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LETTER

Controllable synthesis of CuS nanotubes and nanobelts using lyotropic liquid crystal templates

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Considerable research attentions have been paid to one-dimensional (1D) nanostructures, due to their unique properties and applications in optical, electrical, and magnetic devices [1]. In particular, since the discovery of carbon nanotubes [2], research opportunities have been opened up for a variety of inorganic nanotubes [3–5]. Much many chemical methods have been reported to reach 1D nanostructures, such as self-assembly of 0D nanostructure [6], using capping reagents to control and modify the growth habit of a seed [7]. Especially, template-directed synthesis represents an elegant straightforward route to organize 1D nanostructures and to control the size and shape of nanocrystals [8]. Among the various nanoscale materials, nanobelts have also attracted much interest as potential interconnects and active components in fabricating nanoscale electronic and photonic devices [9].

As a member of the chalcogenides, copper sulfide possesses excellent optical and electrical properties and shows semiconductor or metallic conductivity and transforms to a superconductor at 1.6 K [10]. Copper sulfide with 1D morphologies has been prepared using some chemical methods up to date [11–16]. Herein, we report a controllable synthesis route for the preparation of homogenous CuS nanotubes and nanobelts in the lyotropic nematic media composed of nonionic-anionic mixed-surfactant, which acts as the soft template under moderate condition.

Typically, the synthesis procedure for CuS nanotubes is as follows. 2.50 g $CuSO_4 \cdot 5H_2O$ was dissolved to a transparent solution in 10 ml H_2O containing 2.32 g (1s)-(+)-10-camphorsulfonic acid (CSA) and 12.84 g polyoxyethylene sorbitan monopalmitate (Tween 40) at 333 K. Then the mixture was cooled slowly to 293 K and allowed to silently stand at that temperature for 1 h. Then 2.48 g $Na_2S_2O_3 \cdot 5H_2O$ was added to the above homogeneous mixture and then kept rest for 12 h. The resulting solid was collected, washed using distilled water and ethanol prior to dry in air at room temperature. Then 0.3 g of the precursor solid was put into a Teflon-lined stainless steel autoclave of 40 ml capacity filled with 30 ml absolute ethanol. The autoclave was sealed and maintained at 393 K for 12 h and then cooled down to room temperature. The resultant CuS powders were washed with distilled water and ethanol for several times, dried in vacuum. Similar synthesis using $CuCl_2 \cdot 2H_2O$ in place of $CuSO_4 \cdot 5H_2O$ and thioacetamide in place of $Na_2S_2O_3 \cdot 5H_2O$ was carried out to obtain CuS nanobelts.

Powder X-ray diffraction (XRD) measurements were performed on Philips X'Pert MPD Pro X-ray diffractometer, with graphite monochromatized Cu Kα radiation ($\lambda = 0.15406$ nm) operating at 50 kV. Transmission electron micrographs (TEM) were taken on a JEM-100S Electron Microscope (JEOL), using an accelerating voltage of 80 kV. The ultraviolet and visible light (UV–vis) absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer.

Figure 1a, b shows XRD patterns of the precursors for CuS nanotubes and nanobelts before treatment in

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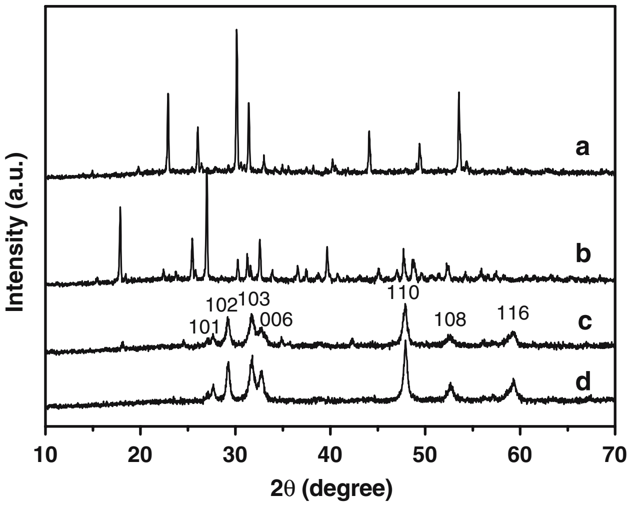


Fig. 1 XRD patterns of (**a**) the precursor for CuS nanotubes before hydrothermal treatment; (**b**) the precursor for CuS nanobelts before hydrothermal treatment; (**c**) CuS nanotubes; and (**d**) CuS nanobelts

the autoclave. The precursor of CuS nanotubes is composed of copper–thiosulfate complexes, as reported in the previous literature [17]. The precursor for CuS nanobelts is Cu(thioacetamide)$_3$Cl complex [18]. Figure 1c, d shows typical XRD patterns of the CuS nanotubes or nanobelts after hydrothermal treatment in autoclave. All the diffraction peaks can be indexed to the hexagonal CuS crystal phase with $a = 3.795$ Å and $c = 16.344$ Å, in agreement with the data of JCPDS No. 06-0464.

