Effect of solvents on morphologies of PbTe nanostructures: Controllable synthesis of hollow and solid PbTe nanocubes by a solvothermal method

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ABSTRACT

We demonstrate a facile solvothermal route to grow hollow and solid PbTe nanocubes. The hollow PbTe nanocubes were successfully achieved when EtOH was used as solvent in the presence of nonionic polymer PEG, while the solid PbTe nanocubes were obtained when EG was used as solvent in the presence of PEG, whilst keeping the other experimental conditions constant. The results indicate that the solvents used in reaction system play a key role to determine the interior structure of PbTe nanocubes. On the basis of the experimental results and analysis, a possible growth mechanism has been discussed in detail for the hollow and solid PbTe nanocubes.

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1. Introduction

Synthesis of inorganic nanostructures with different sizes and morphologies has recently received great attention due to their novel optical and electric properties and potential applications in the fields of electronic and photonic devices. Therefore, much effort has been focused on the design, synthesis, and characterization of inorganic nanostructures with specific sizes and morphologies. Until now, various methods have been employed to synthesize various kinds of nanostructures with different morphologies and special structures, such as nanowires, nanorods, nanotubes, nanobelts, nanocubes, nanoplates, and other nanostructures.

Lead chalcogenides are very important semiconductors with narrow band gap and have potential applications in thermoelectric (TE) and infrared (IR) photoelectric devices [1]. As an important member of Lead chalcogenides, lead telluride (PbTe) is a very promising material for TE applications because of its narrow band gap (0.31 eV at 300 K), face-centered cubic structure and large average excitonic Bohr radius ($\sim$46 nm) [1–4]. Additionally, it has been reported that PbTe and PbTe-based compounds are superior materials for solid-state TE cooling and electrical power generation devices [2, 5–7]. Furthermore, recent works reported that PbTe quantum dot superlattices and bulk compounds with nanostructures have largely improved energy

conversion efficiency compared with their bulk counterpoints [1, 5]. For instance, experimental and theoretical studies have recently shown a great enhancement in the Seebeck coefficient of PbTe nanoparticles [8]. Therefore, the controllable synthesis of PbTe nanostructures with controllable morphologies and sizes has attracted considerable attentions. Thus, various methods have been developed to prepare PbTe nanostructures with different sizes and morphologies, such as nanocrystals [9–12], nanorods [13], nanoboxes [14, 15], hollow spheres, nanotubes [16, 17], nanowires [18–20], pearl-necklace-shaped nanowires [21], dendritic structures [22] and nanocubes [23, 24]. In our present work, we have developed a facile solvothermal method for controllable synthesis of the hollow and solid PbTe nanocubes by using ethanol (EtOH) and ethylene glycol (EG) as solvents, respectively. The results indicate that the solvents used in reaction system play a key role to determine the interior structure of PbTe nanocubes.

2. Experimental procedure

Te powder (99.99%), ethylene glycol (EG, 99.8%) were purchased from Aldrich. polyethylene glycol (PEG, MW 20 000), lead acetate $Pb(CH_3COO)_2$ (99%), sodium hydroxide (NaOH), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%, w/w%), ethanol (EtOH, 99.8%), and butyl alcohol (99.8%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Distilled water was obtained by a water-purification appliance.

In a typical experimental process of the synthesis of hollow PbTe nanocubes, 15 mg polyethylene glycol (PEG, molecular

weight: 20 000) was completely dissolved into 2.5 mL distilled water with the help of continuous magnetic stirring, then 1.8 g NaOH was added and dissolved completely, followed by adding 20 mL ethanol, which makes the ethanol to water ratio of 8 to 1. The solution was stirred for 5 min, then 156 mg $Pb(C_2H_3O_2)_2$ was added and dissolved completely, followed by adding 47 mg Te powder, and 3.8 mL $N_2H_4 \cdot H_2O$ solution (1.9 mL H_2O and 1.9 mL $N_2H_4 \cdot H_2O$), and stirring for 10 min. The mixtures were transferred into a Teflon-lined stainless steel autoclave, sealed and kept at 160 °C for 20 h in a furnace, and cooled to room temperature. The black precipitates were collected and washed with distilled water, and then dried in a vacuum oven at 80 °C for 12 h.

