

Template Synthesis of Ag₂S Nanorods via an Ion-exchange Route

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By using CdS nanorods as template, Ag₂S nanorods were synthesized via a solution-phase ion-exchange route at room temperature. It is important to control a slow reaction speed by adding thiourea into the solution to form complex with Ag⁺ ion during the synthetic process.

Recently, considerable progress has been made in the syntheses of one-dimensional (1-D) nanostructure materials, such as nanowires, nanorods, and nanotubes, because of their novel electrical and optical properties, and potential applications in nanodevices.¹⁻⁴ In order to obtain the desired 1-D nanostructure materials, various preparation methods have been developed, including template directed synthesis,⁵⁻¹⁵ laser-assisted catalytic growth,¹⁶ solution-phase method,¹⁷ and the chemical vapor deposition (CVD) route.¹⁸ Particularly, lots of research on template syntheses of 1-D nanostructure materials have been done. The templates used in these methods are commonly divided into "hard" templates and "soft" ones. "Hard" templates include anodized aluminium,⁵⁻⁷ zeolite,⁸ mesoporous silica^{9,10} and carbon nanotubes^{11,12} as they have inner channels which serve as template. "Soft" templates include DNA chains,¹³ polymer film of poly(vinylalcohol) (PVA),¹⁴ and micelles of cetyltrimethylammonium bromide (CTAB).¹⁵

Herein, we report a template-directed solution-phase approach for the preparation of Ag₂S nanorods at room temperature. The template used was CdS nanorods, which also served as reacting substance. Because of the difference in solubility of sulfides in water, Cd²⁺ ion can be exchanged from CdS by Ag⁺ ion. This method is simple and convenient, and does not need any complicated apparatus. Further, it avoids removing the template as the template has been consumed during the synthetic process.

All chemical reagents are of analytical grade and used as received without purification. The preparation of 1-D CdS nanorods was reported in other literatures in detail.^{19,20} In a typical procedure, 0.170 g AgNO₃ and 0.456 g Thiourea (Tu) were dissolved in 50-mL distilled water. 0.010 g fresh CdS nanorods were ultrasonically dispersed into 50-mL distilled water. Then, these two solutions were mixed together under magnetic stirring. The mixed solution was kept being stirred for 5 h, and then the precipitates were centrifuged and washed with distilled water and absolute ethanol several times each, and dried in vacuum at 60 °C for 2 h.

X-ray powder diffraction (XRD) was carried out on a Philips X'pert PRO SUPER diffractometer with Cu K α radiation ($\lambda = 0.154187$ nm). The transmission electron microscopy (TEM) images were recorded on a Hitachi Model H-800 transmission electron microscope. The ultraviolet and visible light (UV-vis) absorption spectra were taken on a Shimadzu UV 365 spectrophotometer.

The XRD pattern of the synthesized Ag₂S nanorods is shown in Figure 1. All the peaks can be indexed to monoclinic phase Ag₂S with lattice constants of $a = 0.4158$, $b = 0.6915$, $c = 0.7839$ nm, which are consistent with the standard values (JCPDS 14-72, $a = 0.4229$, $b = 0.6931$ and $c = 0.7862$ nm). No obvious peaks of CdS can be detected from XRD measurement.

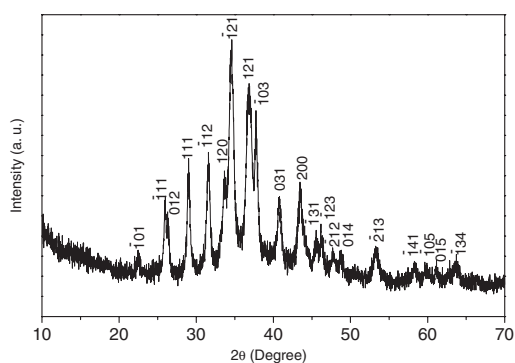


Figure 1. XRD pattern of the Ag₂S nanorods.

