Materials Letters 185 (2016) 165–168

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

In situ facile surface oxidation method prepared ball of yarn-like copper oxide hierarchical microstructures on copper foam for high performance supercapacitor

Dong He, Junning Wan, Hui Suo, Chun Zhao *

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form
11 August 2016
Accepted 20 August 2016
Available online 21 August 2016

Keywords:
Copper oxide
Long-life span
Supercapacitor
Nanocomposites
Energy storage and conversion

ABSTRACT

We have developed an in situ facile surface oxidation method to fabricate three-dimensional (3D) hierarchical ball of yarn-like CuO microstructures on copper foam, which can be directly used as a long-life binder-free electrode for supercapacitors. The electrochemical results demonstrated that this CuO microstructures exhibited a specific capacitance of 762.55 mF cm^{-2}, excellent cycling stability (98.11% retention after 20000 cycles) and good rate capability (81.5% retention upon increasing the current density by 10 times). These features will make ball of yarn-like CuO microstructures attractive for high-performance supercapacitors.

1. Introduction

Supercapacitors have attracted considerable attention due to high power and appropriate energy density, fast charging and discharging capability, and long steady cycle life and relatively environmental benign characteristics, which have been widely used in back-up power system, hybrid vehicles and portable devices [1–4]. Copper oxide is one of the promising transition metal oxides for pseudocapacitors electrodes materials, due to its environmental benign, rich reserve, relatively low cost, easy preparation and good electrochemical performance [5–7]. Various methods have been developed to fabricate CuO electrodes and reveals good electrochemical properties, such as Zhang et al. using hydrothermal method to prepare MnO_2-coated CuO flower-like nanostructures, revealing specific capacitances of 167.2 F g^{-1} [4], Dubal et al. using chemical bath deposition method to prepare micro-roses and micro-woolen like CuO nanosheets, exhibiting maximum specific capacitances of 346 F g^{-1} [3], Pendashteh et al. using sonochemical assisted precipitation method to fabrication copper oxide nanoparticles on graphene oxide nanosheets, revealing specific capacitances of 245 F g^{-1} [8], Allagui et al. adopting bipolar electrochemical method to prepared dendritic CuO structures, exhibiting specific capacitances of 202 F g^{-1} [5] and so on. However, these methods usually contained high temperature annealing process, complex procedures, some using hazardous chemicals and most of them need an electrode preparation process which may influence the electrochemical properties of the materials.

In this work, we have developed an in situ facile surface oxidation method to prepared 3D ball of yarn-like CuO microstructures on copper foam which could directly use for electrode without further procedures. This synthesis strategy adopted copper foam as copper source and current collector at same time, which can decrease the internal resistance of the electrode materials and significantly improve the stability of the electrode materials. The ball of yarn-like CuO/copper foam electrode exhibits a high specific capacitance, excellent cycling stability and good rate capability.

2. Experiment

All reagents used in the experiment were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received without further purification. The copper foam was purchased from Kunshan DESSCO Co., Ltd (China) and cut into 10×10×1.5 mm^3 slices. The copper foam slices were washed with 1 M hydrochloric acid and deionized water under ultrasonic condition several times, then dried under nitrogen atmosphere. The synthesis of three-dimensional (3D) hierarchical ball of yarn microstructures CuO was achieved by surface oxidation method by Zhang et al. with some modifications [9]. Briefly, 5 g of sodium hydroxide was

* Corresponding author.
E-mail address: zchun@jlu.edu.cn (C. Zhao).

http://dx.doi.org/10.1016/j.matlet.2016.08.096
0167-577X/

dissolved in 25 mL deionized water in a 100 mL flask, and 25 mL of 0.125 M ammonium persulfate aqueous solution was then added with vigorously magnetic stirring. Then two pre-treated copper foam slices were immersed in the solution and the flask was settled into an oil bath kettle at 50 °C for 40 min. Then, the copper foam slices were rinsed several times with ethanol and deionized water, and finally dried at 40 °C for 2 h.

The chemical composition and crystallographic information of synthesized products were characterized by X-ray diffractometer (XRD; Shimadzhu 6000) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The morphologies and structures of the as-prepared products were investigated by a field emission scanning electron microscopy (FESEM; JEOL JEM-6700F). The electrochemical characteristics were studied on an electrochemical workstation (Shanghai Chenhua Instrument, CHI660D) by cyclic voltammetry method and galvanostatic charge-discharge method in a three-electrode configuration, the working electrode is the as-prepared CuO/copper foam sample, the counter electrode is a platinum electrode, the reference electrode is Hg/HgO and the electrolyte solution is NaOH solution (5 M).

3. Results and discussion

Fig. 1(a) shows the composition and crystallite phase purity of electrochemical as-prepared CuO/copper foam electrode sample. The peaks marked with triangle can be indexed to the cubic phase of Cu (JCPDS 01–1242). Meanwhile the rest planes marked with asterisk indicated the presence of the monoclinic phase CuO (Tenorite, JCPDS 05–0611), and no peaks of impurities can be detected, confirming the Tenorite copper oxides are pure and well crystalline.

