Facilely synthesis of 3D Cu_xO–Cu nanostructures as binder–free electrode for supercapacitors

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Abstract

3D Cu_xO–Cu nanostructures were synthesized through a simple chemical corrosion method and were employed as binder–free electrodes for supercapacitors. Owing to the direct growth of the active **materials** onto the Cu foam without any **binders**, and the 3D interconnected structure ensures a highly conductive network favorable for electron transfer, the as–prepared electrode exhibit a high specific capacitance of 111 mF cm^{−2} at 0.5 mA cm^{−2} and a better rate capability of 80 mF cm^{−2} at 10 mA cm^{−2}. **Besides, the Cu_xO–Cu//AC asymmetric supercapacitor can deliver a high energy density of 34.36 uWh cm^{−2}, thus showing great potential for supercapacitor applications.**

Keywords: Copper oxide; Supercapacitor; Pseudocapacitance; Nanocomposites; Energy storage and conversion

1 Introduction

Supercapacitors are promising candidates for future energy storage systems due to their high power density, fast charging–discharging rates, safe operation, and long cycle life.^{1,2} Nevertheless, their practical applications are hindered by the relatively low energy density. According to the equation $E = 1/2CV^2$, the energy density of the supercapacitors can be enhanced by increasing the specific capacitance with development of novel electrode materials, and/or broadening the cell voltage by using organic electrolytes.³ However, organic electrolytes usually suffer from high cost, poor ionic conductivity, flammability and high toxicity.⁴ Therefore, the current research interest is focus on the design and synthesise of novel electrode materials with high performance in aqueous solution.

Based on the energy storage mechanism, supercapacitors electrode are generally classified into carbon–based materials, transition metal oxides and conducting polymers, etc.. Among them, transition metal oxide electrode show much higher energy density than electric double layer capacitors due to their multiple oxidation states, and also deliver better cyclic stability than conducting polymers. As a typical metal oxide electrode material, RuO_2 has received extensive attention because of its high capacitance, reversible charge–discharge features and good electrical conductivity.⁵ However, the relatively high cost and toxicity of RuO_2 has seriously restricted their commercial application.⁶ As a result, less expensive metal oxides, such as NiO ,⁷ Co_3O_4 ,⁸ MnO_2 ,⁹ V_2O_5 ,¹⁰ CuO ,¹¹ Fe_2O_3 ,¹² NiCo_2O_4 ¹³ and NiMoO_4 ,¹⁴ etc. have been widely studied as electrodes for supercapacitor. Unfortunately, the poor electronic conductivity of these oxides significantly restricted their specific capacitance, cycling stability and high–power applications.¹⁵ Furthermore, traditional supercapacitor electrodes are fabricated by using binders to press electroactive material

onto the current collector, which will seriously decrease the electrical conductivity of the electrode. An effective way to solve this problem is directly growing electrode materials onto the current collector, which **will** not only simplifies the electrode processing, but also offers remarkable advantages such as easy diffusion of electrolyte, better electrical contact with substrates, sufficient electrochemical reaction of individual nanostructures and enhanced electrode–electrolyte contact area.¹⁶

Among the metal oxides electrode, copper oxide is good candidate for supercapacitors because of their high theoretical capacitance, low cost and friendliness to environment.^{17, 18} At present, copper oxides with various morphologies, such as nanowires,^{19–21} nanosheets,^{22, 23} nanoribbons and nanoflowers,²⁴ nanoneedle arrays,²⁵ and nanofilms,²⁶ have been already reported. Although enhanced electrochemical performances have been achieved, it still remains a great challenge to develop cost–effective and simple methods for the fabrication of nanostructured copper oxide electrodes. In this sense, chemical corrosion appears as an attractive method due to its low growth temperature, cost effectiveness and controllability.²⁷ Moreover, the electrode prepared by chemical corrosion can be directly deposited on substrates without adding polymer binders or conductive additives, which ensure good electrical contact and high electrochemical properties.²⁸ Therefore, in this paper, we present a facile, environmentally friendly approach to large–scale prepare 3D Cu_xO –Cu nanostructures by a **simple** chemical corrosion process. The as–prepared binder–free electrode shows a good electrochemical performance for pseudo–capacitive energy storage. In specific, a high specific capacitance of 111 mF cm^{-2} is obtained in 2 M KOH and 78% of initial value is remained after 5000 times cycling. **Additionally, the Cu_xO –Cu//AC asymmetric supercapacitor was assembled, and it can deliver a high energy**

