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Research paper

Alternating voltage induced electrochemical synthesis of three-dimensionalization copper oxide for lithium-ion battery application

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ABSTRACT

Three-dimensional copper oxide structures composed of single crystal nanosheets have been successfully prepared by a green electrochemical alternating voltage approach. This special structure of copper oxide grown along the [0 1 0] direction can be effective to accommodate the volume expansion during charge–discharge cycles. The obtained product as anode materials in lithium-ion batteries displays outstanding electrochemical performances with a high reversible capacity of 635.2 mA h g^{-1} after 50 cycles at 100 mA g^{-1} close to the theoretical capacity of copper oxide (674 mA h g^{-1}).

1. Introduction

Lithium ion batteries (LIBs) as one of the most important energy storage devices have attracted excessive attention, which is attributed to their application in various electronic devices and rapidly expanding need for LIBs [1–3]. At present, the commercial anode material is typical graphite with low theoretical capacities of 374 mA h g^{-1} [4]. In 2000, Tarascon reported that transition metal oxides could be developed into high capacity candidates for anode materials through a conversion reaction mechanism ($MO_x + 2xLi \leftrightarrow M + xLi_2O$) [5], such as FeO, NiO, Co_3O_4 and CuO [6–8]. Especially, CuO is an interesting transition metal oxide with a narrow band gap (E_g = 1.2 eV) [9] and has been considered as a promising anode material for LIBs which can be mainly contributed to its high theoretical capacity (674 mA h g^{-1}), low cost, environmental benignity and safety [3,10].

The main challenge for using CuO as active anode is its drastic volume expansion of about 174% during charge–discharge cycles [3]. Hence, the most effective way to enhance the electrochemical behaviors of CuO is to accommodate the volume expansion. One typical approach to buffer the volume expansion is to design special structured CuO since the electrical and optical properties of materials are often size- and shape-dependent [11,12]. In this regard, various architectural structure have been fabricated, for instance urchin-like CuO [13], bundle-like CuO nanostructure [11], CuO mesoporous nanosheet cluster [14], CuO nanoribbons [15], CuO hierarchical microspheres [16] and so on. Moreover, the design of CuO structures with exposed high surface energy facets could also be beneficial to enhance electrochemical property. For example, single crystal CuO nanoplatelets with a high percentage of {0 0 1} facets displayed high reversible capacity of 502 mA h g^{-1} after 100 cycles, respectively [17].

In this manuscript, a novel green alternating voltage electrochemical method has been firstly applied to manufacture three-dimensional (3D) structure CuO material. The as-obtained CuO is composed of single crystal nanosheets grown along the [0 1 0] direction. In addition, the electrochemical mechanism of 3D CuO structures composed of single-crystal nanosheets has been also investigated in details. The electrochemical measurements reveal that CuO prepared through alternating voltage exhibits excellent cyclability and rate capability for LIBs.

2. Experimental sections

The 3D structure CuO composed of single crystal nanosheets was prepared by a green electrochemical method using alternating voltage. The electrochemical system was assembled by two Cu wire (purity 99.95%, Sigma–Aldrich) electrodes with the diameter of 0.2 mm utilizing aqueous 2 M, 100 mL NaOH (Shanghai Titan Scientific Co., Ltd.) as electrolyte solution. After applying alternating voltage (11.0 V, 50 Hz) with a TDGC2-0.5 regulator transformer

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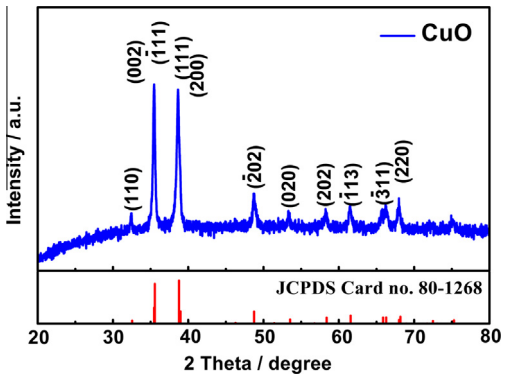

Fig. 1. The XRD pattern of CuO prepared through alternating voltage method.

(Ningbo G.S electronic group Co., Ningbo, China) to the two working electrodes for 4 h, flocculent substances were obtained. Furthermore, the freshly as-prepared substances were rinsed with distilled water until the value of pH was close to 7. Finally, the 3D structure CuO sample was got after calcination at 350 °C for 2 h in Ar.

