



Synthesis of copper sulfide nanowire bundles in a mixed solvent as a cathode material for lithium-ion batteries



Caihong Feng^{a, b}, Le Zhang^a, Zhihui Wang^b, Xiangyun Song^b, Kening Sun^a, Feng Wu^a, Gao Liu^{b, *}

^a School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, PR China

^b Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., MS 70R108B, Berkeley, CA 94720, USA

HIGHLIGHTS

- Novel copper sulfide (CuS) nanowire bundles were successfully synthesized.
- A template- and surfactant-free method in a dimethyl sulfoxide (DMSO)-ethyl glycol (EG) mixed solvent was used.
- The synthesized material exhibit a large capacity and excellent cycling stability and rate capability.
- The unique structure of the CuS nanowire bundles is responsible for their excellent electrochemical performance.

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ABSTRACT

Novel copper sulfide (CuS) nanowire bundles with a diameter of about 6 nm and a length up to several micrometers are successfully synthesized by a template- and surfactant-free method in a dimethyl sulfoxide (DMSO)-ethyl glycol (EG) mixed solvent. The resulting CuS nanowire bundles are used as a cathode material in lithium-ion batteries and exhibit a large capacity and excellent cycling stability and rate capability. The unique structure of the CuS nanowire bundles is responsible for their excellent electrochemical performance.

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1. Introduction

The increasing demand of renewable energy sources continues to inspire an enormous amount of research interest in new electrode materials and electrode materials with new structures for lithium-ion batteries (LIBs). Recent progress has demonstrated that the performance of LIBs not only strongly relies on the electrode materials used but also on the morphology and the microstructure of the electrode materials used [1,2]. Up to now, significantly improved battery performance of various nanoscale materials—including transition metal oxide nanoparticles [3,4], Cu–Si nanocables [5,6], and metal chalcogenides [7,8]—has been reported. The outstanding electrochemical performance is ascribed to the new

nanostructure, which can increase reaction sites, improve cycle life in the face of mechanical strain, and improve efficient charge transport.

Copper sulfides have received considerable attention due to their wide stoichiometric composition (Cu_xS , $x = 1-2$) and diverse applications in energy devices [9,10]. Among them, green covellite copper sulfide (CuS) has been actively investigated as an electrode material for LIBs due to its cost effectiveness, abundance in nature, environmental friendliness, good electronic conductivity (10^3 S^{-1}) and higher theoretical lithium-ion (Li-ion) storage capacity (560 mA h g^{-1}) than that of commonly used cathode material LiCoO_2 (145 mA h g^{-1}) [11–13]. Although CuS is known to suffer from poor capacity retention, and hence a short lifetime, much enhanced electrochemical performance can be expected by nanostructuring CuS or by using an ether-based electrolyte [14,15]. In the past few years, many attempts have focused on the synthesis of novel nanostructures of copper sulfides, including hollow

* Corresponding author. Tel.: +1 510 486 7207; fax: +1 510 486 7303.

E-mail address: gliu@lbl.gov (G. Liu).

spheres and flowers [16–18], one-dimensional (1-D) nanostructures [19–22], and complex hierarchical micro-/nanostructures [23–28]. Among different kinds of nanoscale morphologies, 1-D nanostructures attract wide interest because of their advantages in electronic conduction along the axial direction. The corresponding preparation techniques involved mostly template-based, surfactant-directed, or interface methods. These growth methods usually require the use of special instruments, surfactants, or templates, which will increase the difficulty of operation, the cost, and contamination. A simple method for the large-scale synthesis of CuS nanowire bundles has not been achieved so far. Recent studies have shown that the mixed solvent method is effective in preparing metal chalcogenides with unique morphologies or new nanostructures because of the “magic power” of mixed solvents for shaping nanocrystals [29,30]. The solvent plays an important role in controlling the growth of nanocrystals because of its strong coordination with metal ion or selective binding with crystal plane [28,31,32]. By changing the components and volume ratios of mixed solvents, it is easy to control the size, morphology, and microstructure of the desired materials. For example, urchin-like nickel selenide (NiSe) was synthesized in a ternary solution of diethylenetriamine, hydrazine hydrate, and water by S. Yu and co-workers [30]. The surface topography of these NiSe nanocrystals can be tailored by tuning the composition of the solvents used.

In this work, we report a template- and surfactant-free method for synthesizing CuS nanowire bundles in a dimethyl sulfoxide (DMSO)-ethyl glycol (EG) mixed solvent, which could be scaled up to prepare large amounts of oriented attachment CuS nanowire bundles. The factors influencing formation of CuS nanowire bundles were discussed and the electrochemical properties of as-prepared CuS cathode were investigated as well. The unique structure of CuS nanowire bundles offers many critical features, such as a fast way for both ion and electron transport, many active sites for electrode reactions, and a robust structure for durability [33], which make it a promising cathode material for LIBs with high capacity, excellent rate performance, and high cycling stability.

