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Facile aqueous-phase synthesis of copper sulfide nanofibers

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ABSTRACT

We report a facile aqueous-phase synthetic route to vine-like copper sulfide (CuS) nanofibers prepared by reacting elemental sulfur with Cu^{+}-branched polyethyleneimine (BPEI) complex obtained by the reaction of Cu^{2+} with ascorbic acid in the presence of BPEI. By controlling the concentration of BPEI, we could easily control the morphology of CuS from nanofibers to hollow nanoparticles. We also found that concentration of BPEI and the presence of halide anion would play important roles in the formation of vine-like CuS nanofibers.

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1. Introduction

One dimension nanomaterials including nanorod, nanowire, and nanofiber have obtained much interest for their promising practical applications due to their unique and intrinsic physical and chemical properties compared with their bulk counterparts [1–3]. As an important p-type semiconducting material, 1D copper sulfide (CuS) nanostructures have been attracted more attention because of its unique properties and great potential applications in photo catalysts [4–6], sensors [7], solar cell [8], lithium-ion batteries [9,10], and etc.

Last a few decades, CuS nanostructures with controllable morphologies including rod, wire, plate, spherical, and flower-like structures have been synthesized by various synthetic methods such as microwave [7], solvothermal and hydrothermal [11–13], chemical vapor deposition [14,15], and wet chemical method [16]. For example, Saranya et al. synthesized the CuS nanomaterials by hydrothermal route which the temperature needed to be maintained at 150 °C for 24 h in the autoclave [12]. Ni et al. had successfully synthesized wrapped CuS nanowires in a large scale [13]. The process was operated at 180 °C for a short time via a simple hydrothermal process without the assistance of any surfactants. However, above mentioned synthetic methods need harsh reaction conditions including high reaction temperature, pressure, and toxic organic solvent. Therefore, for the industrial applications, it is strongly needed to develop a new synthetic process producing CuS nanostructures under mild reaction conditions.

In this article, we reports a facile aqueous-phase synthesis of vine-like CuS nanofibers by addition of an ethanol sulfur (S) solution into an aqueous solution containing $CuBr_2$, ascorbic acid, and BPEI at low reaction temperature of 60 °C. The synthesis was conducted using two sequencing reaction, formation of Cu^{+}-BPEI complex by reacting Cu^{2+} with ascorbic acid in the presence of BPEI, and synthesizing CuS nanofibers by reaction of Cu^{+}-BPEI complex with elemental S. By controlling the concentration of BPEI, we could easily control the morphology of CuS from nanofibers to hollow nanoparticles. We also found that the concentration of BPEI and the presence of halide anion would play important roles in the formation of vine-like CuS nanofibers.

2. Experimental

2.1. Synthesis of CuS nanofibers

A 0.02 M S solution was prepared by dissolving 3.2 mg S powder (0.1 mmol, Aldrich) in 5 mL of ethanol at 60 °C in a glass vial. 22.34 mg of copper bromide ($CuBr_2$, 0.1 mmol, Daejung) and 60 mg of BPEI (MW=750,000, Aldrich, 6 mg/mL in the final suspension solution) were dissolved in 2 mL of water to make a 0.05 M $CuBr_2$ solution. After mixing BPEI with $CuBr_2$ solution, 3 mL of L-ascorbic acid solution (0.6 M) was added to the above mixture solution and the resulting mixture was then heated to 60 °C. After 5 min, 5 mL of ethanol S solution was injected using a pipette and the final suspension was obtained and aged at same temperature for 30 min with stirring. After the reaction, the final suspension solution was centrifuged at 3000 rpm for 5 min to remove free BPEI and remained reagents. The precipitate was re-dispersed in water.

2.2. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured using a JEM-2100F

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microscope operating at 200 kV. Scanning electron microscopy (SEM) images were obtained using a LEO SUPRA 55 microscope. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA. X-ray photoelectron spectroscopy (XPS) data was obtained using a Thermo Scientific K-Alpha spectrometer.

3. Results and discussion

Vine-like CuS nanofibers were synthesized by using two sequencing reaction. First, Cu^{+}-BPEI complex was prepared by reacting $CuBr_2$ with ascorbic acid in the presence of BPEI in an aqueous-phase. After reacting $CuBr_2$ with ascorbic acid, the color of the solution changed from blue to green, indicating the reducing Cu^{2+} to Cu^{+} and formation of the Cu^{+}-BPEI complex. Then an ethanol S solution was injected to the reaction solution and aged at 60 °C for 30 min. The color of the resulting suspension solution was blackish green. A typical SEM image of the product shows the formation of 1D vine-like nanofibers with diameter of around 40–80 nm and length of 1–5 μm (Fig. 1a and b). A TEM image of a single nanofiber shows some nanofibers have a tadpole shape consisting of a spherical head with a diameter of around 60 nm (Fig. 1c). In addition, high-resolution TEM (HRTEM) characterization also shows that the nanofiber has lots of stacking faults (Fig. 1d and e).