In a typical experimental process of the synthesis of solid PbTe nanocubes, 15 mg PEG (MW 20 000) was completely dissolved into 2.5 mL distilled water with the help of continuous magnetic stirring, then 1.8 g NaOH was added and dissolved completely, followed by 20 mL EG, which caused the EG/water ratio to be 8:1. The solution was stirred for 5 min, then 156 mg $Pb(C_2H_3O_2)_2$ was added and dissolved completely, followed by 47 mg Te powder and 3.8 mL $N_2H_4 \cdot H_2O$ solution (1.9 mL H_2O and 1.9 mL $N_2H_4 \cdot H_2O$). The mixtures were stirred for 10 min and then transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed and kept at 160 °C for 20 h in a furnace, and cooled to room temperature. The black precipitates were collected and washed with distilled water, and then dried in a vacuum oven at 80 °C for 12 h.

The phase structure of the as-prepared products was investigated by X-ray diffraction (XRD) on a Rigaku (Japan) $D_{max}\gamma_A$ rotation anode X-ray diffractometer equipped with the graphite monochromatized Cu K_α radiation ($\lambda = 1.54178$ Å), employing a scanning rate of $0.02°$ s^{-1} in the 2θ range from 10 to 90°. The morphology and size of the as-prepared PbTe nanocrystals were observed by a Hitachi transmission electron microscope (H-700), using an accelerating voltage of 200 kV. The microstructure of the as-prepared hollow PbTe nanocubes was investigated by transmission electron microscope (JEM 2100), using an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of PbTe nanocrystals prepared by using EtOH as solvent in the presence of nonionic
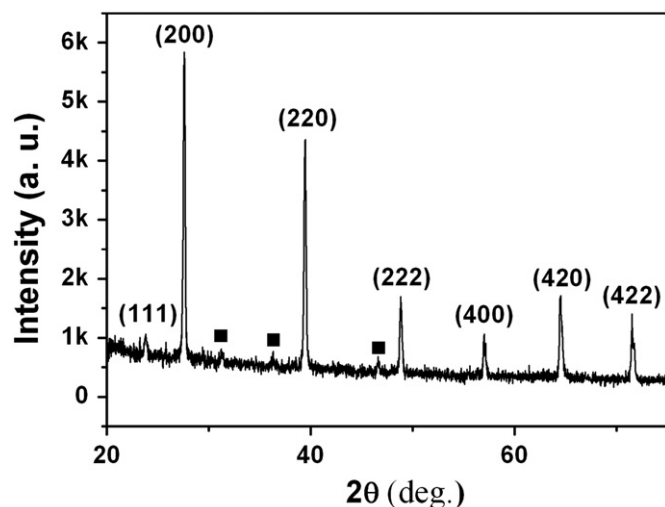
polymer of PEG. XRD pattern shows that all of the diffraction peaks can be perfectly indexed to (1 1 1), (2 0 0), (2 2 0), (2 2 2), (4 0 0), (4 2 0) and (4 2 2) planes of face-centered cubic (fcc) PbTe with space group $Fm\bar{3}m$ (No. 225) and lattice constants of $a = b = c = 6.454$ Å (JCPDS: 78–1905). The lattice constant calculated by refinement of the XRD data is $a = 6.445$ Å, which is consistent with the standard value ($a = 6.454$ Å) of bulk face-centered cubic PbTe. One also can find that there are three weak diffraction peaks at ~ 33, 35 and 48 degrees as indicated with black squares in XRD pattern. A careful examination indicates that these weak diffraction peaks come from of unreacted Te (JCPDS: 36–1452). Thus the XRD result indicates that PbTe compounds have been synthesized by our present method.