2. Experimental

2.1. Materials

Thiourea (ACS reagent, 99.0%), copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), ethylene glycol (EG, anhydrous, 99.8%), and dimethyl sulfoxide (DMSO, GC, 99.5%) were purchased from Sigma–Aldrich. Lithium-ion electrolytes were purchased from Novolyte Technologies, including 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 w/w) with 30% fluoroethylene carbonate (FEC). All chemicals were used without further purification.

2.2. Synthesis of the CuS nanowires bundles

In a typical synthesis, 0.290 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in the mixed solvent (60 mL) with a volume ratio of $V_{\text{DMSO}}/V_{\text{EG}}$ (defined as R) = 1:3 under stirring in a three-neck flask at room temperature. The temperature of the solution was slowly increased to 145 °C and was maintained for 3 h under nitrogen ambience. Then, 5 ml of mixed solution containing 0.274 g of thiourea was added to the solution drop by drop through a syringe under vigorous stirring. Finally, the whole solution was kept at 160 °C for another 2 h. The final products were collected by centrifugation and washed several times by distilled water and ethanol and dried in a vacuum at 60 °C for 12 h.

2.3. Material characterization

The phase composition of the as-prepared samples were characterized by a Philips X'Pert Pro Multipurpose X-ray diffractometer (XRD) using $\text{Cu K}\alpha$ radiation at 45 kV and 40 milliamps (mA), at the 2θ range 20°–85° with 0.02 per step. The Raman spectra of the sample were collected using a Renishaw spectrophotometer equipped with a microscope having a laser wavelength of 532 nm. The morphology of the samples and electrodes was characterized with a JEOL JSM-7500F field emission scanning electron microscope (SEM) system. High-resolution transmission electron microscope (TEM) images were obtained on a Philips CM200 field emission microscope operated at 200 kV.

2.4. Electrochemical measurement

The as-prepared CuS nanowire bundles were studied as cathode materials for rechargeable lithium-ion batteries. The anodes were fabricated by mixing copper sulfur nanowires, Super C 65, carboxymethyl cellulose (CMC), and Polyvinyl Alcohol (PVA) with a weight ratio of 75:15:7.5:2.5 in water. The mixture was blended together using a Polytron PT 10–35 homogenizer at 2500 rpm for

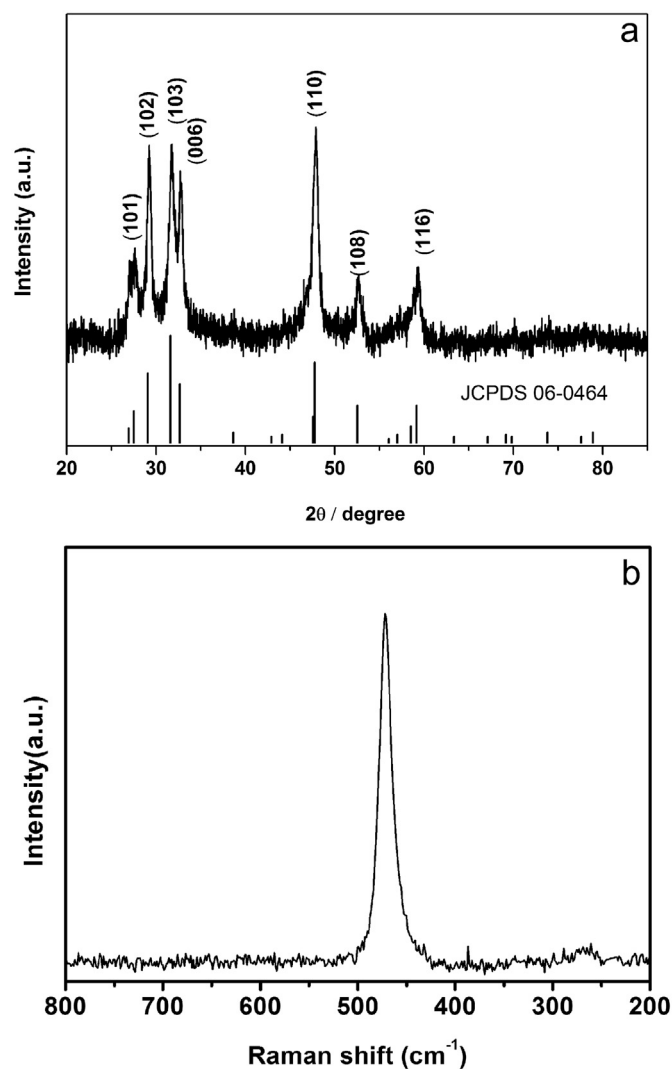


Fig. 1. (a) XRD patterns of as-grown CuS nanowire bundles; (b) Raman spectra of as-grown CuS nanowire bundles.

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