Synthesis and characterization of PbTe micro/nanostructures through hydrothermal method by using a novel capping agent

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MS received 30 March 2013; revised 12 August 2013

Abstract. For the first time, a Schiff base compound derived from 1,8-diamino-3,6-dioxaoctane and 2-hydroxybenzophenone marked as (2-HBP)-(DaDo) was synthesized, characterized and then used as capping agent for the preparation of PbTe micro/nanostructures. Besides the as-synthesized Schiff base compound, $\text{Pb}(\text{NO}_3)_2$ and Te powders were applied as lead and telluride precursors. In addition, effect of preparation parameters like reaction time and temperature in hydrothermal synthesis on the morphology of the final products was tested. The products were analysed with the aid of SEM, XRD, FT-IR and EDS. Based on the obtained results, it was found that pure cubic phased PbTe has been obtained by this method. According to SEM images, it was found that uniform PbTe micro/nanocubes have been obtained at 180 °C for 12 h. On the other hand, by increasing the reaction temperature from 3 to 24 h, the production of cubic-like shapes increased.

Keywords. Nanostructure; chalcogenide; lead telluride; Schiff base; hydrothermal.

1. Introduction

In the past decade, the preparation of low-dimensional materials such as nanorods, nanowires, nanobelts and nanoparticles have attracted much attention due to their unusual chemical and physical properties (Mohandes *et al* 2010; Esmaili *et al* 2011; Hosseinpour-Mashkani *et al* 2012). Synthesis of nano-sized lead telluride (PbTe) as a member of chalcogenides family has attracted significant attention due to its small bandgap (0.31 eV at 300 K) and larger Bohr excitation radius. PbTe nanostructures as semiconductors have been widely applied in many fields such as infrared detectors, photo resistance, lasers and thermoelectric materials (Du *et al* 2002; Shchennikov and Ovsyannikov 2003; Nair *et al* 2004; Zogg *et al* 2004; Harman *et al* 2006). Up to now, various methods have been explored to synthesize lead telluride nanostructures. Wan *et al* (2010) synthesized PbTe nanocubes in hydrazine saturated alkaline solution by using $\text{Pb}(\text{NO}_3)_2$ and Te powder. Sonochemical synthesis of nanocrystalline PbTe with Pb as impurity has been reported by Li *et al* (2003) after sonication for 8 h by using $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and Te powder. PbTe

nanowires with an average diameter of about 30 nm were produced by a hydrothermal process at 180 °C for 24 h using tellurium nanowires as templates and $\text{Pb}(\text{NO}_3)_2$ (Tai *et al* 2008). Flower-like PbTe nanostructures were synthesized using $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and Na_2TeO_3 as precursors under hydrothermal conditions at 240 °C for 24 h (Zhou *et al* 2012). The alkaline hydrothermal synthesis of PbTe nanosheets by using $\text{Pb}(\text{NO}_3)_2$, Na_2TeO_3 and NaBH_4 as starting materials and different surfactants was introduced by Zhu *et al* (2010). Hierarchical superstructures of lead chalcogenides were prepared by microwave-assisted method with $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and Te powder in ethylene glycol (Cao *et al* 2007). Cubic-like nanostructures of PbTe have been obtained via solvothermal route at 150 °C for 12 h in various solvents including ethanol, acetone and *N,N'*-dimethylformamide (DMF) (Zhu *et al* 2008).

It is well-known that the presence of capping agents during the formation of nanostructures has a great effect on the morphology of the final products. Therefore, much attention has been paid to the study of such supramolecular structures, which can act as both template and micro-reactor for the controlled growth of products and it has been proved to be an effective structure director to control the morphology of nanomaterials (Lisiecki *et al* 1996; Jeevanandam *et al* 2000). For example, sodium dodecylbenzene sulfonate (SDBS) (Zhu *et al* 2010),

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sodium dodecyl sulfate (SDS) (Soofivand *et al* 2012), polyvinylpyrrolidone (PVP) (Mohandes and Salavati-Niasari 2013), polyethylene glycol (PEG) (Zhang *et al* 2007) and cetyltrimethylammonium bromide (CTAB) (Esmaili-Zare *et al* 2012) have been applied as current ionic and polymeric capping agents.

Here, a Schiff base compound derived from 1,8-diamino-3,6-dioxaoctane and 2-hydroxybenzophenone marked as (2-HBP)-(DaDo) was synthesized, characterized and then used as capping agent for the synthesis of PbTe micro/nanostructures. Lead nitrate, Te powder, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and NaOH as starting reagents and ethylene glycol as solvent were used in hydrothermal synthesis of PbTe micro/nanostructures. The as-produced PbTe micro/nanostructures were characterized with the aid of XRD, SEM, EDS and FT-IR.

