



Dendritic CuO structures synthesized by bipolar electrochemical process for electrochemical energy storage



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ABSTRACT

Cupric oxide is an inexpensive material with electrochemical behavior that can be used for energy storage applications. Here, we prepare CuO materials by a simple bipolar electrochemical process in deionized water, where a high voltage is applied between two stainless steel feeding electrodes symmetrically surrounding an electrically floating copper plate. CuO is mainly formed in the locally alkaline region facing the anodic pole of the copper plate, where electro-dissolved Cu^{2+} undergo successive reactions of complexation–dehydration with OH^- ions. The morphology, composition, and phase structure of as-prepared materials were characterized by scanning electron microscopy, powder X-ray diffraction, micro-Raman spectroscopy, and Vis-near-IR spectroscopy. We have found that CuO materials are self-assembled in three-dimensional dendritic structures that can grow up to millimeters in size. The electrochemical characterization in 1 mol L^{-1} KOH by cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy shows a capacitive behavior of CuO structures, with an average capacitance value reaching 202 F g^{-1} at 10 A g^{-1} , giving an energy density of 7.0 Wh kg^{-1} for a power density of 2.5 kW kg^{-1} . At 20 A g^{-1} current density, the materials exhibit 90% capacitance retention over 2000 charge/discharge cycles with a coulombic efficiency exceeding 95%.

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1. Introduction

Amongst the different technologies of energy storage, electrochemical supercapacitors have attracted the greatest deal of research activity in recent years, as they may be the adequate solution to powering the fast-soaring market of portable electronic devices, hybrid electric vehicles, as well as storing renewable energy in power grids. Supercapacitors are electrical energy storage devices that narrow the gap between conventional dielectric capacitors and rechargeable batteries by exhibiting remarkably higher power delivery/uptake and higher degree of reversibility when compared to secondary batteries, and higher energy density when compared to electric double-layer capacitors [1–3]. The most commonly used electrode materials in electrochemical storage devices are high surface area activated carbon-based materials, including porous graphite, carbon nanotubes and graphene [1–6], that store electric charge by highly reversible electrostatic principle in the electrochemical double-layer formed at the solid/electrolyte interface. On the other hand, some electronically conducting polymers (such as polyaniline, poly(pyrrole),

polythiophene, poly(3-methylthiophene), and poly(3,4-ethylenedioxythiophene) [7–10]) and nanostructured transition metal oxides (such as RuO_2 , MnO_x , IrO_2 , NiO_x , and CoO_x [11–15]) were found to exhibit the performance of pseudocapacitive or faradaic active materials. They make use of the charge transfer generated by the quasi-reversible faradaic reactions at the electrode material surface or in the bulk near the surface, where the charge, and hence the capacitance, is voltage-dependent. The most studied types of nano-sized metal oxides for supercapacitors are usually large band gap semiconductors and sometimes insulators with poor electric conductivity [11]. As a result, dissipation of excess energy with charge/discharge cycles into Joule heating may make the volume of the device to change and decreases its stability.

On the other hand, cupric oxide exhibits a narrow band gap of 1.2 eV in bulk, and is obtained out of the oxidation of copper, which is an important material in many technological applications, widely available, relatively cost-effective, and nontoxic. Its theoretical capacitance in aqueous alkaline media, assuming one OH^- per one CuO molecule, is estimated by $F/M\Delta V$ (F is Faraday's constant, $\Delta V \approx 1 \text{ V}$ the operating voltage, and M the molar mass) to be 1213 F g^{-1} . However, this rough estimation should be taken with caution as the capacitance of the material is potential-dependent. Different 2D and 3D structures of CuO have been extensively

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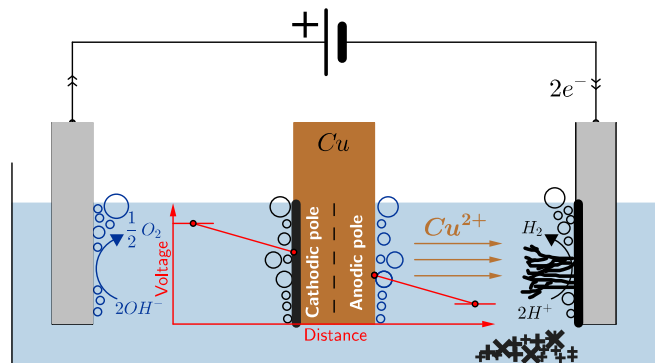


Fig. 1. Bipolar electrochemical cell used for the synthesis of CuO materials, consisting of two stainless steel feeding electrodes surrounding a floating copper plate. The external electric field is at the origin of an interfacial potential difference between the two surfaces of the bipolar copper plate, which will be acting as both an anode (electro-dissolution to Cu^{2+}) and a cathode ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) in the same time.

studied as anode material for lithium ion battery, but just recently as a competitive candidate for supercapacitors applications [16–21]. Li et al. compared the electrochemical energy storage performance in KOH of CuO nanowires, nanosheets and flower-like nanostructured materials grown on copper foam, and reported a morphology-dependent specific capacitance with the highest being 212 F g^{-1} at 0.41 A g^{-1} for the CuO nanosheets [22]. One dimensional CuO nanowires have been also reported by Chen and Xue with pseudocapacitance values of 118, 109 and 102 F g^{-1} in 2 mol L^{-1} KOH, at the current densities 1, 3, and 5 A g^{-1} , respectively [17]. Flexible CuO nanobelts on single-walled carbon nanotubes have been demonstrated as highly stable composite material to charge/discharge cycles, with energy density in the range of 130 to 20 Wh kg^{-1} with power densities from 1.25 up to 50 kW h kg^{-1} [23]. However, the usually adopted techniques of manufacturing either involve hazardous chemicals, high temperature annealing processes and/or complex multi-step procedures making them less attractive.