density of $34.36 \text{ uWh cm}^{-2}$ at a power density of 400 uW cm^{-2} , and still retain 9.56 uWh cm^{-2} at a power density of 8 mW cm^{-2} , which shown that $\text{Cu}_x\text{O-Cu}$ is a promising material for fabricating supercapacitor electrodes.

2 Experimental

2.1 Synthesis of $\text{Cu}_x\text{O-Cu}$ nanostructures

$\text{Cu}_x\text{O-Cu}$ electrode was fabricated by a chemical corrosion method. Cu foams ($2 \times 5 \text{ cm}^2$, 380 g m^{-2} surface density, 1.5 mm thick, was purchased from Changsha Lyrun New Material) were placed in a 50 ml autoclave, then 0.5 mL $30\% \text{ H}_2\text{O}_2$ and 37 mL distilled water was added to keep 75% of its capacity. The autoclave was then sealed and placed in an oven, heated at 90°C for 12 h . Finally, the binder-free electrode was obtained by washed extensively with distilled water and dried at room temperature.

2.2 Material characterizations

X-ray diffraction patterns (XRD, Rigaku D/MAX 2400 diffractometer) were recorded using $\text{Cu-K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) operating at 40 kV and 60 mA . Raman spectra were conducted on the Renishaw inVia Raman microscope under the excitation length of 532 nm . The morphology and microstructure of the samples were characterized by field emission scanning electron microscopy (FESEM, JSM-6701F, JEOL). The atomic concentrations and valence of copper and oxygen were determined by X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Scientific, UK).

2.3 Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical working station

(CHI660E, Shanghai, China) in a half-cell setup configuration at room temperature with 2 M KOH as the electrolyte. A Pt foil and a saturated calomel electrode (SCE) electrode were served as the counter electrode and the reference electrode, respectively. The working electrode was used as-prepared without further treatment and had a geometric surface area of 1 cm². The cyclic stability of Cu_xO–Cu was also evaluated by electrochemical working station within the voltage range of 0–0.4 V.

3 Results and discussion

3.1 Characterizations of Cu_xO–Cu nanostructure

Fig. 1 XRD pattern (a) and Raman spectrum (b) of Cu_xO–Cu nanostructure.

Cu_xO–Cu composite was fabricated by direct chemical corrosion of outer Cu to CuOH, and the subsequent conversion of CuOH into Cu₂O shell. Besides, little amounts of Cu₂O are further oxidized to CuO. The reactions during the hydrothermal process are likely to be as follows²⁷:

XRD patterns show three characteristic peaks located at 36.4°, 42.4° and 61.5°, which can be respectively identified as (111), (200) and (220) diffraction planes of Cu₂O (JCPDS, Card No. 65–3288). In addition, little amounts of CuO were obtained by oxidizing Cu₂O (**Fig. 1a**). Raman spectrum shows several peaks at approximately 108, 150, 218, 281, 334, 620 and 650 cm^{−1}, which

can be attributed to Raman-active modes of Cu_2O (T_{2u} , T_{1u} , $2E_u$, $T_{1u}(\text{TO})$ and $T_{1u}(\text{LO})$)²⁹ and CuO (A_g and B_g),³⁰ respectively (**Fig. 1b**). XPS analysis was performed to further investigate the chemical composition of $\text{Cu}_x\text{O-Cu}$ composite. The full survey spectra consists several distinct Cu signals (2p, 3s, 3p) except the O1s and C1s signals. In **Fig. 2b**, the $\text{Cu}2p_{3/2}$ peak at 932.1 eV implies that Cu element is mainly monovalent, and little amount of Cu (II) has observed from their satellite peak.³¹ Thus, XRD, Raman and XPS results indicate the successful synthesis of $\text{Cu}_x\text{O-Cu}$ composite.

