



Room-temperature vertically-aligned copper oxide nanoblades synthesized by electrochemical restructuring of copper hydroxide nanorods: An electrode for high energy density hybrid device



Xuetao Zhang^a, Jinyuan Zhou^a, Wei Dou^b, Junya Wang^a, Xuemei Mu^a, Yue Zhang^a, Asim Abas^a, Qing Su^a, Wei Lan^{a,*}, Erqing Xie^a, Chuanfang (John) Zhang^{c,**}

^a Key Laboratory of Special Function Materials and Structure Design, Ministry of Education, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, People's Republic of China

^b College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, People's Republic of China

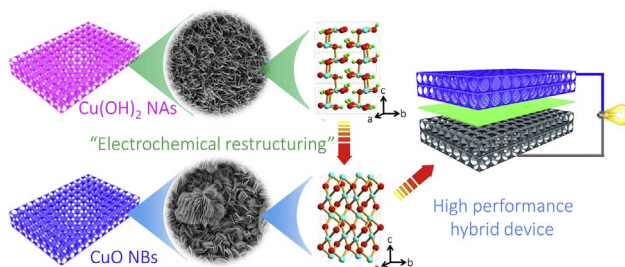
^c Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Chemistry, Trinity College Dublin, Dublin 2, Ireland

HIGHLIGHTS

- CuO NBs on Cu foam were prepared by electrochemical polarization of Cu(OH)₂ NRs.
- CuO NBs exhibits excellent performance in charge storage and rate capability.
- The hybrid device displays high energy/power density and long lifetime stability.
- The hybrid devices can be connected in series and parallel.

GRAPHICAL ABSTRACT

The electrochemical restructured CuO NBs from Cu(OH)₂ NRs on Cu foam for hybrid device.



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ABSTRACT

The fast growing of portable electronics has greatly stimulated the development of energy storage materials, such as transition metal oxides (TMOs). However, TMOs usually involve harsh synthesis conditions, such as high temperature. Here we take advantage of the metastable nature of Cu(OH)₂ and grow CuO nanoblades (NBs) on Cu foam under the electric field at room temperature. The electrochemical polarization accelerates the dissolution of Cu(OH)₂ nanorods, guides the deposition of the as-dissolved Cu(OH)₄²⁻ species and eventually leads to the phase transformation of CuO NBs. The unique materials architecture render the vertically-aligned CuO NBs with enhanced electronic and ionic diffusion kinetics, high charge storage ($\sim 779 \text{ mC cm}^{-2}$ at 1 mA cm^{-2}), excellent rate capability and long-term cycling performances. Further matching with activated carbon electrode results in high-performance hybrid device, which displays a wide voltage window (1.7 V) in aqueous electrolyte, high energy density (0.17 mWh cm^{-2}) and power density (34 mW cm^{-2}) coupled with long lifetime, surpassing the best CuO based device known. The hybrid device can be randomly connected and power several light-emitting diodes. Importantly, such an electrochemical restructuring approach is cost-effective, environmentally green and universal, and can be extended to synthesize other metastable hydroxides to *in-situ* grow corresponding oxides.

* Corresponding author.

** Corresponding author.

E-mail addresses: lanw@lzu.edu.cn (W. Lan), zhangjc@tcd.ie (C.J. Zhang).

1. Introduction

The ever-increasing demands for smart portable electronics greatly stimulate the research and development of advanced energy storage devices (ESDs) [1–8], particularly Li-ion batteries [1] [5] and supercapacitors [9–14]. While supercapacitors possess merits such as high power density, long lifetime and fast rate handling, their energy density is usually quite low [15,16]. Battery-type materials undergo multiple electron-transfer redox reactions, thus deliver much higher charge-storage performance at the cost of rate capability [17,18]. Generally, active materials with the nature of multiple charge-transfer redox reactions and designed with facile electron transport/ion diffusion kinetics usually showcase enhanced charge storage and rate handling [19–22]. In this perspective, through selecting one battery-type redox-active material with elaborately designed electronic/ionic diffusion paths, and further pairing with a capacitive electrode, the resultant hybrid device should exhibit broadened voltage window, much higher energy density and comparable power density compared to that of traditional supercapacitors [23,24].

Transition metal oxides (TMOs) have attracted intensive interests due to their high theoretical charge storage enabled by multiple reversible redox reactions, low cost and environmentally friendly. Copper oxide (CuO), for example, is abundant and possesses a large interlayer spacing and high electrochemical redox activity based on the Cu(II)/Cu(I) redox couple [25,26]. However, the reported CuO-based architectures are far from satisfactory in terms of charge storage performance and rate handling, which are most probably due to the limitations on either electron transport or ion diffusion kinetics, or both. By incorporating CuO into a conductive backbone, the electron transport paths could be considerably enhanced. For instance, reduced graphene oxide, Cu and Ni foams are typically used as substrates to support CuO nanosheets or nanowires [15,27–29]. On the other hand, through reducing the ion diffusion paths and controlling the alignment of the as-obtained CuO flakes/nanosheets, enhanced electron transport and ion diffusion kinetics can be expected. Consequently, both the rate handling and long-term cycling of the CuO-based ESD can be improved.

