# Selected-Control Solvothermal Synthesis of Nanoscale Hollow Spheres and Single-Crystal Tubes of PbTe

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For the first time, hollow PbTe nanospheres with diameters of 80–140 nm have been prepared in an ether/glycerol microemulsion system and PbTe single-crystalline nanotubes with diameters of 60–80 nm have been synthesised in a homogeneous ethanol/glycerol system. They can be facilely controlled via a solvothermal process without any additional catalysts and templates. Two different template mechanisms are discussed herein. The Raman and far infrared spectra of the samples have been investigated at room temperature.

## Introduction

In recent years, one of the important goals of material scientists has been to tailor the structures of materials to obtain special nanomorphologies because the properties of nanomaterials are strongly dependent on the their sizes and shapes.[1−5] Among specific morphologies, hollow nanoscale spheres and tubes have drawn more and more attention.[6,7] Three-dimensional hollow spheres are interesting in the fields of medicine, material science and catalysis due to their hollow structures which make them particularly applicable for drug delivery, medical imaging, protein and enzyme transplantation, encapsulation of products (cosmetics, inks and dyes) and contaminated waste removal.[8] So far, various hollow spheres (SiC, ZnS, CdS, $Ag_2S$ and polymers) have been synthesised by different methods.[9−12] Meanwhile, one-dimensional nanotubes have also attracted attention because of their unique optical, electronic and mechanical properties resulting in promising applications in electrical and optoelectronic nanodevices. Many tubular structures have been fabricated for compounds with layered structures such as C, $MoS_2$ and BN with the assistance of catalysts. Moreover, there have been many tubular materials without layered structures produced by physical template methods.[13] However, the introduction of templates or catalysts to the reaction system means a much more complicated process involving the preparation of catalysts or the selection of templates and may introduce impurities into the final product. Therefore, it is always a challenge for the tubular materials to be prepared by a simple wet chemical route.

PbTe has been intensively studied for more than forty years because it has interesting physical properties which can be applied in many fields such as IR detection, photoconductivity and thermoelectric materials.[14] PbTe nanocrystals have been prepared by various methods.[15] To the best of our knowledge, however, there are no reports regarding hollow PbTe nanospheres and nanotubes. We have successfully synthesised hollow PbTe spheres and nanotubes by a wet chemical method, simply using ether and ethanol as the reaction solvents, respectively. In the solvothermal process, neither physical templates nor catalysts are required. In addition, two different template mechanisms are discussed.

## Results and Discussion

The typical XRD patterns of the products are shown in Figure 1. All the peaks can be indexed as face-centred cubic

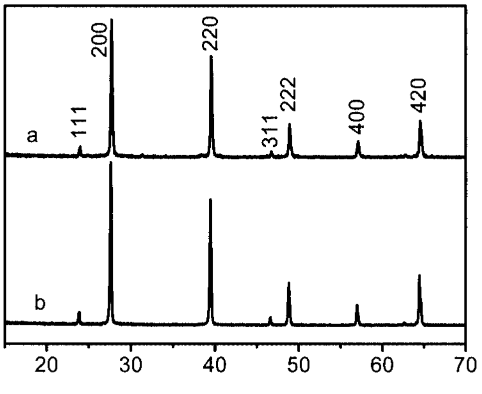

Figure 1. XRD patterns of (a) hollow spheres and (b) tubular PbTe

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PbTe (JCPDS, 38-1435). No peaks of any other impurities are detected, indicating the high purity of the products. In addition, the strong and sharp reflection peaks suggest that the products are highly crystalline.

Figure 2 (see a and b) shows the TEM images of the samples prepared by the process using ether as the solvent. The strong contrast between the dark edge and pale centre is evidence of its hollow nature. Figure 2 clearly displays many hollow PbTe spheres prepared in the products. The proportion of hollow spheres in the samples was estimated to be 25−30% using large numbers of TEM observations. Their external diameter and wall thickness are ca. 80−140 nm and 15−30 nm, respectively. Close observations indicate that the hollow spheres consist of PbTe nanoparticles. The inset of Figure 2 (see b) shows the selected area electron diffraction (SAED) pattern of the hollow PbTe spheres. The SAED exhibits diffuse polycrystalline ring patterns and agrees well with the XRD peaks of the products. It also further confirms that the hollow spheres are constructed from highly crystalline PbTe nanoparticles. In addition, it could be shown that the hollow spheres are sensitive to beam irradiation during TEM examination. This may be related to their thin and porous walls. A similar phenomenon can be also found in former reports concerning hollow spheres.[6,16] In addition to the hollow spheres, some cubes are also present in the samples (Figure 2, c).

