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Featured Letter

Facile route to achieve book-like tricobalt tetraoxide microstructures on copper foam for high performance supercapacitor

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ABSTRACT

We have synthesized book-like Co_3O_4 microstructures on copper form by hydrothermal and annealing process, which can be directly used as binder-free, excellent rate capability and long-life supercapacitor electrode. The random slant book-like Co_3O_4 microstructures were uniformly grown on the Cu substrate, and the electrode exhibited a high specific capacitance of 736.25 F g^{-1} at a current density of 1 A g^{-1}, good coulombic efficiency of 82.6%, excellent rate capability and 78.13% capacity retaining after 5000 cycles of charge and discharge, demonstrating a great potential in high power storage devices application.

1. Introduction

Supercapacitor with the features of high power density, fast charge/discharge properties and long steady cycle life is one sort of modern energy devices which can bridge the gap between traditional dielectric capacitors delivering high power output and batteries storing high energy [1]. The supercapacitors have been wildly used in many fields such as renewable energy production, electric/hybrid vehicles and high-power industrial equipment [2,3]. Recently, the high capacitance transition metal oxides with multiple oxidation states have been widely investigated as pseudo-capacitive supercapacitors electrode materials [4]. For example, Yang et al. synthesized Co_3O_4 nanosheet@nanowire arrays by hydrothermal and annealing treatment that reveals a specific capacitance of 715 F g^{-1} [5]. Tan et al. prepared gold decorated Co_3O_4 nanoparticles via in-situ reduction method, exhibiting a specific capacitance of 681 F g^{-1} [6]. Gou et al. prepared nanoporous Co_3O_4 plates by template method which shows a specific capacitance of 356.6 F g^{-1} [7], and Abouali et al. synthesized Co_3O_4@carbon nanofibers by electrospun method, which exhibits a specific capacitance of 586 F g^{-1} [8]. Though the specific capacitance of Co_3O_4 oxides electrode active materials have been significant improved, the cycle stability and the rate capability still need to be improved.

In this study, we presented a facile strategy for achieving book-like Co_3O_4 microstructures on Cu foam, which can be used as binder-free electrode for supercapacitors. The unique structure of the sample presented good cycle stability, excellent rate capability and low intrinsic resistance, demonstrating its great potential in practical application.

2. Experiment

2.1. Synthesis of the book-like Co_3O_4 microstructures

All the reagents used in this experiment were purchased from Sinopharm Chemical Reagent Co. Ltd (China). The copper foam was purchased from Kunshan Dessco Co. Ltd (China). The copper foam was trimmed into 20 × 15 × 1.8 mm^3 slices, then the slices were cleaned under ultrasonic condition with toluene, acetone, ethanol and deionized water in sequence and dried at 60 °C for 2 h. The book-like Co_3O_4 microstructures were synthesized by a hydrothermal method. Typically, 5 mmol of $Co(No_3)_2$ $6H_2O$ was dissolved in 50 mL of deionized water followed by 5 min of magnetic stirring. Then 12.5 mmol of $CO(NH_2)_2$ was added to the above solution and stirred for 30 min to form a homogeneous solution. Then 35 mL of resulting solution was transferred into Teflon-lined stainless steel autoclave with a pre-treated Cu foam slice inside. The autoclave was sealed and maintained at 110 °C for 12 h, and then cooled down to room temperature. The sample was rinsed with deionized water for several times, followed by annealing at 430 °C for 3 h in a tube furnace under nitrogen atmosphere.

2.2. Materials characterization

Morphologies and nanostructures were characterized with a field-emission scanning electron microscope (FESEM; JEOL-JEM-6700F)

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and transmission electron microscopic (TEM, JEOL-JEM-2100F). The composition and phase of the samples were evaluated by X-ray diffraction (XRD, Shimadzhu-6000) and X-ray photoelectron spectroscopy (XPS; ESCALAB-250).

2.3. Electrochemical measurement

The prepared sample was tested in a three-electrode cell on CHI-760E electrochemical station by cycle voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements.

3. Results and discussion

The XRD pattern of book-like Co_3O_4@Cu foam sample is depicted in Fig. 1(a). The three strong peaks marked with asterisk can be indexed to copper foam substrate with cubic phase of Cu (JCPDS No. 01-1242). The peaks marked with triangle correspond to the (111), (220), (311), (400), (511) and (440) plane of cubic phase of Co_3O_4 (JCPDS No. 65-3103). The rest weak peaks marked with circle are in good agreement of cubic phase of Cu_2O (JCPDS No. 02-1067) which originates from the Cu foam substrate. No other impurity phase can be detected and these results indicate that the product is Co_3O_4.

