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Core-shell $CuO@TiO_2$ nanorods as a highly stable anode material for lithium-ion batteries

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ABSTRACT

A hierarchical nanorod structure containing a CuO core and a TiO_2 shell ($CuO@TiO_2$) was successfully prepared and demonstrated high capacity and cycle stability as an anode material for lithium-ion batteries. The Cu dendrites were prepared by galvanic displacement using an aluminum plate, and a layer of TiO_2 was coated on the Cu dendrites through sol–gel processing. Finally, the $Cu@TiO_2$ dendrites were evolved to $CuO@TiO_2$ nanorods by thermal oxidative annealing. Core–shell $CuO@TiO_2$ exhibited reversible specific capacity (400 $mAhg^{-1}$ at 0.1C) and stable cyclability (97% after 100 cycles). This work suggests a facile and cost-effective strategy for the fabrication of a core-shell structure that has the potential to be useful in energy storage devices.

1. Introduction

Copper oxide (CuO) has been introduced as an anode material for lithium ion batteries (LIBs) due to its high theoretical capacity (674 $mAhg^{-1}$), environmental benignity, safety, and low cost [1]. However, during the Li-alloying/dealloying process, the large volume expansion and contraction of a CuO-based anode results in short cycle life, which hinders its practical applications [2,3]. Because nanostructured materials can accommodate large strain without severe pulverization and because using a specific shell material can limit the volume change of the whole structure, preparation of nano-architecture core-shell structures is a potentially effective method to solve the problems associated with volume expansion [4].

Recently, many researchers have introduced the preparation of various carbon-based core-shell structures, such as CuO@carbon, CuO@CNT, and CuO@graphene [4–6]. As an alternative, anatase-type TiO_2 has proven to be suitable as a shell material due to its small degree of volume change ($<4\%$) during Li-insertion/extraction [7]. Furthermore, anatase-TiO_2 not only buffers volume change to maintain structure integrity, but also makes partial contributions to the specific capacity (theoretical capacity of TiO_2 is $\sim$350 $mAhg^{-1}$).

Herein, we propose the synthesis of a novel $CuO@TiO_2$ nanorod anode material using a simple and reliable process. Cu dendrites are prepared by a galvanic displacement reaction from an aluminum plate. Then, TiO_2 is coated on the Cu dendrites through a sol–gel process. Finally, the $Cu@TiO_2$ dendrites are evolved into $CuO@TiO_2$ nanorods by thermal oxidative annealing. We expect that $CuO@TiO_2$ core-shells as the anode material in LIBs will enhance electrochemical performance (e.g. the specific capacity and cycle stability).

2. Experiments

First, 0.5 g of copper chloride ($CuCl_2$) and 1 ml acetic acid were dissolved in 100 ml distilled water. The clean Al plate was then immersed into the beaker with the as-prepared solution for 15 min at room temperature. After reaction, the deposited Cu dendrites were rinsed thoroughly with distilled water, and then dried in an oven at 50 °C. One hundred milligrams Cu dendrites were ultrasonically dispersed in 80 ml anhydrous ethanol and 0.5 ml titanium tetraisobutanolate (TBOT) was added to a 0 °C suspension in an ice bath over 20 min while stirring constantly. The suspension was immersed in a water bath at 80 °C. The hydrolysis of TBOT was initiated by adding 20 ml water/ethanol mixture (50 ml/l) dropwise. After 2 h, the powders were collected by filtration, washed with ethanol, and then dried in an oven at 60 °C. Finally, core-shell $Cu@TiO_2$ was annealed in a furnace at 500 °C for 2 h.

