel cells, and also, higher energy densities than the conventional dielectric capacitors [1–3]. The most commonly used materials for electrical double layer capacitors (EDLCs) are carbonaceous materials including activated carbon [4], graphene [5] and carbon nanotubes [6], however, relatively low energy density, suffering from poor rate capability and/or poor capacitance retention upon cycling has limited their applications [2]. In contrast, transition metal oxides or hydroxides with variable valence, such as NiO [7], Co_3O_4 [8–10], MnO_2 [11], $Ni(OH)_2$ [12], and $Co(OH)_2$ [13] can provide higher energy density for supercapacitor. Such materials not only store energy like electrostatic carbon materials but also exhibit electrochemical faradaic reactions between electrode materials and ions within appropriate potential windows [2].

Among the transition metal oxides, porous copper oxide (CuO) is noteworthy to explore as a promising candidate due to its low cost, abundant resources, non-toxicity, chemically stable, and easy preparation in diverse shapes of nano-sized dimension. Many methods have been developed to synthesize various CuO nanostructures [14–19], and its supercapacitance behavior has attracted extensive research interest. For instance, Patake et al. [20] synthesized the porous amorphous copper oxide thin films which exhibited a specific capacitance of 36 $F\,g^{-1}$ in 1 M Na_2SO_4

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electrolyte whereas, Dubal et al. [21] reported copper oxide multilayer nanosheets thin films with a specific capacitance of 43 F g^{-1} in 1 M Na_2SO_4 electrolyte. Zhang et al. [22,23] found that CuO with flower-like nanostructures displayed a specific capacitance of 133.6 F g^{-1} in 6 M KOH electrolyte, which is about three-fold higher than commercial CuO powder. However, the specific capacitance of CuO is still lower than other transition metal oxides and exhibited unstable cycling performances. Wang et al. [24] have reported the synthesis of CuO nanosheets arrays directly grown onto nickel foam with higher specific capacitance of 569 F g^{-1}, whereas the method employed is relatively complicated. Although, nanoscale CuO particles possess large surface area and relatively high specific capacitance, the microstructure is easily damaged during electrochemical cycling, resulting in a relatively poor electrochemical stability. Recently, composites based on carbonaceous materials (graphene and graphene oxide) and copper oxides [25–27] have been studied for improved capacitance. Integration of graphene into functional architectures and composites has currently been an active area of research [25,28].

Given this situation, a promising strategy would be to combine supercapacitive material, graphene with low-cost pseudo-capacitive metal oxides such as CuO, which offers both a cost advantage and potentially a high performance benefiting from both mechanisms of electric double layer capacitance and pseudo-capacitance [2,29]. To the best of our knowledge, macro-structured porous copper oxide monoliths synthesized via modified Sol–Gel route without using any acidic or basic medium with a reasonable specific capacitance and better cycling performance have seldom been reported.

Herein, we report a facile, cost-effective and scalable synthesis approach to prepare macro-structured porous copper oxide monoliths (macroCuO) via modified Sol–Gel route. Trimethyl benzene (TMB) is used in the synthesis as an organic structural directing agent to enhance the pore size, pore volume, pore density and surface area of the resulting CuO hybrid. This product is dispersed with graphene nanosheets to give a nanocomposite material (GN/macroCuO) to be used as electrodes for supercapacitors.

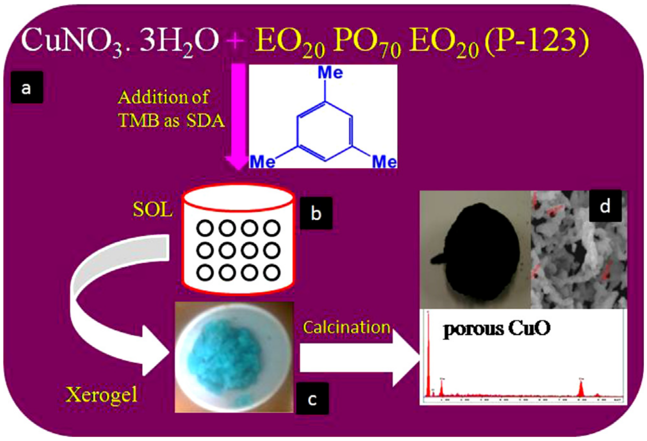
The incorporation of macroCuO into graphene layers is expected to improve electrolyte–electrode accessibility and electrode conductivity by reducing the agglomeration of GN. GN/macroCuO composite has been prepared by ultrasonication of GN and macroCuO. Supercapacitor devices are fabricated using GN/macroCuO nanocomposite electrode materials and performance studies are conducted.