Recently, Zhang et al. obtained CuO nanoflakes on nanoflowers through a solvothermal reaction at 140 °C [12]. While the resultant three-dimensional (3D) heterostructure exhibited a high stored charge, however, the active materials were scratched and processed into conventional electrodes (a combination of carbon black, CB, polyvinylidene fluoride, PVDF and N-Methyl-2-pyrrolidone, NMP), which inevitably loss the advantages brought by CuO as abovementioned. We note that for a potential ESD electrode, both the material synthesis and the electrode fabrication should be simple, low cost and environmentally green. Said otherwise, the facile growth of CuO nanosheets at room temperature is much preferred. However, to the best of our knowledge, neither reports on the synthesis of aligned CuO nanosheets at room temperature, nor the aligned CuO nanosheets as binder-free electrode for the hybrid device have yet been available.

The present article builds on the electrochemical restructuring of vertically-aligned Cu(OH)₂ nanorods (NRs) to CuO nanoblades (NBs) in alkaline media at room temperature (Scheme 1). Important morphological and phase transformation are observed upon continuous galvanostatic cycling. Such an electrochemical route to vertically-aligned CuO NBs is indeed a decomposition and restructuring of Cu(OH)₂ NRs. No extra chemicals or post-treatments are required, rendering this electrochemical restructuring strategy in aqueous solution to obtain CuO NBs *in-situ* being cost effectively and environmentally friendly. The binder-free electrode shows a high stored charge, coupled with high-rate handling as well as long-term stability, which can be ascribed to the rational architecture design: 1) the underlined 3D Cu framework provides efficient electron transport network; 2) the vertically-aligned CuO NBs well expose to the electrolyte, ensuring rapid ion diffusion kinetics and improving the utilization of active material; 3) the electrochemically-induced CuO NBs intimately adhere to the conductive

backbone, leading to a well maintained structure integrity upon repeated charging/discharging. Consequently, when matched with a high-power activated carbon electrode (Scheme 1), the prototype hybrid device displays a wide voltage window (1.7 V) in the alkaline solution, high energy density and power density, as well as long lifetime. The tandem device can readily power several LEDs for a long duration, suggesting the promising application of CuO NBs in high-performance ESDs for portable electronics.

2. Experimental

2.1. Synthesis of Cu(OH)₂ NRs

All chemical reagents were of analytical purity and used as-received. The Cu foam (10 × 15 × 1.5 mm³) was ultrasonically cleaned with acetone, ethanol, and deionized water alternatively. Cu(OH)₂ NRs were grown on the Cu foam through *in-situ* etching at room temperature according to the following procedure. 3.2 g of NaOH was dissolved in 30 mL deionized water under vigorous stirring. Then, 0.913 g of (NH₄)₂S₂O₈ was added to the above solution. A piece of Cu foam (10 × 10 mm²) was vertically immersed into the etching solution for 1 h. Finally, the slice was washed with ethanol and deionized water several times, and then dried under compressed air.

2.2. Synthesis of CuO NBs

The vertically-aligned CuO NBs were grown directly on the 3D Cu foam framework by electrochemical restructuring of the as-obtained Cu(OH)₂ NRs at room temperature. Three-electrode configuration was employed, specifically, the Cu(OH)₂ NRs on the Cu foam was used as the working electrode, while a platinum sheet and Hg/HgO were used as the counter and reference electrode, respectively. The electrolyte was 1 M NaOH. The working electrode was subjected to the galvanostatic charging/discharging (GCD) at different current densities (5, 6.5, 10, 15 mA cm⁻²) in a potential range of 0–0.6 V for a certain cycles. In addition, to explore the phase transformation mechanism, the working electrode was also polarized at a specific potential for 42 h, the duration is roughly similar to GCD for 1200 cycles. For the sake of comparison, we also soaked the working electrode in 1 M NaOH without applying the electric field.

2.3. Material characterizations

The morphologies of the samples were observed on a field-emission scanning electron microscopy (FE-SEM, TESCAN MIRA3 XMU). The length histograms of Cu(OH)₂ NRs and CuO NBs were obtained by measuring sufficient NRs (NBs) ($N > 100$) from SEM images and taking the longest axis of the rods (or NBs) as the length. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns of the studied samples were obtained on a FEI Tecnai F30 at 300 kV. The crystal structures were obtained by X-ray diffraction (XRD, Philips, X'pert pro, Cu K α , 0.154056 nm) and Raman spectroscopy (JY-HR800 micro-Raman, using a 532 nm wavelength YAG laser with a laser spot diameter of ~600 nm). The chemical composition was investigated using X-ray photoelectron spectrometer (XPS, PHI-5702, Mg KR X-ray, 1253.6 eV).

2.4. Electrochemical measurements

Electrochemical measurements (CHI 660E) were accomplished in a three-electrode configuration in 1 M NaOH aqueous electrolyte as detailed previously. The area of CuO NBs electrode immersed in the electrolyte was controlled to 1 cm × 1 cm. Cyclic voltammetry (CV) and GCD tests were performed at various scan rates and current densities, respectively. Electrochemical impedance spectroscopy (EIS) was conducted at the open circuit potential with frequencies ranging from

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