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Facile synthesis of CuO mesocrystal/MWCNT composites as anode materials for high areal capacity lithium ion batteries

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ABSTRACT

CuO mesocrystal entangled with multi-wall carbon nanotube (MWCNT) composites are synthesized through a facile scalable precipitation and a followed oriented aggregation process. When evaluated as anode materials for lithium ion batteries, the CuO-MWCNT composites exhibit high areal capacity and good cycling stability (1.11 mA h cm^{-2} after 400 cycles at the current density of 0.39 mA cm^{-2}). The excellent electrochemical performance can be ascribed to the synergy effect of the unique structure of defect-rich CuO mesocrystals and the flexible conductive MWCNTs. The assembled architecture of CuO mesocrystals can favor the Li-ion transport and accommodate the volume change effectively, as well as possess the structural and chemical stability of bulk materials, while the entangled MWCNTs can maintain the structural and electrical integrity of the electrode during the cycles.

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1. Introduction

Oriented attachment, as a nonclassical crystal growth mechanism, involves the self-assembly of nanoparticles, crystallographic reorganization within the assemblies, and further conversion to mesoscopically structured crystals, namely, mesocrystals [1,2]. Mesocrystals, as a new class of nanostructure solid materials, can be composed of several to thousands of primary nanocrystals with common crystallographic orientation, but without coherent and crystalline material linking them, which can be regarded as mosaic-like quasi-monocrystals with abundant defects. Mesocrystals usually exhibit unique physical/chemical properties, which are derived from the collective interactions of individual nanoparticles as well as the defects [3]. Such superstructures would possess the structural and chemical stability of bulk materials while exploiting the beneficial properties associated with primary nanocrystals and their large reactive surface area, which attracts increasing attention in the fields of catalysis, energy storage and conversion, et al. [4–6].

Transition metal oxide (TMO) is one kind of promising anode materials for the next generation of lithium ion batteries (LIBs) due to their high theoretical capacity, safety performance, and environmental benignity [7–9]. However, the intrinsic low electrical conductivity of TMOs and the drastic volume change during the lithiation/delithiation process hinder their practical applications in high energy and high power devices. Constructing conductive carbon material (including amorphous carbon, carbon nanotube, and graphene) and TMO composites is a common approach to solve these problems [10]. Another typical strategy is to synthesize nano-sized TMOs with unique morphology, since nanostructured materials can increase the specific surface area and thus facilitate the lithiation/delithiation process [11]. Despite the great development of nanomaterial anodes, the issues of the low tap density, high processing costs, and potential nano-toxicity effects associated with nanomaterial synthesis and processing are still up in the air [6]. In this context, mesocrystals may be the most suitable candidate to solve the above obstacles. The defects within the mesocrystals are active sites for the electrochemical lithiation/delithiation processes. When used as anodes for LIBs, the inherent uniform porosity and defects in mesocrystals not only can favor the fast Li-ion transport and electrochemical reactions exceedingly [12,13], but also can accommodate the concurrent volume change effectively [14]. On the other hand, as nanoparticle assemblies, mesocrystals have much larger size than nanoparticles, which lead to a convenient and non-hazardous processing. Especially, the high tap density of the micron-sized mesocrystals shows great advantage in fabricating the electrodes with high energy density and power density per unit volume or area [15,16], which is of significance for applications in portable electronic microdevices and thin-film LIBs [17]. However, the rational designing and fabricating the mesocrystalline materials aiming to TMO anodes is still infrequently reported.

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Herein, for the first time, we fabricated the CuO mesocrystal composites incorporated with multi-wall carbon nanotubes (MWCNTs). When tested as anodes for LIBs, the CuO mesocrystal/MWCNT composites present high areal capacity and cycling stability. A reversible discharge capacity as high as 1.11 mA h cm^{-2} (equivalent to a specific capacity of ~572 mA h g^{-1}) can be delivered after 400 cycles at the current density of 0.39 mA cm^{-2} (~200 mA g^{-1}). The main reason for the excellent electrochemical performances of the CuO mesocrystal/MWCNT composites are analyzed and discussed.

2. Experimental

2.1. Synthesis of CuO mesocrystal/MWCNTs composites

All the reagents were of analytical grade and used without further purification. Typical procedures for the synthesis of CuO-MWCNT composites were as follows: Firstly, 0.65 g of MWCNTs and 9.8 g of $Cu(NO_3)_2 \cdot 3H_2O$ were dispersed/dissolved in 1 L of deionized water under supersonic treatment for 30 min Then 240 mL of $NH_3 \cdot H_2O$ solution (1.5 M) was added into the above mixed suspension under constant stirring. Next, 70 mL of NaOH solution (10 M) was added dropwise into the as-prepared suspension to form a blue precipitate. The suspension was further heated at 80 °C for 24 h to obtain the final product, CuO mesocrystal/MWCNTs composites. For comparison, CuO mesocrystal materials were also prepared in the absence of MWCNTs by a similar procedure.

