

A surfactant-assisted photochemical route to single crystalline HgS nanotubes

Ting Ren, Shu Xu, Wen-Bo Zhao, Jun-Jie Zhu*

Key Lab of Analytical Chemistry for Life Science, Department of Chemistry, Nanjing University, Nanjing 210093, PR China

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Abstract

A surfactant-assisted photochemical method has been developed to prepare tube structural single crystalline mercury sulfide (α -HgS). The HgS nanotubes have well-defined structure with the wall thickness of 20–30 nm. The as-prepared HgS nanotubes were characterized by employing techniques including X-ray powder diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, selected area electron diffraction, high-resolution transmission electron microscopy. The characterizations of the products in various stages exhibited the probable reaction process could be divided into three steps in sequence: the formation of the nascent poly(vinylpyrrolidone) (PVP)-coated HgS particles, their assembly and crystal growth. It was found that PVP served as dispersant and stabilizer in the formation of the homogeneous nascent HgS particles and more importantly, the direct UV photocrosslinking of PVP was exploited to induce the assembly of the PVP-coated particles and the growth to tube structure.

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1. Introduction

Recently, One-dimensional (1D) nanostructures, such as nanotubes, nanorods and nanowires are known to have many fascinating physical properties, and are of great importance in both basic scientific research and potential technological applications [1]. Many unique and interesting properties have been proposed or demonstrated for nanoscale 1D materials, such as superior mechanic toughness, higher luminescence efficiency, enhancement of thermoelectric figure of merit, and lowered lasing threshold [2]. 1D nanostructures are also ideal systems for investigating the dependence of electrical transport, optical properties and mechanical properties on size and dimensionality [3]. Thus, downscaling a broad range of materials to 1D nanoscopic structures is currently the focus of rapidly increasing interest.

Up to now, various methods for generating 1D nanostructures have been developed, such as vapor deposition methods [4], solvothermal methods [5,6], solution-phase methods based on capping reagents [7] and template-directed synthesis method [8,9]. In all these methods, for obtaining nano-materials with well-defined 1D structure, the stable growth circumstance is required. In the current years, photochemical methods have increasingly become important for the synthesis of nanoparticles, nanocomposites and the control of morphology because of the easier accessibility, greater safety, and manipulation at room temperature [10–15]. Moreover, the photochemical approach has the advantage in the crystal growth for its very stable circumstance. However, this method has not been widely adopted in synthesis of nanomaterials with 1D structure.

Herein, a surfactant-assisted photochemical approach (UV irradiation) was developed for the preparation of tube-like HgS nanoparticles. Mercury sulfide is a kind of technologically interesting material in quantum electronics [16] and is widely used in many fields such as ultrasonic transducers

* Corresponding author. Tel.: +86 25 83594976; fax: +86 25 83317761.
E-mail address: jizhu@nju.edu.cn (J.-J. Zhu).

[17,18], electrostatic image materials [19], photoelectric conversion devices [17–19] and infrared sense [20]. Some methods for the synthesis of nanostructural mercury sulfide have been reported in the past few years [20–24]. However, up to now, few references reported the preparation of one-dimensional mercury sulfides for the difficulty in control of the growth of the particles in a certain direction [21]. In our experiments, due to the controllability and the relatively slow growth rate of the nanotubes under UV irradiation, the as-prepared HgS products had more uniform tube-like structure with homogeneous wall thickness compared with the reported mercury sulfides nanotubes. Probable mechanism for the photochemical formation of the HgS nanotubes was presented. Both the presence of PVP and ultraviolet irradiation were found to play important parts in the fabrication of tube-like structure.

2. Experimental

All the reagents used in our experiments were of analytical purity, and were used without further purification. Mercury acetate was purchased from Shanghai Second Chemical Reagent Factory (China). Sodium thiosulfate and ammonia solution were purchased from Nanjing Chemical Reagent Factory (China). Absolute ethanol and acetone were purchased from Shanghai Chemical Reagent Factory. Poly (vinyl pyrrolidone) (PVP-K30, MW 40,000) was purchased from Huakang Co. Chemical Reagent Factory (China). Distilled water was used in our experiments.