The typical morphologies of the as-prepared samples are characterized by TEM. From the TEM images, it can be seen that the precursor for CuS nanotubes is in a sheet-like morphology (Fig. 2a), while the precursor for CuS nanobelts, synthesized with CuCl$_2$·2H$_2$O and thioacetamide, is in a belt-like morphology (Fig. 2b). Figure 3a shows that the CuS nanotubes have inner diameters of 100–250 nm, outer diameters of 200–500 nm and lengths up to several micrometers. Figure 3c indicates that the morphology of CuS nanobelts are very uniform, with width of about 300 nm and lengths up to several hundred micrometers. Figure 3b, d provide a further insight into the nanostructures of the two CuS one-dimensional nanocrystals. From the head part of the single nanotube as shown in Fig. 3b, specially, it might confirm that these nanotubes form through the rolling of the sheet-like structure of precursor.

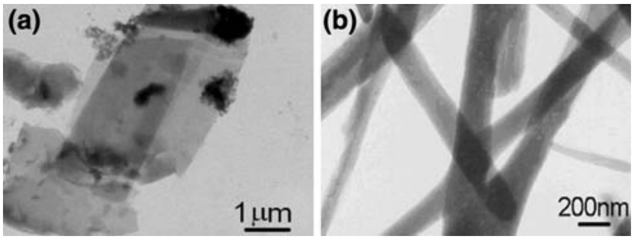


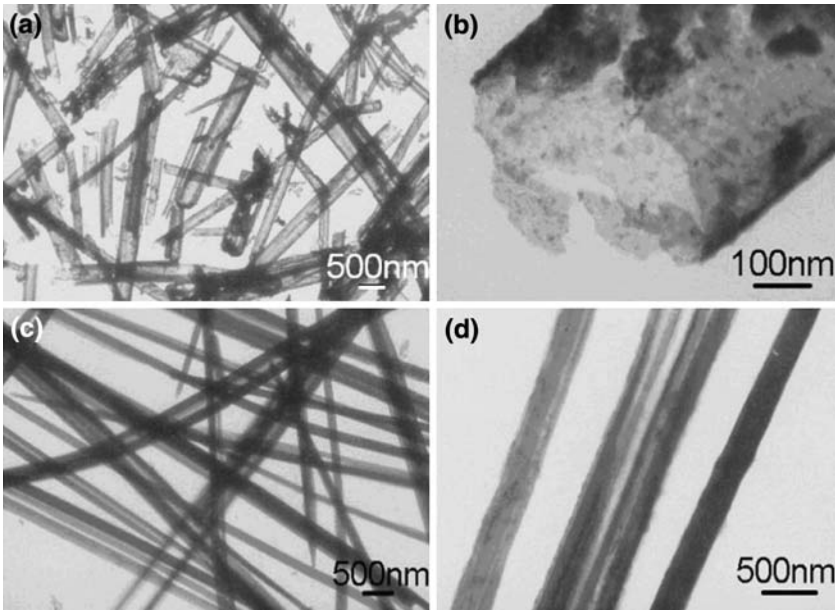
Fig. 2 TEM images of (**a**) the precursor for CuS nanotubes before hydrothermal treatment; and (**b**) the precursor for CuS nanobelts before hydrothermal treatment

The UV–vis absorption spectra present the optical properties of CuS nanotubes and nanobelts. Figure 4a shows the absorption spectrum of the CuS nanotubes, which displays a sharp peak at 255 nm, while the UV–vis spectrum of CuS nanobelts shows an absorption peak at 235 nm (Fig. 4b). Compared with the absorption onset of bulk CuS, the appearance of the two new absorption peaks might be due to the defects at the interface of nanocrystalline CuS, as color centers [19].

