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Hydrothermal synthesis of copper sulfide with novel hierarchical structures and its application in lithium-ion batteries

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ABSTRACT

Novel stick-like CuS hierarchical structures have been fabricated by a hydrothermal approach use β-cyclodextrin as ligand and structure-directing agent. SEM and TEM characterizations show that the CuS stick-like structures are composed of tens to hundreds of well-arranged and self-assembled nanoplates with a thickness of about 25 nm. The mechanism for the formation of the final stick-like hierarchical structures is proposed and discussed. β-cyclodextrin is found to be the key factor in controlling the morphologies. Meanwhile, the possibility of using CuS as the electrode material for lithium ion batteries (LIBs) is studied. Electrochemical measurements reveal that the as-prepared CuS exhibits outstanding cycle stability, indicating that it might find possible application as a cathode material for LIBs in the long term.

1. Introduction

Many studies have been conducted for improving the performance of lithium ion batteries (LIBs) [1–3]. It is well-known that the capacity of the cathode materials is generally much lower than that of the anode materials. This is a main barrier for enhancing the specific energy of LIBs [4]. Among the various candidates for cathode materials, copper sulfide (CuS) is a promising cathode material for the application in low voltage battery system [5–7]. CuS has a high theoretical capacity (560 mAh g^{-1}), a good electrical conductivity (10^{-3} S/cm) and flat discharge curves when cycled *versus* Li^+/Li^0 [8–10]. It has been demonstrated that the properties of CuS are determined predominantly by their crystal structure, size and morphology. Therefore, the synthesis of CuS materials with well-controlled size and shape is of great significance for their applications. Up to date, various morphologies of CuS such as nanowires, thin film, hollow spheres, and some complex hierarchical micro-/nanostructures have been synthesized and used as cathode materials for LIBs [11–14].

In this work, novel CuS nanoplate-based hierarchical structure cathodes for LIBs were produced by a facile hydrothermal method. The hierarchical nanostructures exhibit outstanding cyclic stability and long cycle life.

2. Experimental

2.1. Chemical and synthesis

The CuS hierarchical structures were prepared according to the method described elsewhere with a minor modification [15]. All the reagents were analytical grade and used without any further purification. In a typical synthesis, 2 mmol $Cu(NO_3)_2{\cdot}3H_2O$, 4 mmol thiourea and 1 g β-cyclodextrin were dissolved in a mixed solution of 30 ml water and 10 ml anhydrous ethanol. The mixture was vigorously stirred for about 10 min, then transferred to an autoclave of 50 ml capacity. The autoclave was heated to 120 °C for 12 h. After naturally cooling to ambient temperature, the resulting black precipitate was collected by centrifugation, washed sequentially with double-distilled water and ethanol, respectively, and then dried at 60 °C in air.

2.2. Material characterizations and performance measurements

The crystal structures and microstructures of the materials were characterized by X-ray diffraction (XRD, Rigaku/Max-3A, Cu Kα, λ = 1.5406 Å), scanning electron microscopy (SEM, JEOL JSM-6330F) and transmission electron microscopy (TEM, JEOL 2010, 200 kV).

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The FTIR spectra were recorded on a MAGNA-IR 750 FTIR spectrometer.

The working electrode was prepared by mixing CuS with acetylene black and polyvinylidene fluoride in a weight ratio of 72:18:10 in N-methylpyrrolidinone. The coin-type batteries (CR2025) were assembled with lithium metal as the counter/reference electrode and 1 M $LiPF_6$ in ethylene carbonate, diethyl carbonate and ethylmethyl carbonate (1:1:1 vol.) as electrolyte. The automatic charge/discharge equipment (LAND CT2001A) was used to perform the galvanostatic charge/discharge tests in a potential range of 1.8–2.6 V at 0.2 C (1 C = 560 mA g^{-1}) at room temperature.

3. Results and discussion

3.1. Characterization of the products

Fig. 1A shows the XRD pattern of the products synthesized by hydrothermal treatment at 120 °C for 12 h. The diffraction peaks can be readily indexed to the standard diffraction data of the hexagonal phases of CuS (JCPDS Card File No. 06-0464). No characteristic peaks from impurities can be detected. Compared with the standard pattern, the diffraction peaks are much broadened, indicating the formation of crystallites with small size.

The morphology and size of the as-prepared CuS were investigated by SEM and HRTEM. As shown in Fig. 1B and C, the products are mainly make up of CuS stick-like microstructures with diameters around 3 μm and lengths of tens micrometers. And the stick-like hierarchical structures are composed of tens to hundreds of self-assembled, well-arranged and oriented nanoplates, and the mean thickness of the nanoplates is about 25 nm. Although the entire stick is too large and thick for the HRTEM observation, we could still obtain the HRTEM image of a nanoplate. Fig. 1D is the corresponding HRTEM image, giving resolved lattice fringes of (1 0 2) planes (d_{102} = 0.298 nm). The SAED pattern in Fig. 1d shows that the nanoplate is single crystal with a hexagonal phase corresponding to covellite CuS.