The crystalline structure was determined via X-ray diffraction (XRD) recorded in a Rigaku D/max 2550 VB^+ 18 kW X-ray diffractometer with Cu Kα radiation in a 2θ range from 20° to 80° with a scanning rate of 0.1° s^{-1}. Scanning electron microscopy (SEM, JSM-6510LV), transmission electron microscopy (TEM, JEM-2100F) and high resolution transmission electron microscopy (HRTEM, JEM-2100F) were performed to analyze the morphologies of samples. The elemental compositions of the samples were investigated through energy dispersive X-ray (EDS) analysis. Coin-type half-cells (CR2016) were assembled to explore the lithium storage behaviors of as-obtained products. The detailed procedure was similar with the previous report [18]. The mass loading of the electrode material is 1.1–1.3 mg. Cyclic voltammetry (CV) tests were carried out at various scan rates on Solartron Analytical between 0.01 and 3.0 V (vs Li^+/Li). Galvanostatic charge/discharge cycles

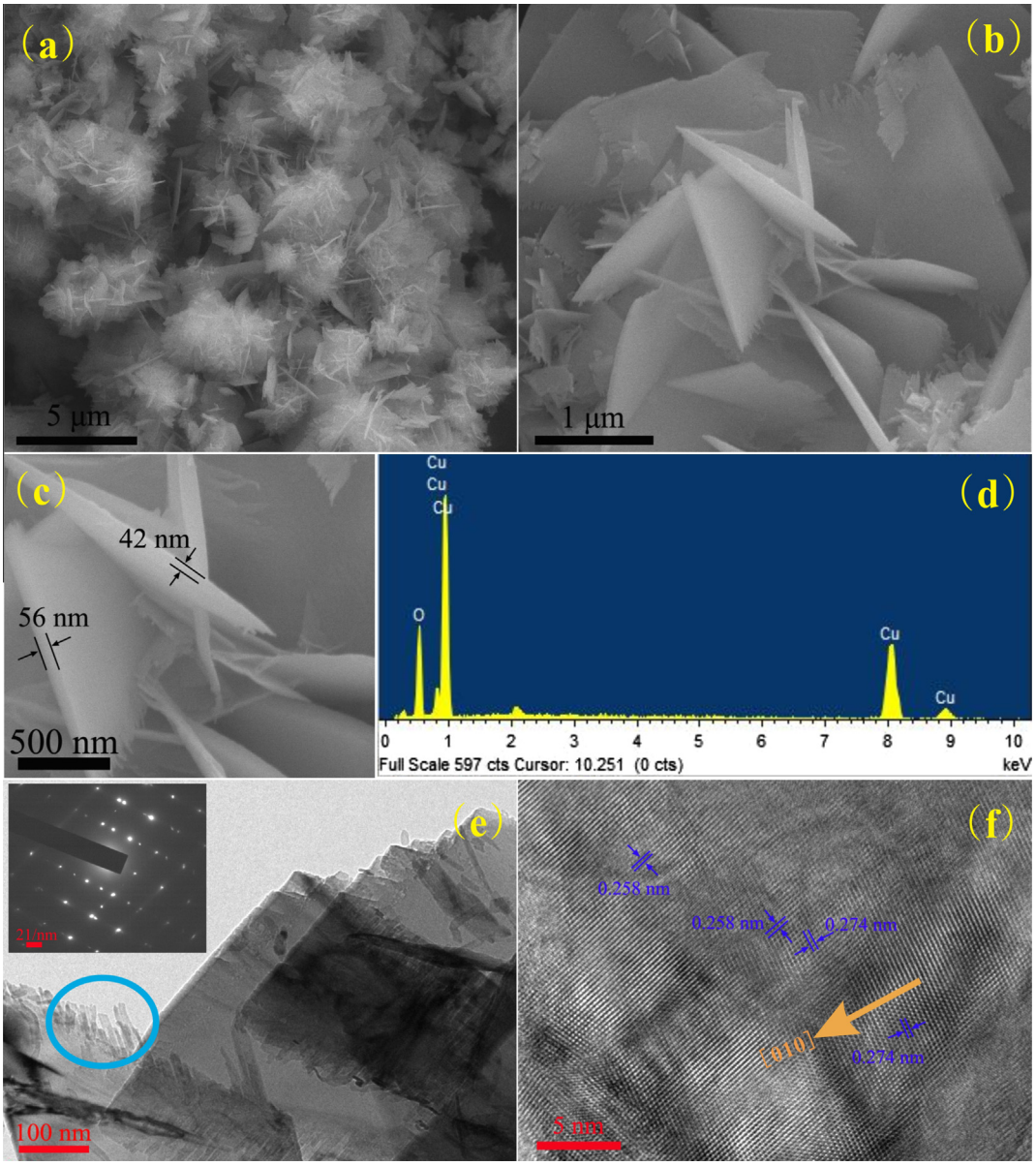

Fig. 2. The SEM images (a–c) of 3D flower-like CuO sample with different magnifications. (d) EDS spectrum of as-obtained CuO sample. TEM (e) and HRTEM (f) images of as-obtained 3D CuO composed of single-crystal nanosheets. Inset in (e) is SAED pattern.