The XRD pattern was recorded using a Philip X'pert X-ray diffractometer at a scanning rate of $4^\circ/\text{min}$ in the 2θ range from 20° to 80° , with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418\text{\AA}$). The TEM and ED images were recorded on a JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV. The HRTEM images were recorded on a JEOL-4000EX transmission electron microscope, using an accelerating voltage of 400 kV. The X-ray photoelectron spectra (XPS) were recorded on ESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg $K\alpha$ X-ray as the excitation source. Differential scanning calorimetry (DSC) thermograms were measured on a Perkin–Elmer instrument (Pyris 1 DSC) in aluminum pans at $20^\circ\text{C}/\text{min}$ under a flowing nitrogen atmosphere. FT-IR measurements were carried out with a JASCO IR-460.

In a typical procedure, 3.0 g PVP was dissolved in 50 ml distilled water in a glass beaker, 1.27 g $\text{Hg}(\text{CH}_3\text{COO})_2$, 2 ml 25% $\text{NH}_3(\text{aq})$ and 2.5 g $\text{Na}_2\text{S}_2\text{O}_3$ was added to the PVP solution. Ammonia solution was added to adjust the pH of the solution to 10. Then the mixture solution was placed about 10 cm away under a 500 W, column-like, high-pressure mercury lamp ($\lambda > 290\text{ nm}$) and exposed to ultraviolet irradiation for 30 h at room temperature. After the reaction finished, the red precipitates were washed with distilled water and absolute ethanol, and dried in air.

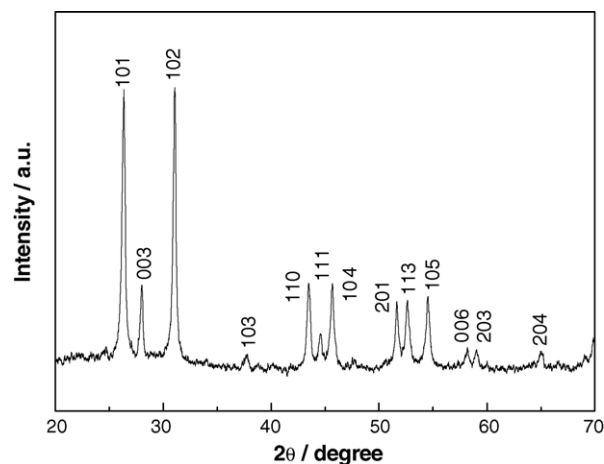


Fig. 1. The XRD pattern of the as-prepared HgS nanotubes.

3. Results and discussion

To study the crystalline structures of the products, XRD measurements were carried out at room temperature. The XRD pattern of the product was shown in Fig. 1. In the figure, no peaks of any other phases were detected, indicating the high purity of the product. All the diffraction peaks could be indexed to be a pure hexagonal phase HgS (cinnabar). The calculated cell parameters are $a = 4.174\text{ \AA}$, $c = 9.483\text{ \AA}$, which is in good agreement with the literature values of $a = 4.149\text{ \AA}$, $c = 9.495\text{ \AA}$ (JCPDS, No. 6-0256).

The as-prepared HgS nanotubes were also characterized by XPS measurements for the evaluation of their composition. Fig. 2 exhibited the corrected XPS spectra of the as-prepared HgS sample. The C 1s peak lies at 299.5 eV, which should be corrected to 284.6 eV. All the other peaks were corrected accordingly. The wide XPS spectrum was shown in Fig. 2a. No peaks of other elements except C, O, Hg, and S were observed on the picture. Fig. 2b and c showed the high-resolution XPS spectra of Hg 4f and S 2p, respectively. The two strong peaks taken for the HgS region at 99.35 and 103.4 eV were assigned to the Hg 4f binding energy. The peaks measured in the S energy region detected at 160.5 and 161.6 eV were attributed to the S 2p transitions. According to the measurements of the Hg 4f and S 2p peak areas, the ratio of Hg to S was calculated to be 1.1:1, which presents very close ratio of 1:1 HgS in the resultant products.