Fig. 1(b)-(d) show the surface morphologies of as-prepared CuO/copper foam electrode examined by SEM. From the low magnification image of the as-prepared sample (Fig. 1(b)), we can find the surface of copper foam was almost fully covered by a layer of 3D ball of yarn microstructures, having a diameter from 2 μm to 10 μm, while presenting spherical and qusi-spherical 3D structures. Meanwhile some typical crystalline structure of Tenorite can be found between the 3D ball of yarn microstructures. The individual image of 3D ball of yarn microstructure was revealed in Fig. 1(c), the microstructure was self-assembled by hierarchical multilayer nanosheets having 20–100 nm width and 1–3 μm length (Fig. 1(d)). These microstructures can dramatically improve the active sites for redox reactions and promote the contact area between electrode and electrolyte, also may result in better charge transfer and ion diffusion. The whole surface oxidation process may follow equation:

$$\mathbf{Cu} + 4\mathbf{NaOH} + (\mathbf{NH_4})_2\mathbf{S_2O_8} \rightarrow \mathbf{CuO} + 2\mathbf{Na_2SO_4} + 2\mathbf{NH_3}\uparrow + 3\mathbf{H_2O} \quad (1)$$

To further demonstrate the chemical composition and purity of the as-prepared CuO samples, X-ray photoelectron spectroscopy (XPS) was performed. Fig. 2(a) shows the complete spectrum of as-prepared samples, indicating the presence of Cu and O on the copper foam. Fig. 2(b) reveals that the C 1 s peak is at 284.6 eV which can be attributed to the vacuum oil contamination of the vacuum pump of the XPS equipment [10–12], since the whole synthesis process did not contain any carbon source. Fig. 2 (c) shows the pattern of Cu 2p core level, we can observe that the peak assigned to binding energy of Cu 2p 3/2 is at 933.6 eV with two shake-up satellites peaks at 940.4 and 943.5 eV, also the peak assigned to binding energy of Cu 2p 1/2 is at 953.6 eV with

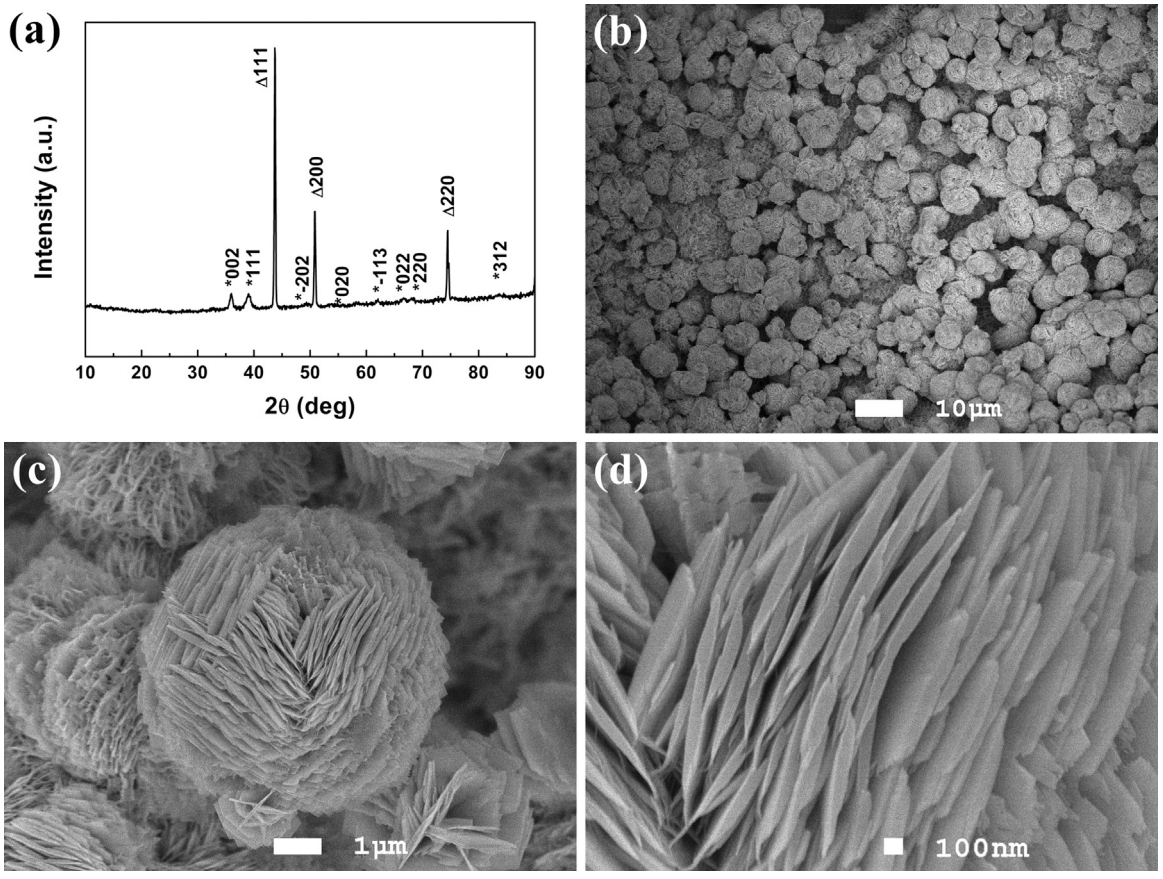

Fig. 1. (a) The XRD patterns of the as-prepared CuO sample; (b)(c) Low and high magnification SEM images of CuO electrode; (d) The individual image of 3D ball of yarn microstructure.