In this work, we report the preparation of hierarchically micro-structured CuO materials by bipolar electrochemical method, consisting of placing symmetrically an electrically floating copper plate between two stainless steel driving electrodes in deionized water. The applied voltage was set to 300 Vdc so that it ensures the generation of a high enough interfacial potential difference between the copper plate surfaces to initiate its electro-dissolution (see Fig. 1). The physicochemical and structural characterization of the obtained CuO materials was carried out using scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray detector (EDX), powder X-ray diffraction (XRD), micro-Raman spectroscopy and Vis-near-IR spectroscopy. Using a conventional three-electrode configuration in 1 mol L^{-1} aqueous KOH solution, cyclic voltammetry (CV), galvanostatic charge/discharge measurements, and potentiostatic electrochemical impedance spectroscopy (PEIS) were performed to evaluate the electrochemical energy storage performance of the CuO structures.

2. Experimental

2.1. Synthesis of CuO dendritic structures

Copper oxide materials were synthesized using an open bipolar electrochemical configuration, as shown in Fig. 1. A typical setup consists of two parallel stainless steel plates ($1 \times 5 \text{ cm}^2$ working area with an inter-electrode distance of 5 cm) in 50 ml deionized water, with a floating copper plate ($2 \times 5 \text{ cm}^2$, 2-mm thick, 99.9%

purity) suspended half way in between. The copper plate was initially cleaned with concentrated nitric acid for 5 min and thoroughly washed with deionized water and ethanol. The dc power supply is a programmable Sorensen (Ametek) XG 300-5 set to 300 Vdc . The current reading plateaued at an average of 5 mA over the first 1.5 h of the experiment, and steadily increased to about 50 mA by the end of the 3 h (see SI Fig. 1).

2.2. Morphological, structural and optical characterization

Unless otherwise mentioned, all characterization results are shown for the black deposit that was collected from the bottom of the electrochemical cell (see Fig. 1) by series of centrifugation and washing with deionized water, and subsequently stored in ethanol. The morphological characterization was performed by topographical inspection of both sides of sacrificial copper plate, the stainless steel cathode, and a droplet of CuO materials on carbon tape using VEGA3 XM (TESCAN) SEM. SEM-coupled EDX was employed for elemental analysis, and was conducted with both two-dimensional mapping and point modes. The powder XRD patterns for crystal identification were recorded in the 2θ geometry between 30° and 70° at 0.005° 2θ step size with a Bruker D8 Advance DaVinci multipurpose X-ray diffractometer (Cu K_α radiation; $\lambda = 1.5406 \text{ \AA}$), operating at 40 kV tube voltage and 40 mA current. The Raman spectra were measured at room temperature in the back scattering configuration with a Renishaw inVia Raman microscope equipped with near-IR 785 nm and visible 514 and 488 nm wavelengths lasers. The illuminated area on the sample was about $1 \mu\text{m}^2$, that was carefully deposited out of the CuO solution on a clean microscope slide. Absorptance measurement in the visible and near-IR light regions (using a tungsten halogen light source) was carried out with an Ocean Optics HR2000 high-resolution spectrometer right on the anode-facing side of the copper plate. The spectrometer was connected to a fiber optic reflection probe (Ocean Optics R200-7-SR) that was fixed at 4 mm from the copper surface. A reference spectrum from a standard reflectance specimen was used to store baseline absorptance and reflectance.

2.3. Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge/discharge, and ac potentiostatic electrochemical impedance spectroscopy (PEIS) were conducted at room temperature with a BioLogic VSP-300 electrochemical workstation, in a standard three-electrode cell filled with 1 mol L^{-1} KOH aqueous solution. The working electrode was prepared by depositing 0.1 mg of CuO materials onto the cross-section of a 6 mm -diameter graphite rod (mass loading $\approx 0.35 \text{ mg cm}^{-2}$), and left to dry for 30 min under an incandescent lamp. The active material fully covered the cross-section surface of the graphite current collector. A Pt wire served as a counter electrode and a standard calomel electrode (SCE) as reference. The potential window in the CV and galvanostatic measurements was set to $0\text{--}0.5 \text{ V}$ to avoid interference with the oxygen evolution reaction. EIS was conducted at open-circuit potential with a 10 mV amplitude sinusoidal signal between $f = 500 \text{ kHz}$ down to 50 mHz using 10 points per decade.

3. Results and discussion

3.1. Synthesis mechanism

The electrochemical solution used for the synthesis of CuO materials is deionized water, which is a poor bipolar conductor of electricity but not a perfect insulator due to auto-dissociation

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