The dimensions and morphologies of the resultant products were studied by TEM measurements. Fig. 3 showed a TEM image of the as-prepared HgS nanotubes. The external diameter of these tubes was in the range of 100–150 nm, while the wall thickness was in the 20–30 nm ranges. It was apparently observed that the boundary of the wall of the tube was quite well defined. The electron diffraction patterns (inset of Fig. 3) taken on different individual nanotubes were essentially the same, which indicated the single crystalline structure of HgS nanotubes. HRTEM measurements were also used to study the HgS nanotubes. However, we found that it

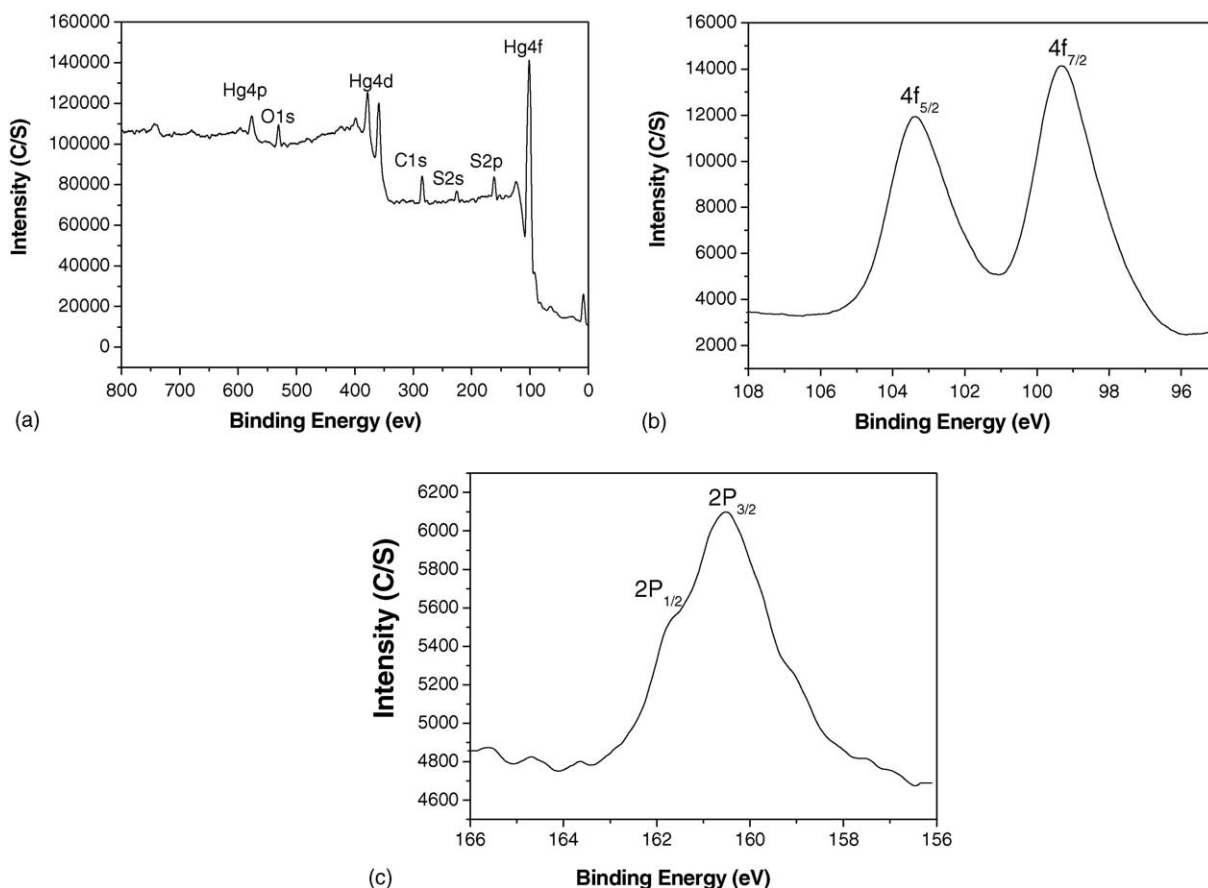


Fig. 2. The XPS spectra of the as-prepared HgS nanotubes.

