A Novel in situ Template-controlled Route to CuS Nanorods via Transition Metal Liquid Crystals

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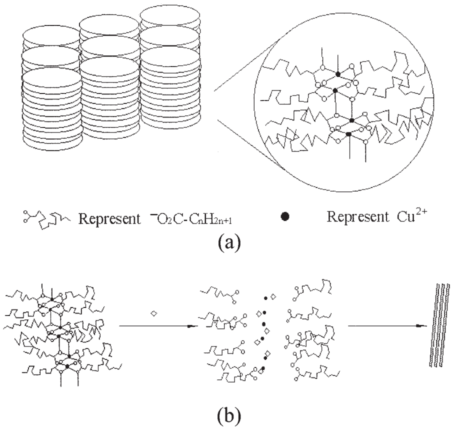
A novel and simple route, called in situ template-controlled (ISTC) method, has been developed to fabricate low-dimensional CuS nanorods by firstly taking advantages of TMLC's semi-ordered arrangement.

Developing a controlled-synthesis route is always one of the most important goals of materials scientists. Since Iijima[1] discovered multiwalled carbon nanotubes in arc-discharge apparatus, the fabrication of low-dimensional nanomaterials has been the focus of considerable interest because of their potential applications in mesoscopic research, nanostructured composite materials, and the development of nanodevices. However, up to now, it is also much challengeable to fabricate or synthesize these low-dimensional materials owing to their extremely small size and their anisotropy. The control of nucleation and growth of low-dimensional nanostructural materials is becoming critical.

The ubiquitous presence of liquid crystal display (LCD) has made liquid crystal (LC) perhaps the most popular and familiar class of advanced materials in the modern life.[2] The LC consists of two categories, lyotropic LC and thermotropic LC. Under proper conditions, LC presents the semiordered arrangement that is common at solid crystal state, and semi-fluidity that is the attribute of liquid state. Owing to its promising characteristics, many researchers have been thinking about taking it as template to controllably produce low-dimensional nanoscale materials. Very recently, various nanoscale semiconducting superlattices have been generated by direct-template synthesizing in a lyotropic organic LC,[3] and our recent work on preparation of ZnS nanowires also made use of lyotropic organic LC.[4] However, to our best knowledge, the synthesis of nanomaterials by using thermotropic LC as the template has not, as yet, been reported.

In the last decade, a new class of LC containing transition metals, so called metallomesogen, has burst into the field.[5] Transition metal liquid crystals (denote as TMLCs hereafter) belong to thermotropic LC. Some of TMLCs, the molecular figures presented in Scheme 1, are composed of long-chain symmetrical molecules and transition metal cations,[6] and others are made of asymmetrical ones and transition metal cations.[7] To date, most of these new TMLCs have been of only academic interest, but their special properties have brought about expectations that are attracting an increasing number of researchers. Herein, we just use these special structures of TMLCs to provide a novel route to controllably synthesize CuS nanorods. As far as we know, this method is first developed to fabricate low dimensional nanomaterials.

Transition metal chalcogenides including sulfides, selenides and tellurides are often found in minerals and they have a number of commercial applications in pigments, semiconductors, fluorescence devices and even superconductors.[8] It is well known that copper sulfides are useful minerals, and their mineralogical and technological properties have been studied extensively,[9] furthermore copper sulfides exhibit fast-ion conduction at high temperature.[10] Traditionally, copper sulfides have been synthesized by solid-state reactions,[11] and self-propagating high-temperature synthesis.[12] Recently, Parkin reported a low-temperature route to synthesize copper sulfides via elemental reaction in liquid ammonia.[13] But only the mixture of $Cu_{1.8}S$, $Cu_{7.2}S_4$, $Cu_{1.96}S$ was obtained, moreover, during their experiments, several manipulations had to be carefully carried out at −77 °C in thick-walled glass vessels, and all operations had to be conducted with care and behind a safety screen.



(a)

(b)

Scheme 1. (a) Schematic representation of the hexgonal columnar mesophase of copper(II) carboxylates[4,5] and (b) the reaction process of production of CuS nanorods.

In this letter, we explored an in situ method to fabricate low-dimensional CuS nanorods by taking advantage of the ordered array of the metal cations chelated with organic molecules, which acts as a template in the process. The low-dimensional CuS nanorods have been prepared by using the molecules ($[Cu_2(O_2C–C_{17}H_{35})_4]$, shown in Scheme 1a as the copper source and gaseous H_2S as the sulfur feedstock under the temperature at which the coordination compounds show anisotropic LC properties. Comparing with the above-mentioned methods, CuS was produced here under a relatively lower temperature. It is orderly embedded in the TMLCs where anions combine with the cations, and TMLCs, serving as the templates, assisted the oriented growth of crystals. TMLCs also show more stable arrangements than lyotropic LC to be served as soft template.