The morphology of the prepared Co_3O_4@Cu foam electrode is investigated by SEM and TEM methods (Fig. 1b–f). The surface of Cu foam substrate is fully covered by book-like microstructures and these microstructures are not perpendicular to the substrate, but slant and clustering as shown in Fig. 1(b). From Fig. 1(b and c), it is also found that the thickness and length of the Co_3O_4 leaves is less than 100 nm and 8 μm, respectively, and several leaves are clustering together like a slant semi-opened book. From the higher magnification SEM image (Fig. 1d), we can find that the leaf is composed of small nano particles with some gullies on the leaves, which can provide more specific surface area than smooth and plane surface, and make the structures more stable during the ions insertion/desertion processes. The TEM image confirms that the book-like microstructures were consist of nanoparticles with diameters around 20 nm and gullies with the thickness less than 10 nm (Fig. 1e). The lattice fringes in the HRTEM image (Fig. 1f) can be clearly observed and the lattice spacing is 0.232 nm, corresponding to the (222) plan of Co_3O_4. The result is in accordance with the XRD result and further confirms that the book-like microstructures are consist of Co_3O_4 nanoparticles.

XPS characterization was carried out to investigate the atomic valence states of the sample. The complete spectrum of the sample indicates the presence of C, Co, O and Cu elements and no obvious impurities can be found (Fig. 2a). In high resolution Co 2p spectrum (Fig. 2b), the two main peaks located at 779.5 and 794.6 eV are corresponding to the Co 2p3/2 and Co 2p1/2 spin-orbit peaks of Co_3O_4, respectively, and both peaks can be further fitted into two components, which can be assigned to Co^{3+} at 779.6 and 794.6 eV as well as Co^{2+} at 781.3 and 796.3 eV [9]. At meantime, the shake-up satel-

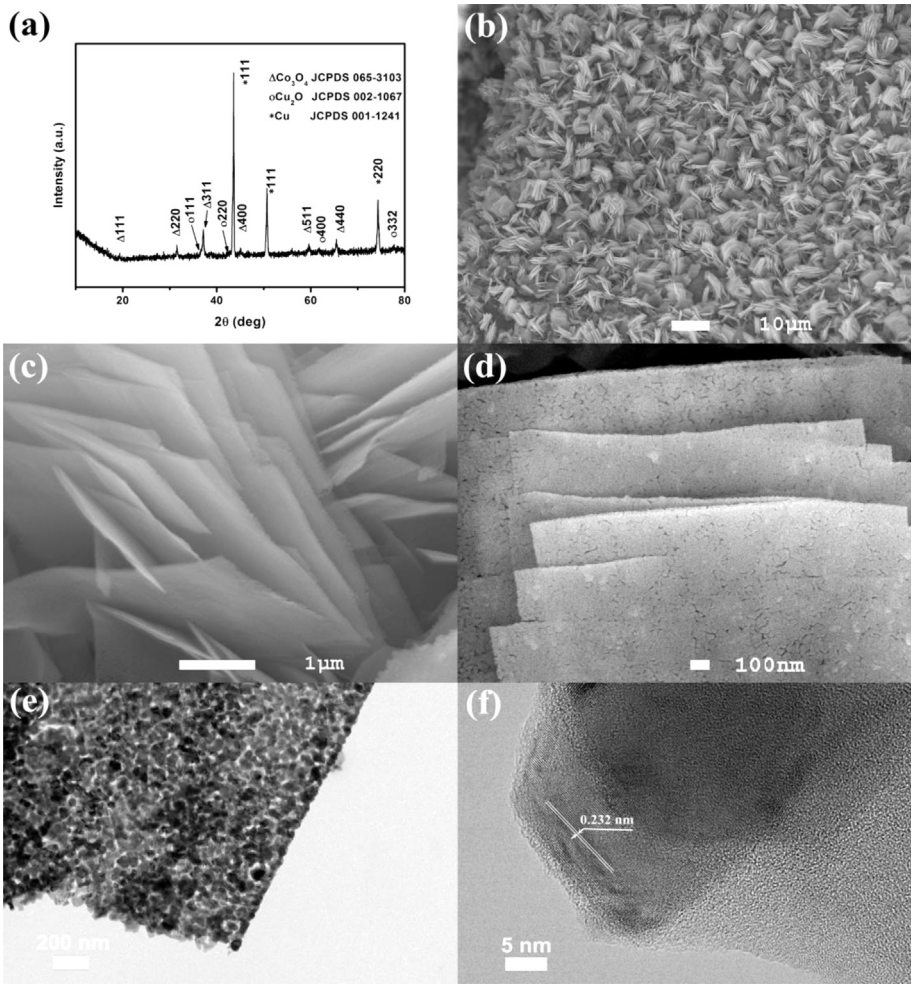

Fig. 1. (a) The XRD patterns of the book-like Co_3O_4 electrode sample; (b) Low magnification SEM images of Co_3O_4 electrode; (c) and (d) high magnification SEM images of Co_3O_4 electrode; (e) the TEM image and (d) the HRTEM image of Co_3O_4 electrode.