Powder XRD patterns of the product show the presence of diffraction peaks at 29.4°, 31.8°, 47.9°, 52.8°, and 59.5°, which can be assigned to (102), (103), (006), (110), (108), and (116) planes of the hexagonal phase of CuS (Fig. S1 in Supporting information, *P63/mmc*, a = 3.792 Å and c = 16.344 Å, Joint Committee on Powder Diffraction Standards (JCPDS) file No. 06-0464), respectively. We did not find any diffraction peaks of other sulfide or oxide phase. XPS Cu 2p core level spectrum of the CuS nanofibers shows the presence of two peaks at 931.8 eV for Cu $2p_{3/2}$ and 951.08 eV for Cu $2p_{1/2}$, respectively, which corresponds to Cu^{2+} in CuS (Fig. 2a) [17]. The XPS S 2p core level spectrum indicates the S $2p_{3/2}$ and S $2p_{1/2}$ peaks at 161.18 and 162.28 eV, respectively, showing the presence of CuS (Fig. 2b).

In the present synthesis, Cu^{+}-BPEI complex synthesized by the

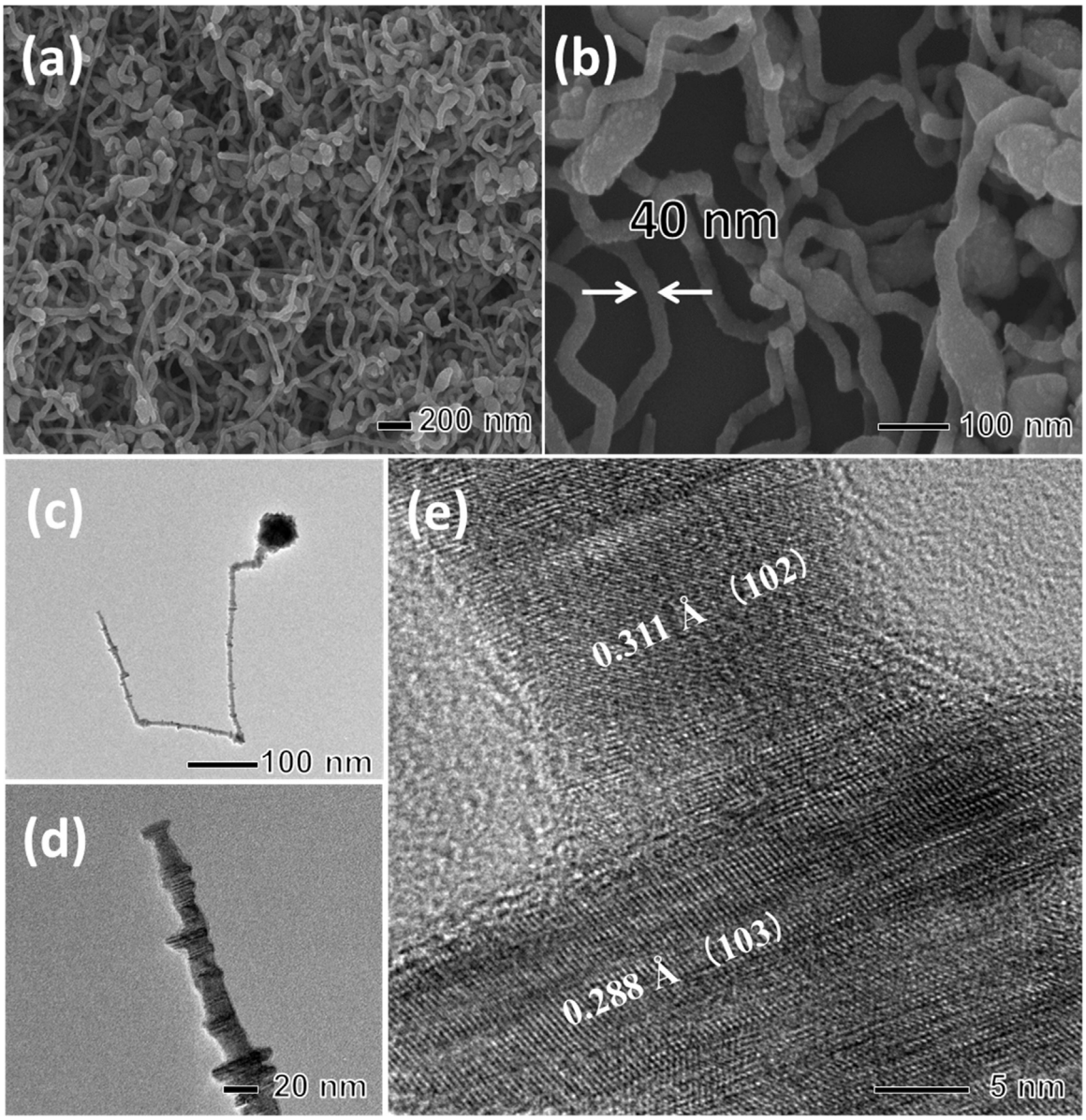

Fig. 1. (a and b) SEM and (c–e) TEM images of vine-like CuS nanofibers synthesized by reacting elemental S with Cu^{+}-BPEI complex obtained by the reaction of Cu^{2+} with ascorbic acid in the presence of BPEI.

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