Figure 2 (see d−g) shows tubular PbTe prepared in the process using ethanol as the solvent. The yield of the nanotubes in the sample was about 20%. The external diameter and wall thickness of the nanotubes are ca. 70 nm and 15 nm, respectively. Their lengths are about several hundred nanometers. Most nanotubes have closed ends and a few have open ends. The microstructure of tubular PbTe was further characterised by HRTEM and SAED. The HRTEM images looking down onto the wall and open end of the nanotubes are given in Figure 2 (see f−h), where the inset is the corresponding open end ED pattern. The regular spacing of the observed lattice planes is ca. 0.32 nm which is consistent with the separation of the (200) planes of c-PbTe. It shows that the nanotube is single-crystalline, structurally uniform and dislocation free. Moreover, the SAED patterns taken from various regions of an individual nanotube are essentially the same. It can also be concluded that the nanotubes synthesised using the present procedure are single-crystalline in structure. According to the HRTEM images and the SAED pattern, it can be concluded that the nanotubes grow along the [100] direction.

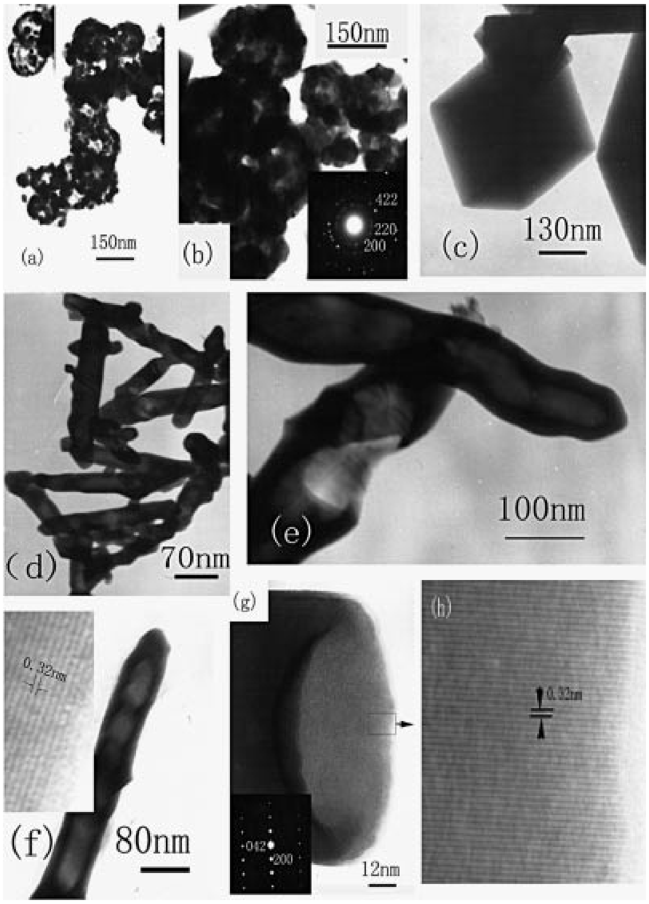
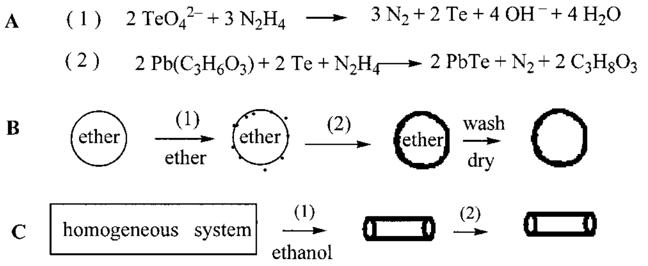


Figure 2. TEM images of (a) and (b) hollow PbTe spheres and (c) a few cubes, the inset shows the hollow sphere ED patterns; (d) Tubular PbTe TEM images and (e) their magnification images. (f) HRTEM images of the wall and (g) the open end of the nanotubes, the inset show the corresponding ED patterns