2. Experimental

2.1. Chemicals and Materials

Copper nitrate trihydrate (Sigma Aldrich as a precursor), soft template Pluronic P-123, (Sigma Aldrich), structural directing agent 1, 3, 5-Trimethylbenzene, TMB (Merck). Graphene (99.5 % purity) was purchased from Sisco Research Laboratories Pvt. Ltd.

Porous copper-oxide monoliths were prepared by dissolving 2.0 g Cu $(NO_3)_2.3H_2O$ (50 wt%, Sigma–Aldrich) in 2.0 g of ultrapure water (50 wt %) and 2.0 g of Pluronic P-123 (14.81 wt%, $M_w = 5800$, Aldrich) in 11.5 g of ultrapure water (85.19 wt %) followed by addition of 2 g of TMB at 25 °C. The gel was heated for 1 h at 55 °C on a magnetic stirrer to form the paste which gradually became light blue in colour. The resulting gel was aged for 2–3 days at room temperature (xerogel formation) and then calcined at 650 °C for 2 h at a heating rate of 1 °C/min followed by cooling at a rate of 1 °C/min to room temperature in an ELLITE furnace. The overall protocol for the synthesis is shown in Scheme 1.



Scheme 1. (a) Cu $(NO_3)_2$.$3H_2O$ solutions mixed with Pluronic P-123 solution followed by addition of TMB as a SDA (b) Light blue colour solution formed (SOL). (c) Heat cum magnetic stirring at 55 °C followed by ageing for 2–3days resulting into cross linking of precursor with P-123 (Xerogel) (d) Calcination of the resulting xerogel at 650 °C results into porous copper oxide monoliths.

2.2. Fabrication of supercapacitor based on GN/macroCuO nanocomposite modified glassy carbon electrode (GCE)

GCE was mechanically polished with a 0.05 mm alumina slurry and then sequentially sonicated in dilute nitric acid, anhydrous ethanol and redistilled water for 15 min. Next, the cleaned GCE was dried under nitrogen stream. GN and macroCuO in the ratio of 1:1 by weight were dispersed in 100 ml of distilled water by ultrasonication for 1 h to obtain a homogeneous GN/macroCuO suspension. Finally, the solid was filtered, washed several times with distilled water and alcohol and dried at 100 °C for 12 h in a vacuum oven. 10 mg of this composite was dispersed in 5 mL dimethylformamide by sonicating in an ultrasound bath for 30 min to form a stable suspension. The suspension of 10.0 μL was cast onto the GCE surface by a micropipette, and then thoroughly dried under an infrared lamp. Subsequently, the electrode was rinsed several times by distilled water and dried in air before use; the final obtained electrode was denoted as GN/macroCuO/GCE. For comparison, the GN/GCE was prepared using the GN dispersion alone by following the same procedure.

2.3. Structure characterization

After calcination of the xerogel, XRD patterns of the sample was obtained on a Bruker D-8 advance diffractometer in the diffraction angle range $2\theta = 20–120°$, using monochromatic Cu kα radiation ($\lambda = 1.5410$). The surface pore morphology and average pore diameter of the obtained sample was carried out by field emission scanning electron microscopy (FESEM) using S-4800 field emission SEM system (FEI Quanta 200) operating at 20.0 kV equipped to perform elemental chemical analysis by energy dispersive X-ray spectroscopy (EDX). The FFT, SAED patterns of macroporous CuO and HRTEM image of the resulting GN/macroporous CuO composite was investigated by JEOL JEM 2100F microscope operated at 200 kV using an Orius SC1000 camera. Nitrogen adsorption desorption measurements of the sample was performed by physisorption of N_2 at 77 K over a Micromeritics ASAP 2010. Before calcination of the sample TGA/DTA and FTIR analysis were carried out by Perkin-Elmer thermal analyzer (using alumina reference crucible at the heating rate of 10 °C/min) and Shimadzu-8400S spectrometer respectively