The crystal structure, morphology, and chemical composition were determined by X-ray diffraction (XRD, D8 ADVANCE/BRUKER AXS), scanning electron microscopy (SEM, JEOL), transmission electron microscope (TEM, JEOL JEM ARM 200F), and X-ray energy dispersive spectroscopy (EDS), respectively. The working electrodes

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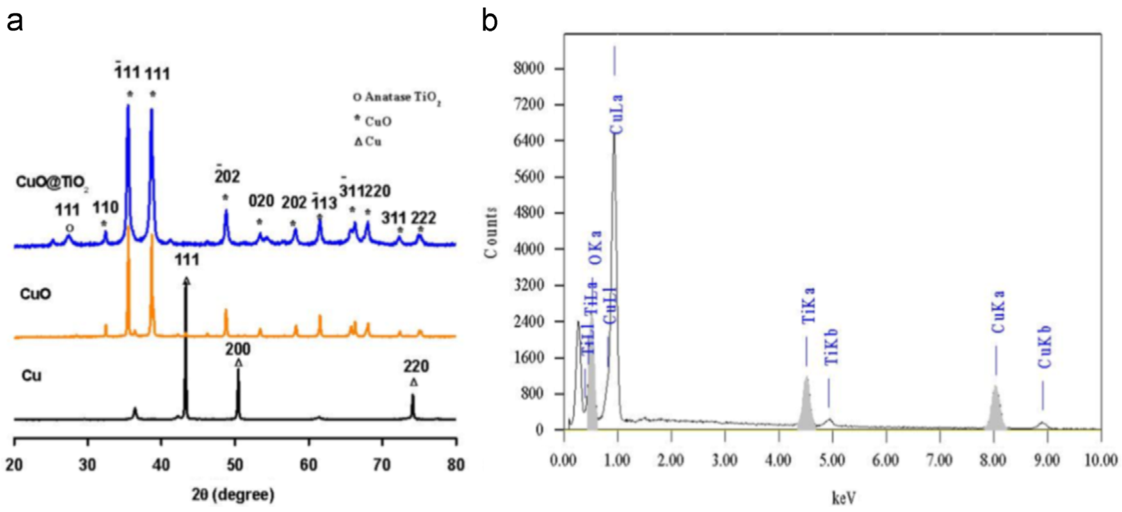

Fig. 1. XRD spectrum of bare Cu, CuO, and CuO@TiO_2 annealed at 500 °C (a); EDX spectrum of core-shell CuO@TiO_2 (b).

were prepared by casting slurry (CuO@TiO_2: acetylene carbon: polyvinylidene fluoride = 70:15:15 wt %) onto a copper foil. Coin-type test cells were assembled using an anode material as a working electrode, Li foils as both counter and reference electrode, 1 M solution of $LiPF_6$ in a mixed solvent (ethylene carbonate: diethyl carbonate: dimethyl carbonate = 1:1:1 wt %) as an electrolyte, and polypropylene foil as the separator. The loading mass of the active materials were kept at 1.26 mg. These cells were assembled in an argon-filled glove box and cycled at different rates from 0.03 to 3 V.

3. Results and discussion

Cu dendrite powder was easily obtained from the galvanic displacement reaction due to the large difference in the reduction potential between Cu^{2+} (0.34 V) and Al (−0.16 V) in an aqueous $CuCl_2/CH_3COOH$ electrolyte [8]. XRD analysis (Fig. 1a) confirmed that the as-prepared Cu dendrite was a pure, face-centered cubic Cu metal (JCPDS No. 85-1326). After sol–gel coating and thermal oxidative annealing, strong and clear diffraction peaks of the monoclinic CuO phase (JCPDS No. 80-1917) were exhibited and the peaks of Cu completely disappeared. Anatase TiO_2 peaks (JCPDS: No. 21-1272) also appeared which implied that the amorphous TiO_2 transitioned to crystalline TiO_2 after annealing. Further evidence of successful TiO_2 coating on CuO was shown by the EDS analysis, which revealed that the average weight ratio of TiO_2 to CuO is 28.9% (Fig. 1b).