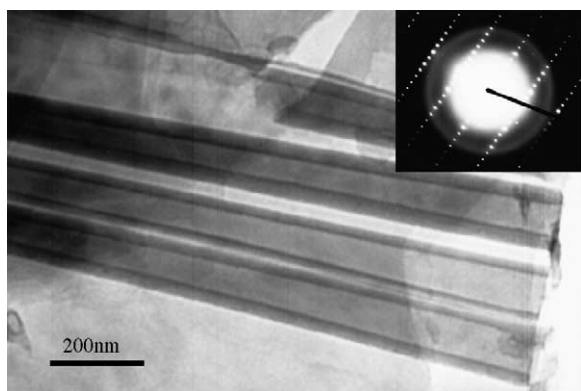
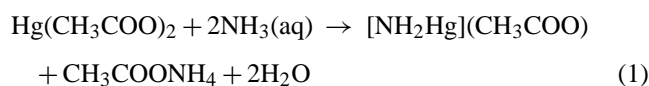


Fig. 3. TEM image of α -HgS nanotubes and the electron diffraction pattern (inset) taken from an individual nanotube.

was difficult to record high-resolution electron microscopy images of HgS nanotubes, because of the high sensitivity of HgS, like that of bismuth [25], to electron beam irradiation during the examination, which is expected due to its low melting points.

In order to discuss the growth mechanism of HgS nanotubes, various stages of the reaction process were studied by using TEM measurement; the results were shown in Fig. 4. When the solution was mixed directly with sodium thiosulfate-

fate, a black precipitate was immediately formed, because aqueous solution of mercury (II) salts was easier to hydrolyze. However, if ammonia was added to the solution, white colloids begin to form by the following reaction:



As shown in Fig. 4a, the white $[\text{NH}_2\text{Hg}](\text{CH}_3\text{COO})$ colloids were slightly agglomerated particles with an average size of 40 nm.

The addition of sodium thiosulfate to the white colloids mixture solution can lead to the formation of thiosulfate complexes [24]. As a result, dissolution can be observed. The mercury(II) ions were released from the thiosulfate complex, while sulfide ions were released from thiosulfate ions in alkaline media under irradiation. The reaction was described as follows [26]:

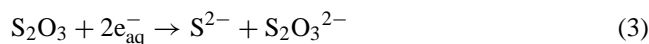


Fig. 4b showed the TEM image of the sample taken from the solution after irradiation for 20 min. In the image, the

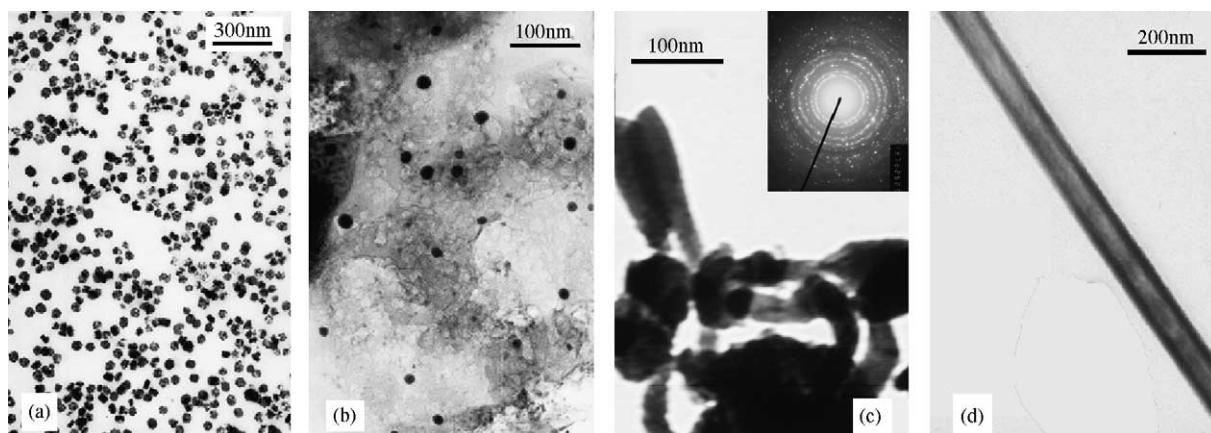


Fig. 4. TEM images of different stages of the reaction process for HgS nanotubes: (a) obtained white colloids before adding $\text{Na}_2\text{S}_2\text{O}_3$, (b) the initial product after 20 min photoirradiation, (c) the intermediate product after 5 h photoirradiation, (d) an individual HgS nanotube.