According to the literatures,[6b–d] we made the copper stearates ($Cu_2(O_2C–C_{17}H_{35})_4$) as the TMLC at first, whose transition temperature is about 119 °C. Dry H_2S was imported to the TMLCs in its mesogenic phase (LC phase) at 120 °C for 11 h. The color of the mesophase changed from celeste to indigo blue, and it showed semifluidity after a while. At the end of the reaction we detected some black precipitates over the TMLC. The black precipitates were filtered out, washed with distilled water and absolute alcohol in subsequence, and then dried in vacuum at room temperature for 4 h.

In order to detect the transition temperature of copper stearates [$\mathrm{Cu_2(O_2C{-}C_{17}H_{35})_4}$] to the TMLC, which plays an important role in the process of synthesizing CuS nanorods, the DSC[14] pattern of the copper stearates is taken and from which one can see that the compound becomes glassy in appearance at 117–122 °C, closed to the transition point in the literature.[6]

The XRD[15] pattern of the products is shown in Figure 1, and all its reflection peaks can be indexed to the hexagonal CuS phase with the parameters $a = 3.786$ Å and $c = 16.337$ Å, which are very close to the reported data ($a = 3.792$ Å and $c = 16.344$ Å). The average crystalline size of CuS estimated by the Scherrer equation based on the XRD linewidths is about 40 nm. In addition, the 002 and 006 planes become obviously stronger than those in the traditional bulk CuS, which indicates the oriented growth of the crystal. The result can also be proved by the observation of TEM[16] images (Figure 2a), in which we can see that the most products are of rod-like morphology.

In the case of the formation of CuS and the properties of TMLC, the reaction could be described as follows:

$$\mathrm{Cu_2[(O_2C{-}C_{17}H_{35})_4] + 2H_2S \xrightarrow{130\,^{\circ}C} 2CuS + 4HO_2C{-}C_{17}H_{35}}$$

CuS nanorods obtained from our method are result from the reaction at gas-LC interface. In this process, lots of discotic TMLC constructed to a semiordered column-like arrangement (shown in Scheme 1b). The infiltration of H_2S won't change the ingredients of the TMLC in a short time. When H_2S molecules touched the interface of the TMLC, S^{2-} anions appeared and penetrated into the semifluid TMLC, and then the S^{2-} anions combined with the Cu^{2+} cations. Because of the semiordered column-like arrangement of TMLCs, the nanocrystals synthesized here show rod-like shape (Figure 2a). Accompanying with the proceeding of replacement of ligands by S^{2-} anions, more and more ligands escape out and the columns tend to topple down. It can be expected that it was very difficult to the formation of pure one-dimensional CuS and the escaped cations will promote the formation of nanoparticles facilely (Figure 2b). So the CuS obtained by this method is mostly made of rod-like fibers (The yield for rod-like fibers is beyond 85% from several typical TEM images.) and a small portion of particles, which is consistent with TEM images.

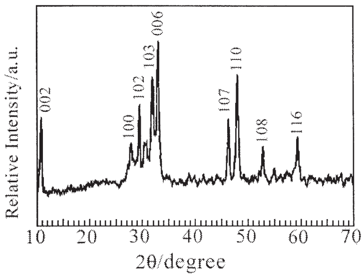


Figure 1. The XRD pattern of as-prepared CuS.

In summary, a novel utility of TMLC is introduced to the field of constructing inorganic nanocrystals. CuS nanocrystals are in situ synthesized and show rod-like morphology. The possible mechanism to prepare copper sulfides is discussed. With respect to the future research work, we hope that we can take advantage of other TMLCs to manufacture other more important inorganic nanocrystals.

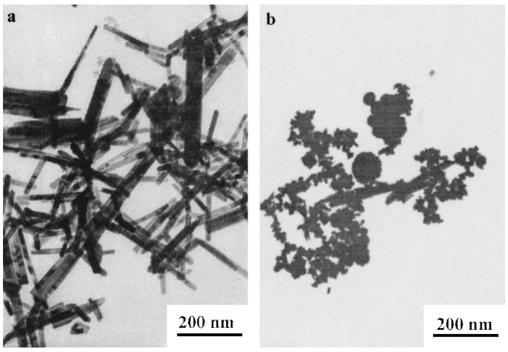


Figure 2. TEM images of as-prepared CuS.

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14 The DSC analysis was carried out with a Shimadzu DSC-50, enwrapped with nitrogen atmosphere. The rate flow was 20.00 ml/min.

15 The XRD analysis was carried out with a Japan Rigaku D/max-γ rotation anode X-ray diffractometer using Ni-filtered Cu Kα radiation at 25 °C.

16 TEM images were taken with Hitachi H-800 transmission electron microscope at the acceleration voltage 200 kV.