The morphologies and sizes of the Cu dendrites were determined by SEM. The lengths of stems and branches were ~10 and ~3 μm, respectively. The diameters of the branches were ~100 to 200 nm (Fig. 2a). After sol–gel coating, SEM and TEM images confirmed that a uniform TiO_2 shell completely covered the Cu core (Fig. 2b and e). However, the dendrite structure of bare Cu was completely destroyed and only aggregated particles were found after annealing (Fig. 2c). This may be attributed to the aggregation tendency of complex structures to decrease their surface energy at high temperatures [9]. In contrast, a SEM image showed that Cu@TiO_2 dendrites evolved into CuO@TiO_2 nanorods. The diameters and lengths of the nanorods were ~200 nm and ~2 μm, respectively (Fig. 2d). The morphology evolution from dendrites to nanorods indicated that the TiO_2 shell can limit the aggregation tendency of core CuO during the annealing process, as illustrated in Fig. 2f.

Electrochemical lithium storage properties of bare CuO and CuO@TiO_2 were evaluated as an anode material in a half-cell configuration. Fig. 3a and b show the galvanostatic charge–discharge voltage curves of the anodes constructed from bare CuO and CuO@TiO_2 at a rate of 0.1C. In the first discharge of bare CuO (Fig. 3a), the monotonic slope at ~1.5 V versus Li is ascribed to lithium insertion into the CuO matrix and the consequent formation of Li_xCuO. Then, the predominant structural destruction occurs to form a Cu_2O phase exhibiting a long, distinct plateau around ~1.5 V versus Li. Further metallic reduction (Cu^0) is also seen. The discharge specific capacities of bare CuO were 413, 273, and 251 mAh g^{-1} for 1st, 2nd, and 3rd cycles, respectively. The initial capacity loss was due to irreversible solid electrolyte interphase (SEI) formation, which occurred during the 1st cycle. Compared with bare CuO, the CuO@TiO_2 nanorods exhibited a much higher initial discharge capacity of 743 mAh g^{-1} for the 1st cycle and then dropped to 400 mAh g^{-1} for the 2nd cycle (Fig. 3b). Such high initial capacity can be attributed to the fact that the large surface area of CuO@TiO_2 nanorods consumed more Li and electrolyte than that of CuO microparticles to form a SEI layer. The specific capacities of the CuO and CuO@TiO_2 electrodes cycled between 0.03 and 3 V under various C regimes are reported in Fig. 3c. The bare CuO electrode delivered a capacity of about 260 mAh g^{-1} at a rate of 0.1C; this value decreased to 64 mAh g^{-1} when the rate was increased to 2C. However, the CuO@TiO_2 displayed higher reversible capacities even at a high scan rate (230 mAh g^{-1} at 2C). The superior high rate specific capacity of CuO@TiO_2 nanorods can be attributed to their larger specific surface area, which supplies more reactive sites to facilitate the insertion/extraction of lithium ions. Fig. 3d compares the cycling performance of CuO@TiO_2 with bare CuO. The capacity of the CuO decayed much faster, to less than 30% after 100 cycles, which is ascribed to the serious volume expansion of bare CuO during Li insertion/ extraction. As expected, the CuO@TiO_2 anode exhibited significantly improved cyclic stability compared to the bare CuO anode. The capacity of the CuO@TiO_2 was maintained at 97% over 100 cycles which can be explained as follows. We have monitored the morphologies of the active materials, CuO and CuO@TiO_2 after 100 cycles. The coin-cells were carefully opened and the active materials were characterized by SEM (in Supporting Information). CuO particles were completely pulverized and aggregated together, while the rod structure of CuO@TiO_2 was still maintained due to the TiO_2 shell, which constrained the volume change (Fig. 1 S). The stable crystalline TiO_2 shell efficiently improved the mechanical strength caused by the small volume change during the Li insertion/extraction process [10]. Also, the nanorod core-shell structure was able to accommodate larger strain without destruction [11]. We also observed that the specific capacity of CuO@TiO_2 slightly declined for the first 20 cycles before gradually