The morphology and size of the as-prepared PbTe nanocrystals were characterized by transmission electron microscope (TEM).
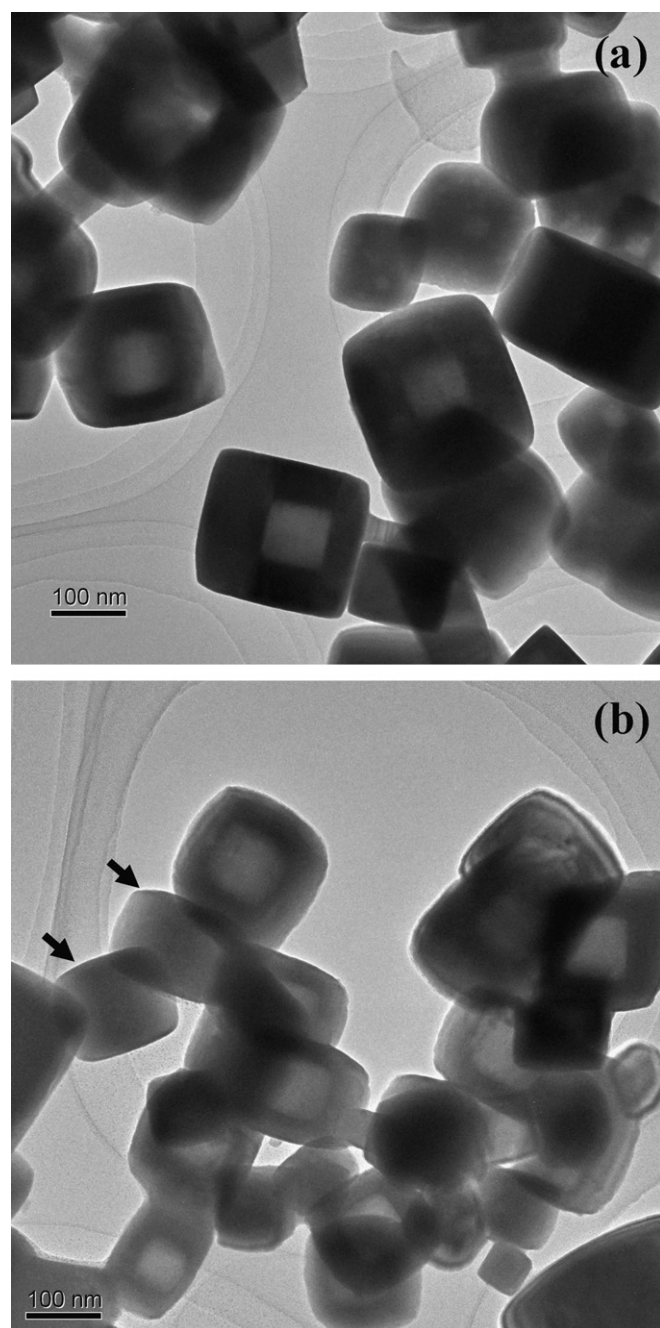
Fig. 2. Typical TEM images of hollow PbTe nanocubes prepared by using EtOH as solvent in the presence of nonionic surfactant PEG at 160 °C for 20 h.

Fig. 1. XRD pattern of hollow PbTe nanocubes prepared by using EtOH and PEG as solvent and shape controller, respectively.
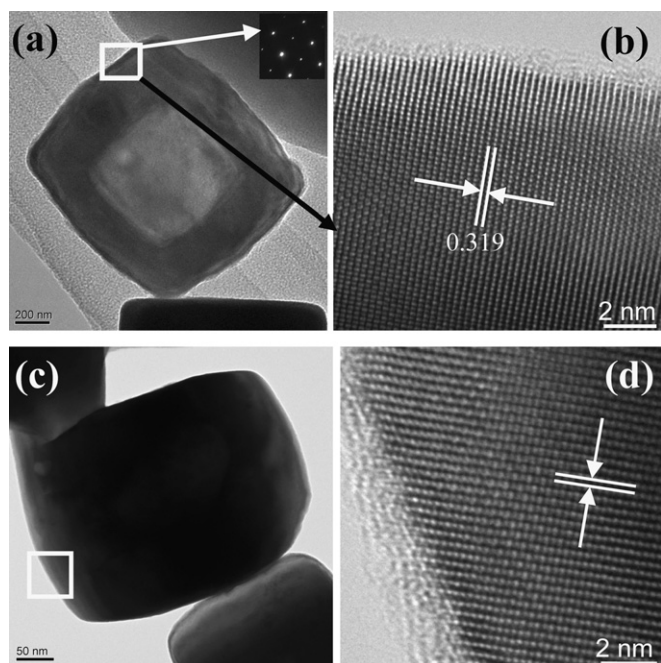
Fig. 3. (a) TEM image with SAED pattern as the inset of an individual hollow PbTe nanocubeand (b) the corresponding HRTEM image of the marked area, indicating that the hollow nanocube is a single crystal. (c) and (d) TEM image and corresponding HRTEM image of an individual solid PbTe nanocube.