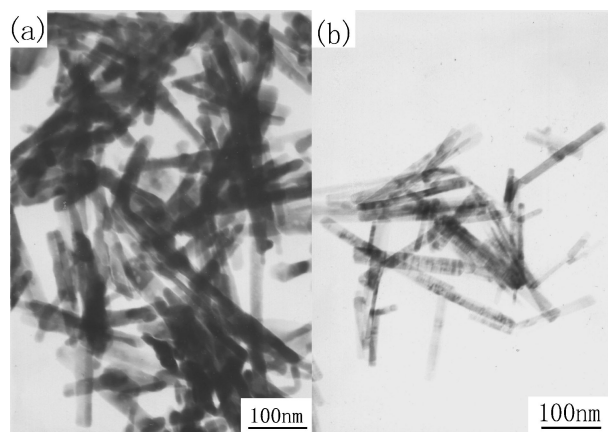


Figure 2. TEM images of (a) the prepared Ag₂S nanorods and (b) the initial template CdS nanorods.

The morphology of the obtained Ag₂S sample is shown in Figure 2a. From this image it can be seen that the product is composed of nanorods. The sizes of these nanorods are approximately 10–15 nm in width and up to several hundred nanometers in length. Figure 2b shows the TEM image of the initial CdS nanorods that were used as template. The sizes of these CdS nanorods are similar to those of the Ag₂S nanorods shown in Figure 2a. That's to say, the product retained the morphology of the template.

Figure 3 shows the UV-vis spectrum of the as-prepared product obtained from the supernatant of the product powders dispersed in absolute ethanol by applying ultrasonication. There is a broad peak at about 530 nm in Figure 3. The band gap of Ag₂S nanorods calculated from this UV-vis spectrum is 2.34 eV. Compared with the direct band gap (1.3 eV) of bulk Ag₂S,²¹ the Ag₂S nanorods show obvious blue shift in UV-vis absorption.

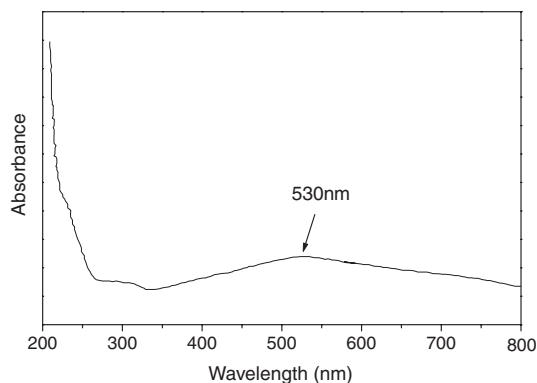


Figure 3. UV-vis absorption spectrum of the as-prepared Ag₂S nanorods.

CdS and Ag₂S are all faintly soluble in water. The solubility of Ag₂S is much lower than that of CdS. So when CdS is added into AgNO₃ solution, Ag⁺ ion can replace Cd²⁺ ion in CdS and form Ag₂S. Through this ion-exchange process, CdS can be completely transformed into Ag₂S. When the ion-exchange process is slow enough, the obtained Ag₂S can retain the morphology of the initial CdS.

It is known that the reaction speed is relevant to the concentration of reactors in solution, so by controlling the concentration of metal ions in solution we can control the ion-exchange speed. Adding ligands into the metal ion solutions can dramatically decrease the concentration of metal ions. In our experiments, Tu is served as ligand. We have conducted the reaction without the adding of ligand, the reaction completed in a much shorter time and the obtained product was made up of irregular nanoparticles instead of nanorods. We have also studied the effect of different ligands in the experiments. In preparing Ag₂S we have tried EDTA, NH₃·H₂O and trisodium citrate, respectively. All the results were not reasonable; the obtained products were composed of nanorods and nanoparticles. It is reported that the stability constant of Ag-Tu complex is much higher than that of [Ag(NH₃)₂]⁺, Ag-EDTA and Ag-trisodium citrate complexes,²² so in the case of using Tu as the ligand, the concentration of Ag⁺ ion is the lowest. As a result, the ion-exchange speed is the slowest. Only this reaction speed is favorable for retaining the morphology of the initial template.

In summary, Ag₂S nanorods are successfully prepared by using CdS nanorods as template via an ion-exchange route at room temperature. The ion-exchange process is controlled by

adding proper ligand into the solution to form complex with Ag⁺ ion. This method provides a simple and convenient way for preparing 1-D nanostructure materials.

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