Understanding the mechanism for the formation of tubular structure from the precursory sheet-like structure is particularly intriguing. The lyotropic nematic media composed of nonionic–anionic mixed-surfactant provides an ideal template for the growth of artificial sheet-like structure. The process for the formation of the nanotubes can be divided into three main steps. (1) Based on the condensation mechanism of anionic surfactant molecules with cationic inorganic species, the CSA molecules condensed into aggregations with Cu^{2+} ions intercalate into the interspaces between the headgroups of surfactant Tween 40 to form CSA–Cu ion pairs. (2) The nonionic surfactant Tween 40 as the lyotropic nematic media is essential to stabilize the CSA–Cu ion pairs and to bring out the lamellar assembly. The lamellar micelles are formed side by side with the hydrophilic head groups and the hydrophobic tail groups of the two-surfactant molecules. Then, the metallic ions are confined in the aqueous interface of mixed-surfactant lamellar micelles. (3) The 2D sheets formed by deposition reaction in between the lamellar micelles scroll up to 1D nanotubes. The driven force for the rolling behavior is attributed to the decrease of the surface free energy of the sheet-like structure controlled by reaction conditions. During the heat treatment with gradually elevated temperatures, these sheets begin to loosen at the sheet edge and then scroll into nanotubes. The above process is schematically shown in Fig. 5.

The major mechanism for formation of CuS nanobelts, however, provides an interesting comparison. The precursor for CuS nanobelts seems rigid, compared to the precursor of CuS nanotubes, and difficult to roll-up to nanotubes at low-temperature hydrothermal condition. The interlayer interaction of this kind of belts might not be diminished from the belt edge, and

Fig. 3 TEM images of (**a**, **b**) CuS nanotubes; and (**c**, **d**) CuS nanobelts



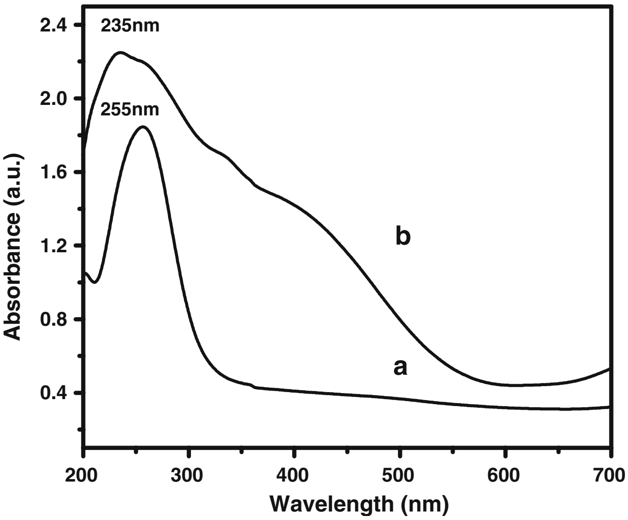


Fig. 4 UV–vis absorption spectra of (**a**) CuS nanotubes and (**b**) CuS nanobelts

the rolling of these belts into tubules should not be expected [20]. The detailed structural characterization still needs to be carried out further.

In summary, CuS nanotubes with inner diameters of 100–250 nm, outer diameters of 200–500 nm and length up to several micrometers and CuS nanobelts with width of about 300 nm and lengths up to about several hundred micrometers have been prepared by using lyotropic nonionic-anionic mixed-surfactant liquid crystal as template. The lamellar liquid crystal offered a confined hydrophilic environment for a sheet-like precursors of CuS for nanotubes or nanobelts. CuS nanotubes are obtained by performing hydrothermal treatment on the sheet-like precursor, which underwent a ‘‘rolling-up’’ process to form nanotubes. The mixed-surfactant template synthesis strategy provides a feasible route to the synthesis many related materials with 1D nanostructures.

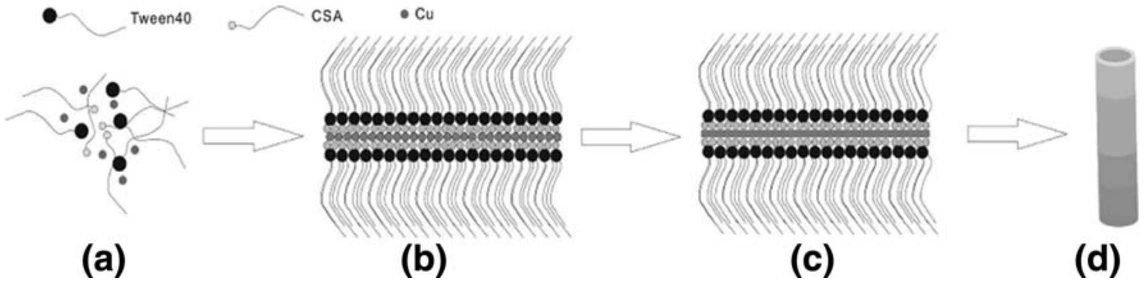


Fig. 5 Schematic shown of the rolling-up mechanism for the formation of CuS nanotubes: (**a**) homogeneous solution of CSA, Tween40, and Cu^{2+}, (**b**) assembly of CSA, Tween 40 and Cu^{2+} in a sheet-like structure, (**c**) precursor of CuS nanotubes, (**d**) rolling-up of the sheet-like structure into nanotubes under hydrothermal conditions

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