Fig. 4. XRD pattern of solid PbTe nanocubes prepared by using EG as solvent in the presence of surfactant PEG.

Fig. 2 shows typical TEM images of PbTe nanocrystals prepared by using EtOH as solvent in the presence of nonionic polymer PEG at 160 °C for 20 h. The TEM images clearly show that the as-prepared PbTe nanocrystals exhibit the good cubic morphology with edge length of about 60–250 nm. One can find that most cubic nanocrystals exhibit a strong contrast difference with dark edge and bright center, showing hollow interior structure. However, one also can find that a few nanocubes have solid interior structure as indicated by arrows in Fig. 2(b). Thus the TEM observations clearly confirm that the hollow PbTe nanocubes were achieved by using EtOH as solvent in the presence of nonionic polymer PEG.

The microstructure feature of the as-prepared hollow PbTe nanocubes was further studied by selected area electron diffraction (SAED) and high-resolution TEM (HRTEM). Fig. 3(a) is TME image of a single hollow PbTe nanocube used to make detailed investigations of crystallinity and microstructure. Fig. 3(b) is a typical SAED pattern that was obtained by aligning the electron beam perpendicular to one of the faces of the hollow nanocube. The spot pattern clearly indicates that the hollow nanocube is single crystal and can be indexed based on a face-centered cubic cell with lattice parameter of $a=6.454$ Å, consistent with the XRD result described above. In HRTEM image, the spacing is 0.319 nm, which corresponds to the (2 0 0) planes of face-centered cubic PbTe. Thus, the above spot SAED pattern and the clear lattice fringes indicate that the hollow PbTe nanocubes prepared by our present method are highly crystallized with high quality single crystal feature. As we observed in TEM images (Fig. 2(b)), a few nanocubes have solid interior structure. Fig. 3(c) and (d) shows a typical TEM image and corresponding HRTEM image of an individual solid PbTe nanocube. The clear lattice fringes also indicate that the solid PbTe nanocubes prepared via our present method have single crystal with highly crystallized feature. The measured spacing is also about 0.319 nm, corresponding the (2 0 0) planes of face-centered cubic PbTe.

In order to understand the effect of solvents on the morphologies of PbTe nanocrystals, a comparative experiment was conducted
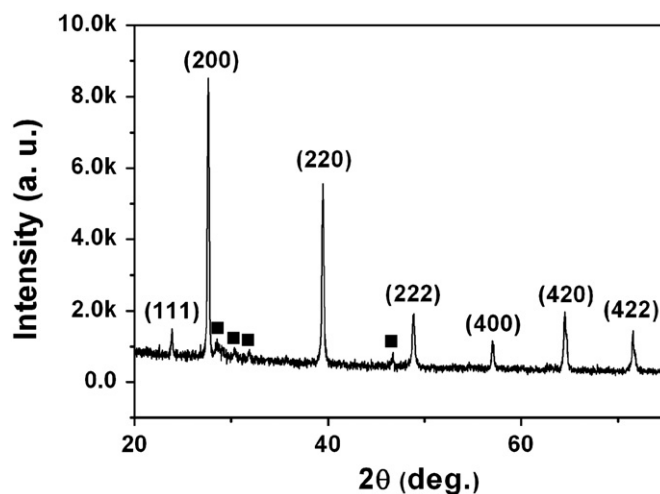
by using EG as solvent instead of EtOH, whilst keeping other experimental conditions constant. Fig. 4 is a typical XRD pattern of PbTe nanocrystals prepared by a solvothermal process in the presence of nonionic polymer PEG, in which EG was used as the solvent instead of EtOH. Again, one can see that all of the diffraction peaks can be easily indexed to face-centered cubic (fcc) PbTe with space group $Fm\bar{3}m$ (No. 225) and lattice constants of $a=b=c=6.454$ Å (JCPDS: 78–1905), although there are three weak diffraction peaks at ∼29, 31, 32 and 48 degrees as indicated with black squares in XRD pattern (Fig. 4). After a careful examination, one can find that these weak diffraction peaks come from unreacted Te. Thus the experimental result indicates that PbTe can also be successfully synthesized by using EG as solvent in the presence of nonionic polymer PEG.