To investigate the reaction process, a series of experiments was carried out. When $Pb(NO_3)_2$ was not added to the reaction system, only Te nanocrystals formed. On the other hand, Pb was not produced when $Na_2TeO_4$ was left out of the reaction system. Moreover, a large amount of Te mixed with some PbTe was obtained when the reaction proceeded for a short time and then more PbTe and less Te were produced when the reaction time was continually increased. Based on the above results and the former reports,[15,17,18] all the reactions can be described according to part A in Scheme 1. Firstly, the $Na_2TO_4$ was reduced to Te by hydrazine. Secondly, the PbTe was formed slowly through a redox reaction between $Pb(C_3H_6O_3)$, Te and hydrazine. Here, glycerol was used as the complexing reagent to form a complex, $Pb(C_3H_6O_3)$. The complex served to reduce the speed of reaction (2) because the $Pb(C_3H_6O_3)$ sharply decreased the free $Pb^{2+}$ concentration in the solution. It is well-known that a slow reaction rate is favourable for crystallisation as well as separating the growth step from the nucleation step.[19] Thus, highly crystalline PbTe was obtained in our experiments and the ED, XRD and HRTEM of the products also confirmed this. For the detailed formation process of the hollow spheres, we assume the process to be a template-interface route. Because the ether was insoluble in the glycerol, the whole system can be described as a microemulsion state. The ether could form stable microscale oil droplets in glycerol at a moderate temperature. When Te nanoparticles were formed through reaction (1) in an ether/glycerol system, many Te particles accumulated on the surface of the oil droplets and formed a template-interface. The reaction then progressed according to Equation (2). Finally the shell-core structure formed. Moreover, the hollow spheres can be obtained when the ether is removed by washing and drying of the product. The whole process can be described diagrammatically as in part B of Scheme 1.



Scheme 1. A) Illustration of the hollow spheres formation process by a template-interface route B) Illustration of the nanotube formation process by a self-generated template route C

In order to discuss the formation mechanism of PbTe nanotubes, some experiments were carried out. Te nanotubes could be obtained in the products (the images not shown here) when $Pb(NO_3)_2$ was not added to the ethanol/glycerol reaction system. This phenomenon can also be found in the literature.[17,18] Moreover, more PbTe and less Te were obtained when the reaction time was continually increased. In addition, it is worth noting that the diameter of the Te nanotubes obtained was almost the same as that of the PbTe nanotubes. Based on these results, we propose a self-generated template process. Firstly, some Te nanotubes were produced according to reaction (1) in the ethanol/glycerol homogeneous system and then according to reaction (2) considerable tubular PbTe formed using the Te nanotubes as the templates. Some similar template syntheses have been reported.[20–22] Accordingly, we are inclined to describe the formation process of the PbTe nanotubes as a self-generated template route. It can be described according to part C in Scheme 1. However, the detailed mechanism needs to be further studied.

The room temperature Raman and far infrared spectra of the hollow PbTe nanospheres are shown in Figure 3. Peaks at 121, 137 and 154 $cm^{-1}$ are observed as indicated in Figure 3 (a). Among them, the peaks marked with asterisks are related to the vibrational modes of a thin $TeO_2$ layer on the PbTe nanocrystals.[23,24] The wide band with the peak at ca. 154 $cm^{-1}$ corresponds to the mixed plasmon-phonon modes of the PbTe nanoparticles forming hollow nanospheres. It is worth noting that the frequency is lower than that for bulk PbTe. This can be explained by the effect of dimensional quantization as the average PbTe nanocrystal radius decreases. This phenomenon has also been observed by others.[25] Figure 3 (b) shows the far infrared spectrum of the hollow PbTe nanospheres. The peaks (marked with asterisks) at 81 and 110 $cm^{-1}$ are related to two $TeO_2$ infrared active modes.[26] The other peaks in part b of Figure 3 corresponded to the infrared active modes of the hollow PbTe nanospheres.[25] Here, the wide band from 50 to 70 $cm^{-1}$ is split into two bands appearing at 57 and 61 $cm^{-1}$. A similar phenomenon has been reported in the literature.[27] From Figure 3 (see a and b), it can be also shown that the frequency of the mixed plasmon-phonon mode (at 154 $cm^{-1}$) in the Raman spectrum of the hollow PbTe nanospheres is almost same as that (at 151$cm^{-1}$) in the infrared spectrum. Additionally, the Raman and far infrared spectra (not shown here) of the PbTe nanotubes were similar to the above Raman and far infrared spectra of the hollow PbTe nanospheres, respectively.