Fig. 2 XPS full survey spectra (a) and $\text{Cu}2p$ spectra (b) of $\text{Cu}_x\text{O-Cu}$ composite.

Fig. 3 FESEM images of $\text{Cu}_x\text{O-Cu}$ at low-magnification (a) and high-magnification (The inset red section is at magnification $\times 20,000$) (b).

Fig. 3 shown the surface morphology of the as-prepared composite, the roughness of sample increased due to the formation of oxide. High magnification FESEM image shows that abundant

copper oxide particles with the size ranges from 200 nm to 1.0 μm firmly decorated on the surface of Cu foam (**Fig. 3b**). In addition, the cracks on the film surface lead to a porous architecture, which is favorable to enhance their electrochemical performance.

3.2 Electrochemical characterizations of the nanostructured Cu_xO –Cu electrode

The as-prepared 3D Cu_xO –Cu nanostructure was directly applied as the binder-free electrodes for supercapacitor in a three-electrode configuration using 2 M KOH as the electrolyte. The CV curves of Cu_xO –Cu under different scan rates of 10, 20, 40, 60, 80 and 100 mV s^{-1} is shown in **Fig. 4a**. The peak intensities of both cathode and anode increased as the scan rate changed from 10 to 100 mV s^{-1} . No obvious changes in shape and peak potential separation of CV curves indicate the excellent charge–discharge reversibility. Based on literature reports about CV of Cu_xO in alkaline electrolytes, the redox reactions can be ascribe to the transition between Cu^+ and Cu^{2+} species as follows:

Fig. 4b shows the galvanostatic charge–discharge curves for Cu_xO –Cu electrode in the potential range of 0–0.40 V at various current densities. The specific capacitance is calculated according to the following equation (4):

$$C = I \times \Delta t / (\Delta V \times A) \quad (4)$$

where C (mF cm^{-2}) is the specific capacitance, I (mA) is the charge–discharge current, Δt (s) is the discharging time, ΔV (V) represents the potential drop during discharge, and A (cm^2) is the area of the active material.

The specific capacitances of Cu_xO –Cu composite calculated from discharging times were 111, 106.5, 101, 93, 87, 82 and 80 mF cm^{-2} , corresponding to the current densities of 0.5, 1, 2, 4, 6, 8

and 10 mA cm^{-2} , respectively (**Fig. 4c**). $\text{Cu}_x\text{O-Cu}$ electrode can remain 72% of its specific capacitance as the current density increases from 0.5 to 10 mA cm^{-2} , which displays its outstanding rate capability. Moreover, as shown in **Fig. 4d**, it is notable that $\text{Cu}_x\text{O-Cu}$ electrode remained 78% of the initial value after a continuous cycling of 5000 times. In EIS result (**Fig. 4e**), the slope of Warburg impedance in low frequency region is closer to 90° , which indicates a predominately capacitive behavior.

Fig. 4 CV curves at different scan rates (a), galvanostatic charge–discharge curves at different current densities (b), the specific capacitance calculated from discharge curves at different current densities (c), the cycle life (d) and the EIS plots (e) of $\text{Cu}_x\text{O-Cu}$ electrode in 2 M KOH aqueous electrolyte.

The relatively good capacitive performance can be ascribed to: (1) the direct growth of the active material onto the Cu foam without using any binder is beneficial to easy diffusion of

electrolyte, better electrical contact with substrates, sufficient electrochemical reaction of individual nanostructures and enhanced electrode–electrolyte contact area;¹⁶ (2) the 3D interconnected structure ensures a highly conductive network which can effectively transfer sufficient electrons to the active material.³² Thus, high electrochemical capacitor properties as well as convenient preparation of Cu_xO–Cu indicate that it has great potential for supercapacitors and other technological areas.