Fig. 5 shows typical TEM images of PbTe nanocrystals prepared by using EG as solvent in the presence of nonionic polymer PEG at 160 °C for 20 h. The TEM images clearly show that the as-prepared PbTe nanocrystals exhibit the cubic morphology with smooth surface. From the as-obtained TEM images with different magnifications as presented in Fig. 5, one can find that the as-prepared PbTe nanocubes have distribution with edge lengths of ∼80–160 nm. Interestingly, the center section of the as-prepared PbTe nanocubes with no a pocket of space in the interior as shown by arrows in Fig. 5(a) is not transparent under irradiation of electric beam, indicating that the interior of the as-prepared PbTe nanocrystals is solid instead of hollow. Thus the PbTe nanocrystals prepared by using EG as solvent in a solvothermal process are solid nanocubes.

The above results clearly indicated that the cubic morphology PbTe nanocrystals were obtained by using both EtOH and EG as solvent in a solvothermal process in the presence of nonionic polymer PEG, showing that nonionic polymer PEG plays an important role for controllable growth of cubic morphology PbTe nanocrystals. It has been reported previously that PEG, as a nonionic polymer, contains many hydrophilic (i.e., –C–O–C, –OH) and hydrophobic (i.e., –CH$_2$–CH$_2$–) sites. There are lone pair electrons on the oxygen atom of every repeating unit, and oxygen of the ether groups possesses strong basic properties, offering a possibility that PEG polymer can combine with the Pb^{+} ions to form Pb^{2+}–PEG complex [25–27]. Although the exact role of PEG in the solvothermal process is still not clear, the above-mentioned facts maybe allow us to assume that the Pb^{2+}–PEG complex plays a key role for the formation of PbTe nanocrystals with cubic morphology. In the present case, when Te particles gradually
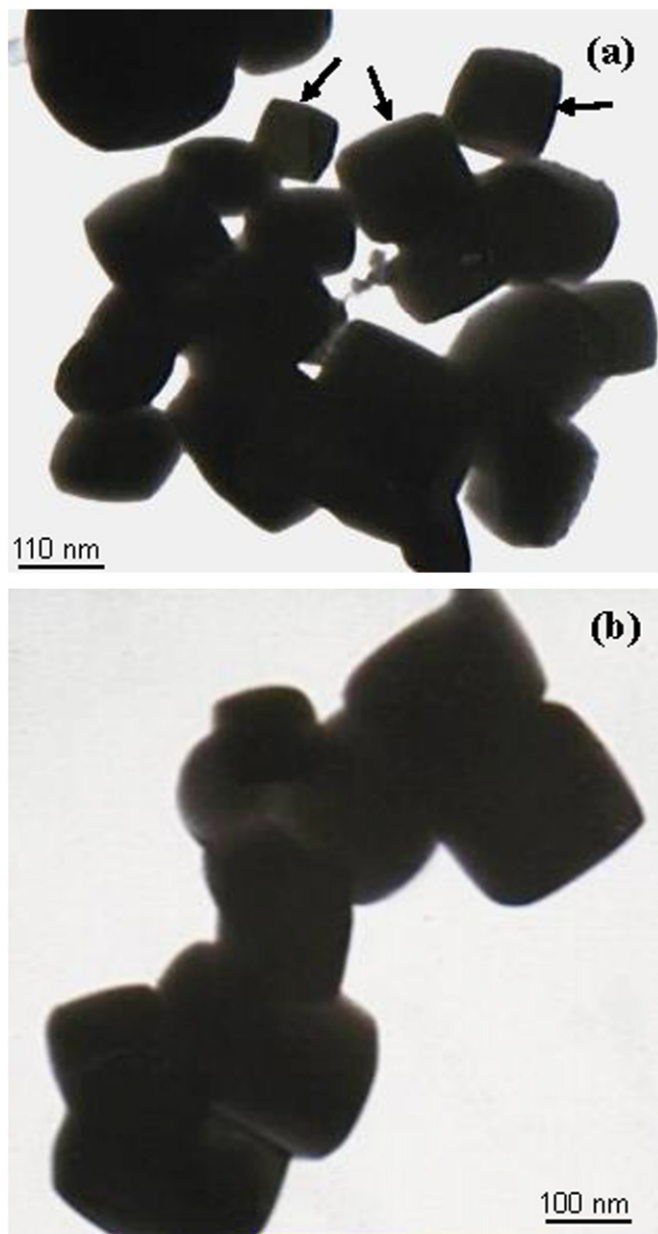
Fig. 5. TEM images of the as-prepared solid PbTe nanocubes by using EG as solvent.
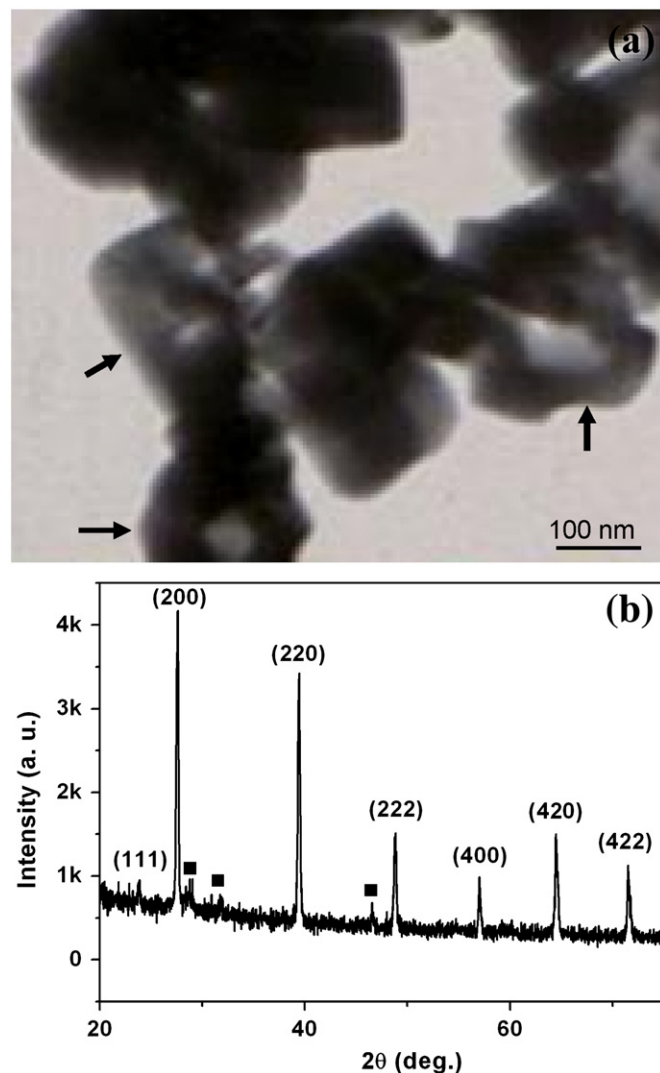