monodispersed particles with the size of 20–30 nm were observed. It may be some HgS nascent particles first formed under the photoirradiation. As shown in Fig. 4c, the product had exhibited the tendency of tubular morphology after 5 h photoirradiation. However, the boundary of the wall of the tube was not well defined. The electron diffraction pattern (inset of Fig. 4c) demonstrated the polycrystalline structure of these tubes composed of small particles. An individual HgS nanotube in the resultant products was shown in Fig. 4d. It was found that the dimension of wall thickness was consistent with that of the nascent nanoparticles.

To further prove the important roles of both PVP and ultraviolet irradiation in the synthetic process of HgS nanotubes, the differences in the resultant products were investigated in the absence of PVP or UV irradiation. Without the PVP in the reaction, the photochemical reaction only produced the irregular HgS nanoparticles instead of the tube-like morphology (Fig. 5a), which indicated that the large particles grew from the aggregated nascent HgS particles, and this kind of

aggregation is irregular. On the contrary, the assembly of the PVP-coated nascent particles under ultraviolet irradiation was ordered. When the mixture solution was placed in 40 °C water bath instead of ultraviolet irradiation and other conditions were kept unchanged, it was found that only dispersed regular single crystalline HgS particles could be observed (Fig. 5b). In spite of the presence of PVP, the assembly of the particles into tubular structure will not take place without ultraviolet irradiation. All the evidences proved that the formation of tube-like morphology could be attributed to the cooperative action of PVP and ultraviolet irradiation.

Based on above discussions, a mechanism for the formation of the HgS nanotubes is proposed. The synthetic process is a PVP-assisted photochemical route. In this process, the surfactant PVP plays roles on at least two aspects: preventing the aggregation of the HgS nascent nanoparticles and inducing the formation of tube-like HgS nanoparticles via photochemical reaction. To our knowledge, at most conditions PVP served as both stabilizer and dispersant. In the

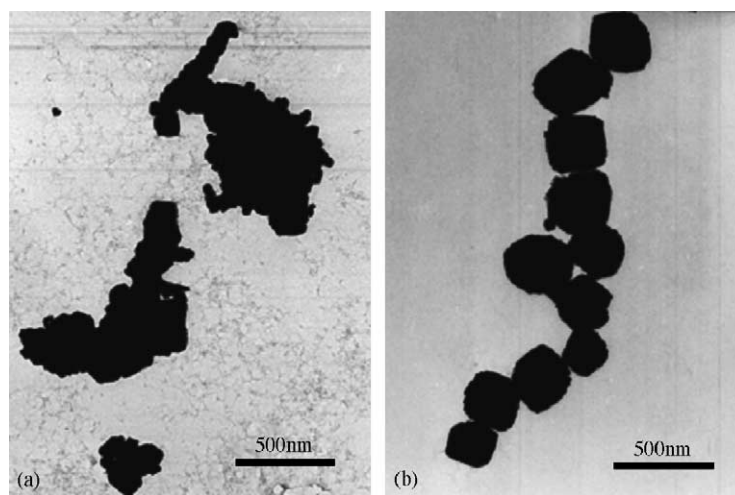


Fig. 5. TEM images of the HgS nanoparticles: (a) without PVP addition in the presence of ultraviolet irradiation, (b) with PVP addition in the absence of ultraviolet irradiation.

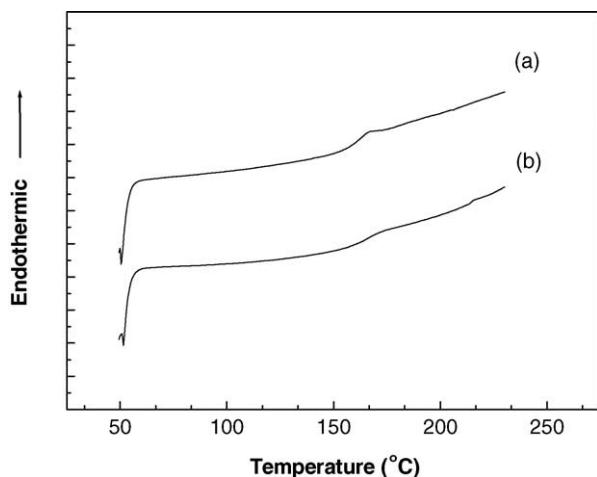


Fig. 6. DSC thermal curves of the PVP: (a) before photoirradiation, (b) after 30 h photoirradiation.