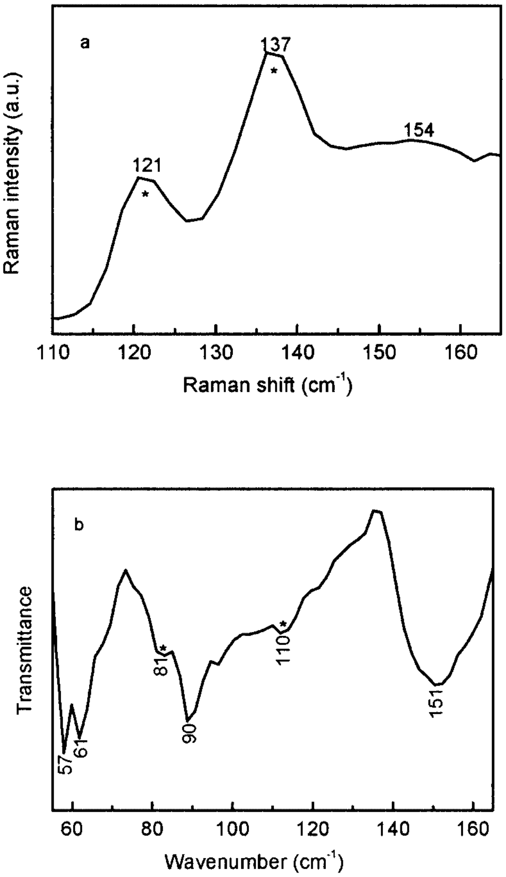


Figure 3. (a) the Raman and (b) far infrared spectra of the hollow PbTe nanospheres

## Conclusion

In conclusion, hollow nanoscale spheres and single-crystal tubular PbTe have been synthesised via facile solvothermal processes for the first time. Two different models, template-interface and self-generated template routes, have been proposed to explain the formation mechanism of hollow PbTe nanospheres and nanotubes. The present study will not only open up great opportunities for novel morphologies of PbTe and their applications to be investigated, but might also be extended to the synthesis of hollow spheres and nanotubes of other materials.

## Experimental Section

All chemical reagents in this work, such as $Pb(NO_3)_2$, $Na_2TO_4 \cdot 2H_2O$, ether, ethanol, glycerol and hydrazine were of A.R. grade and were purchased from the Shanghai Chemical Company, China. They were used as received without further purification.

**Preparation of Hollow Nanoscale Spheres and Tubular PbTe:** In a typical procedure, $Pb(NO_3)_2$ (0.5 mmol) and $Na_2TO_4 \cdot 2H_2O$ (0.5 mmol) were added to a mixture of ether (18 mL) and glycerol (18 mL). The mixture was then stirred vigorously to form a microemulsion phase. After this, hydrazine (10 mL) was added to the microemulsion system and stirring was continued for 10 min. Finally, the mixture was transferred into a 60 mL Teflon-lined autoclave and the autoclave was sealed and heated at 160 °C for 20 h. The autoclave was then allowed to cool to room temperature without assistance. The grey precipitate was filtered and washed several times with distilled water and absolute ethanol to remove impurities and was then dried in vacuo at 60 °C for 4 h. Finally the product (PbTe hollow spheres) was obtained. The whole method, appropriate for the preparation of PbTe nanotubes, was similar to the above process except for the use of ethanol instead of ether as the reaction solvent.

**Sample Characterisation:** The X-ray diffraction (XRD) patterns for the products were recorded on a Philips X'pert diffractometer with Cu-$K_{\alpha 1}$ radiation ($\lambda$ = 1.54178 Å). The morphologies and structures of the products were examined by transmission electron microscopy (TEM) using a Hitachi H-80 instrument. The high-resolution TEM study was carried out using a JEOL 2010 microscope. The samples used for characterisation were dispersed in absolute ethanol and were ultrasonicated before TEM and HRTEM. The Raman spectrum was recorded with a LABRAM-HR Confocal Laser MicroRaman Spectrometer with 514.5 nm radiation from a 10-mW argon ion laser at room temperature. The far infrared spectroscopic measurements were performed with a Nicolet Nexus 870 spectrometer. The powders were dispersed in silicon oil and were studied at room temperature.

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