Fig. 6. (a) Typical TEM images of the PbTe nanocrystals using butyl alcohol as solvent, showing some nanocrystals exhibit a hollow interior structure. (b) XRD pattern of the as-prepared PbTe nanocrystals.

dissolve into solvent to form Te^{2-}, the Pb^{2+} and Te^{2-} reacts to form cubic PbTe nanocrystals with temperate role of Pb^{2+}–PEG complex, the selective adsorption of the polymer PEG and their respective counter-ions on the PbTe crystal faces, leading to the formation of PbTe nanocrystals with cubic morphology.

Although the PbTe nanocrystals formed in both EtOH and EG solvent exhibit the similar cubic morphology, the nanocrystals synthesized by using EtOH as solvent exhibit a hollow interior feature, while the nanocrystals fabricated by using EG as solvent has a solid interior feature. The results indicate that the solvents have a great effect on the interior feature of PbTe nanocrystals prepared by our present method. Since EtOH and EG have different viscosity, we propose that the viscosity of the solvent may have a great effect on the interior feature of PbTe nanocrystals prepared via our present method. To confirm our conclusion, we have further performed an experiment by using butyl alcohol as solvent, whilst keeping other experimental conditions constant. It was reported that the viscosity of butyl alcohol is 2.98 cP,

which is larger than that of EtOH (1.1 cP), but smaller than that of EG (16.1 cP). Fig. 6(a) shows a typical TEM image of PbTe nanocrystals prepared by using butyl alcohol as solvent. The as-prepared PbTe nanocrystals also have cubic morphology due to the role of nonionic polymer PEG as above discussed in detail. In addition to nanocubes with solid interior, one can find that some nanocrystals demonstrate a hollow interior structure as marked by arrows in Fig. 6(a). XRD was used to characterize the composition and phase structure of the as-prepared PbTe nanocrystals. Fig. 6(b) is a XRD pattern of the as-prepared PbTe nanocrystals by using butyl alcohol as solvent. The diffraction peaks can also be easily indexed to face-centered cubic (fcc) PbTe with space group $Fm\bar{3}m$ (No. 225) and lattice constants of $a=b=c=6.454$ Å (JCPDS: 78-1905). Again, one can find three weak diffraction peaks at $\sim$29, 31, 32 and 48 degrees as indicated with black squares in XRD pattern. These weak diffraction peaks come from unreacted Te. Thus the XRD result indicates that PbTe can also be successfully synthesized by using butyl alcohol as solvent in the presence of polymer PEG. Our above experimental results confirmed that the viscosity of solvent used in the formation of PbTe nanocrystals plays an important role to determine the interior structure feature.

Our above experimental results clearly demonstrate that the solvents with different viscosity have great effect on the interior structure of PbTe nanocrystals formed via the present route. It has been reported that the escape rate in general decreases with increasing solvent viscosity [28]. Therefore, we suggest that the different morphologies of PbTe nanocrystals might mainly determined by the escape rate of the solvent encapsulated in the interior of the newly formed nanoparticles. The previous research works indicated that the escape rate of solvent encapsulated in the interior of the newly generated nanoparticles could determine the final morphologies of nanoparticles [29]. For instance, hollow Cu_2O nanocubes in simple solution-phase reduction systems using Triton X-100 as solvent in the presence of a small amount of ethanol were successfully prepared. In work the authors suggested that ethanol would gradually escape while the primary particles of Cu_2O were generated during the process of ripening and post-treatment. The spaces of the interior enlarged with the escape of ethanol, and hollow nanocubes were finally produced [29]. Here, we suggest that the viscosity of the as-used solvents in the formation of PbTe nanocrystals could play a key role to determine the escape rate of solvent encapsulated in the interior of the newly generated nanoparticles and then determines the interior structure of the nanocrystals. Since the viscosity of EtOH is much smaller than that of EG, therefore escape rate of EtOH is higher than that of EG, so EtOH encapsulated in the interior of the newly formed PbTe nanoparticles would gradually escape while the primary particles of PbTe were generated during the process of ripening. The spaces of the interior enlarged with the escape of ethanol, leading to the formation of hollow PbTe nanocubes. The growth process of hollow PbTe nanocubes is similar to the formation mechanism of hollow Cu_2O nanocubes [29]. Compared with EtOH, EG has a higher viscosity, so EG encapsulated in the interior of the newly generated PbTe nanoparticles would not easy to escape while the primary particles were produced during the process of ripening and post-treatment, leading to the formation of solid nanocubes. It therefore seems reasonable to conclude that the escape rate of the solvent encapsulated in the interior of the newly generated nanoparticles in the growth process of nanocrystals determines the final interior structure of PbTe in the above two systems, although we still don't have a clear picture of how solvent escape influences nanomaterial shape. In conclusion, the above experimental results and analysis indicate that the nonionic polymer PEG plays an important role to determine the cubic morphology of PbTe nanocrystals, while escape rate of solvent encapsulated in the interior of the newly generated nanoparticles plays a key role to determine the interior structure of PbTe nanocubes.

4. Conclusion

In summary, hollow and solid PbTe nanocubes have been successfully synthesized by a facile solvothermal method by simple adjusting the solvent. The hollow PbTe nanocubes were successfully achieved by a simple solvothermal process when EtOH was used as solvent in the presence of nonionic polymer PEG. The solid PbTe nanocubes were synthesized when EG was used as solvent. The results indicate that the nonionic polymer PEG plays an important role to determine the cubic morphology of the as-prepared PbTe nanocrystals. While escape rate of the as-used solvent encapsulated in the interior of the newly generated nanoparticles in the growth of nanocrystals plays a key role to determine the interior structure of PbTe nanocubes. A possible growth mechanism for the growth of hollow and solid PbTe nanocubes has been proposed based on the experimental results and analysis.

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