2.2. Characterizations

The as-prepared products were characterized using powder X-ray diffractometry (XRD, X'Pert Pro diffractometer with a Cu Kα radiation), scanning electron microscopy (SEM, Sirion 200) and transmission electron microscopy (TEM, JEOL-2010) equipped with an energy dispersive spectroscopy (EDS) detector. Thermal gravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris 1 Thermal Gravimetric Analyzer with a heating rate of 10 °C/min from 50 °C to 700 °C under air flow.

2.3. Electrochemical measurement

Electrochemical performances of the products were tested using CR2032 coin cells. Electrodes were prepared by coating the slurry consisting of active material, polyvinylidene fluoride (PVDF), and acetylene black (8:1:1 by weight) onto a copper foil. Then the copper foil was cut into round disks with diameter of 12 mm as the working electrodes (the specific weight of active material loaded in each disk electrode is about 1.947 mg/cm^2). The coin cells were assembled in an Ar-filled glove box, using lithium foil as the counter electrode and Celgard 2325 as the separator. The electrolyte consisted of 1 M $LiPF_6$ solution in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1 by volume). The charge/discharge measurement, cyclic voltammetry (CV) measurement, and electrochemical impedance spectroscopy (EIS) for the cells were conducted on the Neware BTS TC53 battery test system and Zahner Zennium electrochemistry work station, respectively.

3. Results and discussion

Fig. 1a shows the XRD patterns of the obtained CuO precipitates and CuO-MWCNT composites. The diffraction peaks of the pristine CuO can be perfectly indexed to monoclinic phase CuO (JCPDS card No. 45-0937), while the CuO-MWCNT composites show an additional faint diffraction peak at 26°, which can be attributed to the (002) plane of the MWCNTs. TGA results (Fig. 1b) show that the CuO-MWCNT composites consist of 83 wt% CuO and 17 wt% MWCNT. The morphological features of the products were examined by scanning electron microscopy (SEM). The obtained CuO displays micro-sized flower-like structure composed of intersecting nanosheets (Fig. 2a). By comparison, CuO architectures entangled by three-dimensional (3D) networks are formed in the addition of MWCNTs (Fig. 2b). The transmission electron microscopy (TEM) image reveals that the CuO sheets have two different morphologies: regular sheet with a smooth surface and bundle-like assemblies with jagged surface (the inset of Fig. 2c), indicating that the bundle-like assemblies are the intermediates for the final CuO sheets. Furthermore, the high resolution TEM (HRTEM) investigation reveals that the assemblies have a common crystallographic orientation with some discontinuous areas marked by white circles in Fig. 2c, which implies that the as-prepared CuO are mesocrystals and the oriented attachment is the potential growth mechanism. The lattice spacing of 0.28 nm corresponds to the (011) plane of CuO. Meanwhile, the corresponding SAED pattern (Fig. 2d) also shows a typical mesocrystal characteristic with elongated diffraction spots, which is due to the misorientations deviating from perfect oriented attachment within the assemblies. Fig. 2e and f display the typical TEM images of the CuO-MWCNT composites. From the TEM images, the coexistence of CuO and MWCNTs can be clearly observed and the lattice spacings are corresponding to the (011) plane of CuO and the (002) of carbon nanotubes, respectively, demonstrating MWCNTs are indeed incorporated into CuO mesocrystals to form CuO-MWCNT composites.

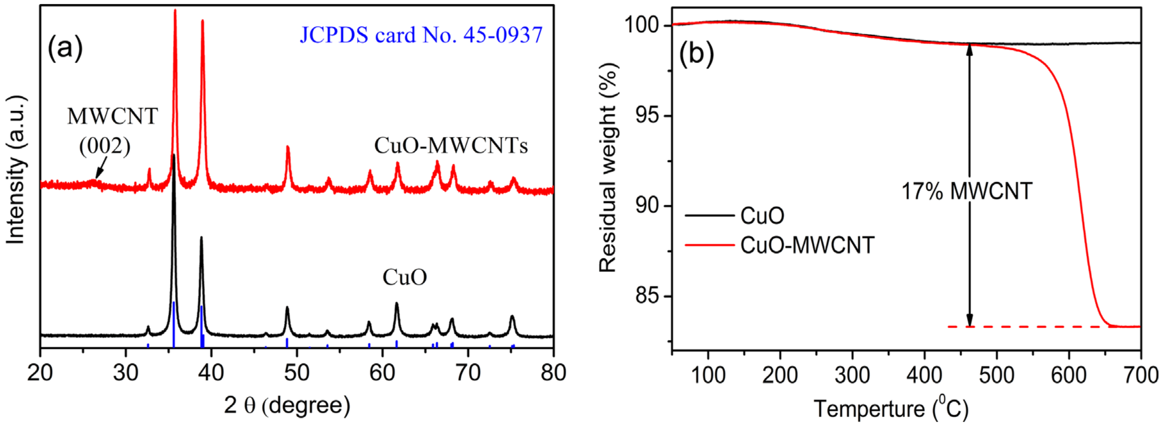

Fig. 1. XRD patterns (a) and TG curves (b) for the CuO and CuO-MWCNT composites.

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