3.3 Electrochemical characterizations of the Cu_xO–Cu//AC asymmetric supercapacitor

To further investigate the capacitive performance of the Cu_xO–Cu nanostructured structure, an aqueous asymmetric supercapacitor was assembled by using of Cu_xO–Cu and commercial activated carbon (AC, obtained from Nanjing JCNANO Tech. Co. Ltd., China) as positive and negative electrodes, respectively. As for asymmetric supercapacitor, the charge on both the electrodes was matched by balancing the areal specific capacitances of the Cu_xO–Cu and AC electrodes. The geometric area of the electrodes was balanced by the following equation³³: $C_+S_+\Delta V_+ = C_-S_-\Delta V_-$, where C_- , C_+ , S_+ , S_- , and ΔV_+ and ΔV_- are the capacitance, surface area and potential windows of the negative and positive electrodes, respectively.

Fig. 5a shows the CV curves of Cu_xO–Cu//AC asymmetric supercapacitor in 2 M KOH aqueous solution at various scan rates between 0 and 1.6 V, and the CV curves demonstrate a typical capacitor behavior of Cu_xO–Cu//AC. Additionally, the nonlinearity of the galvanostatic charge–discharge curves (**Fig. 5b**) confirms the contribution of the redox reaction from metal oxides, which agrees well with the CV curves. As shown in **Fig. 5c**, the specific capacitances calculated from the discharge time are 96.63, 87.69, 79.88, 52.75, 37.50, 30.50 and 26.88 mF cm⁻² at the current densities of 0.5, 1, 2, 4, 6, 8 and 10 mA cm⁻², respectively. **Fig. 5d** shows the

Ragone plot of the Cu_xO–Cu//AC based asymmetric supercapacitor. The energy and power density are calculated based on the equations (5) and (6):

$$E = 1/2 \times C \times (\Delta V)^2 \quad (5)$$

$$P = E/\Delta t \quad (6)$$

Where C (mF cm⁻²) is specific capacitance, E (uWh cm⁻²) is energy density, P (uW cm⁻²) is power density, Δt (s) is discharge time, ΔV (V) is potential window during discharge. The asymmetric supercapacitor can deliver a high energy density of 34.36 uWh cm⁻² at a power density of 400 uW cm⁻², and still retain 9.56 uWh cm⁻² at a power density of 8 mW cm⁻². This result show a improved energy density than previously report of GQDs//PANI (0.093 uWh cm⁻² at 7.52 uW cm⁻²)³⁴, NiO//VN (1.0 uWh cm⁻² at 0.6 mW cm⁻²)³⁵, and nearly close to Bi₂O₃//MnO₂ (maximum areal energy and power density are 43.4 μWh cm⁻² and 12.9 mW cm⁻², respectively)³⁶. Based on the present results, it is believed that the Cu_xO–Cu//AC asymmetric supercapacitors have great potential for various flexible applications.

Fig. 5 CV curves at different scan rates (a), galvanostatic charge–discharge curves at different current densities (b), the specific capacitance calculated from discharge curves at different current densities (c) and Ragone plots (d) of the as-assembled $\text{Cu}_x\text{O-Cu//AC}$ asymmetric supercapacitor.

4 Conclusions

In conclusion, $\text{Cu}_x\text{O-Cu}$ nanostructures were synthesized through a simple chemical corrosion method. Owing to the 3D interconnected structure without any binder, the as-prepared $\text{Cu}_x\text{O-Cu}$ composite exhibit the highest specific capacitance of 111 mF cm^{-2} in 2 M KOH at a current density of 0.5 mA cm^{-2} , and can maintain 78% of initial capacity after a continuous cycling of 5000 times. Moreover, the $\text{Cu}_x\text{O-Cu//AC}$ asymmetric supercapacitor can deliver a high energy density of $34.36 \text{ uWh cm}^{-2}$ at a power density of 400 uW cm^{-2} , and still retain 9.56 uWh cm^{-2} at a power density of 8 mW cm^{-2} . It is anticipated that this work can be extended to other metal oxide/metal foam composites for applications in many fields, such as energy storage, catalysis,

sensing, and electrocatalysis for pursuing performance.

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