3.2. Formation mechanism of the CuS stick-like hierarchical structures

β-cyclodextrin (β-CD) plays an important role in the formation of CuS stick-like hierarchical structures. β-CD is one of the well-known supramolecular compounds [16]. The hydroxyls on β-CD molecules can strongly coordinate with heavy metal ions such as Cu^{2+} ions. After being introduced to the reaction mixture, the Cu^{2+} ions would be attracted by the β-CD to form the Cu-β-CD complex. The complexes might serve as a molecular template in control of the crystals growth. When the reaction temperature was increased, the thiourea in the solution can be decomposed to release S^{2-} to react with the Cu-β-CD complex. Once the CuS nanocrystals were formed during the hydrothermal process, β-CD would selectively bind to the specific surface of the preformed CuS, leading to the seeming restriction of crystal growth. Fig. 2A shows the FTIR spectra of the products prepared at 120 °C for 12 h and the pure β-CD, respectively. The absence of the transmittance bands at 756 cm^{-1} and 946 cm^{-1} indicates that the free β-CD has almost disappeared in the final products. The dramatic decrease and the shift of peak positions at 705 cm^{-1} and 575 cm^{-1} can be interpreted as the "fixed" nature of the β-CD that prevents the skeletal vibration and pyranose ring vibration. The FTIR results confirm that there is strong interaction between Cu^{2+} ions and the hydroxyl to allow β-CD to

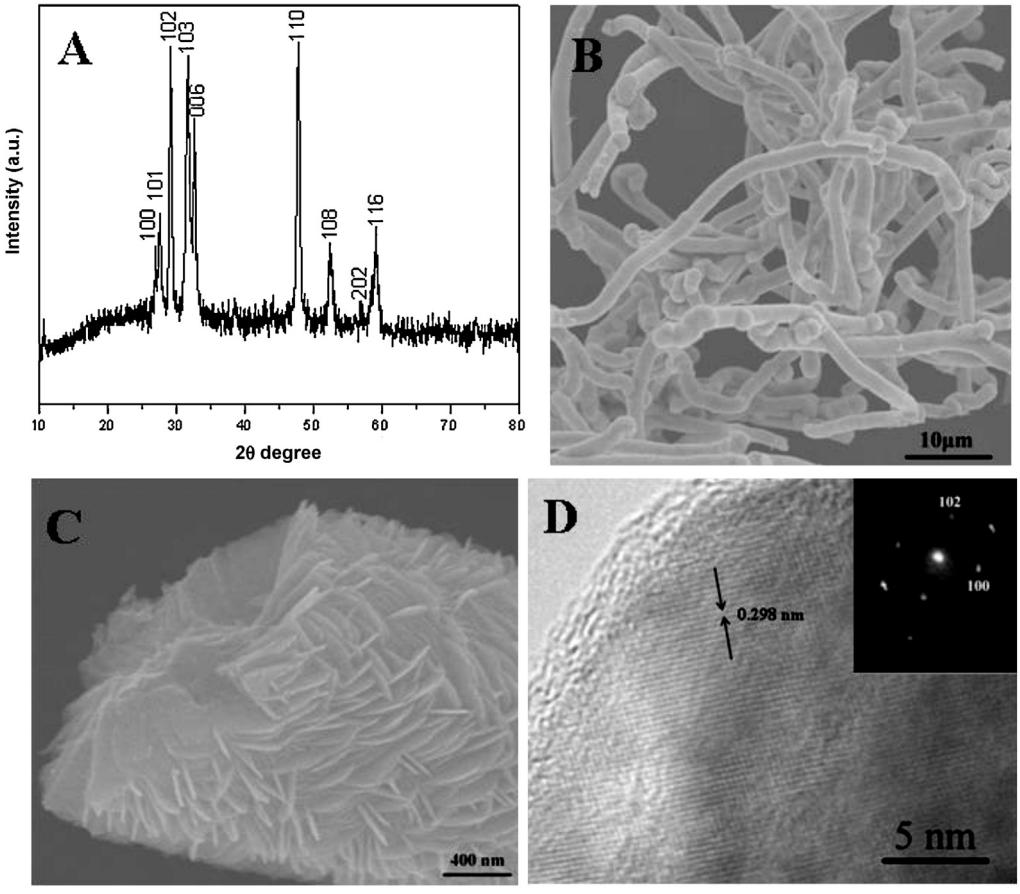

Fig. 1. XRD pattern (a), SEM images (b, c) and HRTEM image (d) of the products prepared at 120 °C for 12 h. The inset in d shows the SAED pattern.