synthesis of HgS nanotubes, due to the high surface activity, once the HgS nascent particles were formed, the PVP molecules would strongly and rapidly adsorb on their surfaces. As a polymeric capping reagent, PVP could limit the aggregation of the initial reactant and form a stable colloid solution. On the other hand, PVP is a homopolymer, whose individual unit contains an amide group. Lactam in PVP structure is a hydrophilic and strongly polar group. Very little is known about photochemistry of 2-pyrrolidone moiety. However, basic amide and lactams photoreactions are expected like: β -cleavage, inter- and intramolecular photoreduction, photorearrangements, etc. Since all these reactions are inter-mediated by radicals, it is valid to suggest that radicals at the polymer backbone are also formed. The crosslinking takes place by recombination of these radicals [27]. Fig. 6 showed the DSC results for the PVP in our system before and after ultraviolet irradiation. The glass transition temperature (T_g) of the PVP after photoirradiation was increased around 6 °C and ΔC_p was decreased 0.056 J/g °C, revealing that the PVP may undergo photo cross-linking. The FT-IR spectra were also recorded to further prove the photocrosslinking of the PVP (presented in Fig. 7). A new peak at 1576 cm^{-1} appeared in the IR spectrum of the PVP after irradiation compared to before irradiation, which can be attributed to C–N stretching frequency of acylamide. The PVP after irradiation also exhibited a stronger IR vibration band at 1015 cm^{-1} , which is the C–N stretching vibration of secondary amine. These changes can be explained as the cleavage of the pyrrolidone substituent. That is, the photochemistry of the pyrrolidone substituent, a cyclic amide, will lead the crosslinking of PVP. Therefore, in the presence of ultraviolet irradiation, the HgS nascent particles would be fabricated to the tube-like assemblies via the photocrosslinking of PVP coated on their surfaces and further grew into the single crystalline tubes. Here, the PVP-coated particles in photochemical reaction can be considered as an in situ template to generate tubular nanostructures. Since the tube was ordered crosslinked with the

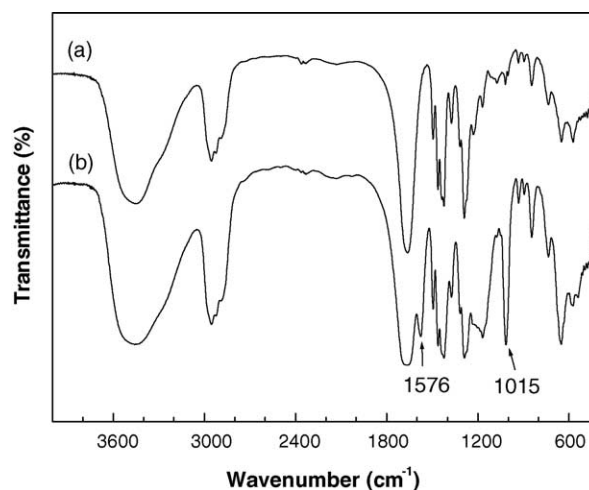


Fig. 7. FT-IR spectra of the PVP: (a) before photoirradiation, (b) after 30 h photoirradiation.

PVP-coated nascent particles, the wall thickness of the final tube is consistent with the diameter of those particles, which supports the proposed mechanism.

4. Conclusion

In summary, we have successfully prepared the HgS nanotubes by PVP-assisted photochemical route. Direct UV photocrosslinking of PVP was exploited to induce the formation of tube-like morphology. This method provides a convenient and efficient route to the fabrication of one-dimension structural materials and hopes to be a generic approach. Next we will devote to the synthesis of other materials with such structure and research the photochemical effect on other surfactants.

Acknowledgments

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