2. Experimental

2.1 Materials and characterization

All the reagents for the synthesis of the capping agent and PbTe micro/nanostructures such as 1,8-diamino-3,6-dioxaoctane, 2-hydroxybenzophenone, methanol, $\text{Pb}(\text{NO}_3)_2$, Te powder, ethylene glycol, hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) and NaOH were purchased from Merck company (pro-analysis) and used without further purification. The Fourier transform infrared spectra were performed using KBr pellets on FT-IR spectrometer (Magna-IR, 550 Nicolet) in the range of $400\text{--}4000\text{ cm}^{-1}$. The powder X-ray diffraction (XRD) patterns were collected from a diffractometer of Philips company with X'PertPro monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$). A Cam Scan MV2300 scanning electron microscope (SEM) was used to investigate morphology of the products. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. ^1H NMR spectrum of (2-HBP)-(DaDo) was recorded by BRUKER (400 MHz) in CDCl_3 .

2.2 Synthesis of Schiff base compound

A typical procedure for the synthesis of (2-HBP)-(DaDo) compound is as follows: a solution containing 2 mol of 1,8-diamino-3,6-dioxaoctane in 50 mL of methanol was added dropwise into a solution involving 4 mol of 2-hydroxybenzophenone in 50 mL of methanol. The mixture was refluxed at $70\text{ }^\circ\text{C}$ under magnetic stirring for 12 h to produce a yellow precipitate. The obtained yellow precipitate was filtered and washed with methanol several times and finally dried at $50\text{ }^\circ\text{C}$ in vacuum for 12 h. The chemical reaction for the preparation of (2-HBP)-(DaDo) is seen in scheme 1. The as-obtained Schiff base compound was characterized by ^1H NMR and FT-IR.

2.3 Synthesis of PbTe micro/nanostructures

In a typical process, 2 mmol of Te powder, 0.02 g of NaOH and 3 mL of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (85%) were dissolved in 30 mL of ethylene glycol under magnetic stirring. When the Te powder was completely dissolved, colour of the reaction became purple. Then 2 mmol of $\text{Pb}(\text{NO}_3)_2$ plus 0.3 g of the Schiff base dissolved in 30 mL of ethylene glycol was added into the above solution dropwise. The resultant mixture was put into a Teflon-lined stainless steel autoclave with a volume capacity of 100 mL. The autoclave was then sealed and maintained at 160, 180 and $200\text{ }^\circ\text{C}$ for 12 h, respectively. Then, the container was cooled to room temperature naturally. The black precipitates obtained were collected, washed with methanol and distilled water several times and dried at $50\text{ }^\circ\text{C}$ in vacuum for 12 h. To investigate the effect of reaction time on the morphology of the products, the experiment was done at $180\text{ }^\circ\text{C}$ for 3, 6, 9 and 24 h in the same conditions, respectively. The preparation conditions have been illustrated in table 1. As shown in table 1, samples 1–7 were related to PbTe micro/nanostructures synthesized by hydrothermal method at different conditions. The products were characterized by XRD, SEM and EDS.

3. Results and discussion

3.1 Characterization of Schiff base compound

^1H NMR spectrum of the as-produced (2-HBP)-(DaDo) in the range of 0–20 ppm is shown in figure 1(a). ^1H NMR spectrum expanded in the range of 6.6–7.7 ppm attributed to the aromatic hydrogens are seen in the inset. ^1H NMR

Scheme 1. Chemical reactions for preparation of as-used Schiff base.

Table 1. Preparation conditions for synthesis of PbTe micro/nanostructures.

Sample	Temperature (°C)	Time (h)	Morphology	SEM image
1	160	12	Irregular shapes including nanocubes	Figure 2(a)
2	180	12	Micro/nanocubes	Figure 2(b)
3	200	12	Nanoparticles	Figure 2(c)
4	180	3	Irregular shapes including nanocubes, nanoparticles and nanorods	Figure 4(a)
5	180	6	Agglomerated particles plus a small amount of nanocubes	Figure 4(b)
6	180	9	Micro/nanocubes	Figure 4(c)
7	180	24	Micro/nanocubes and small amount of nanorods	Figure 4(d)

Figure 1. ^1H NMR (a) and FT-IR (b) spectra of as-synthesized Schiff base.

(400 MHz, CDCl_3) data for this compound is as follows: δ : 15.65 (*s*, 2H, OH); 6.607–7.471 (*m*, 18H, aromatic); 3.469–3.739 (*t*, *s*, 12H, $-\text{CH}_2-$). These results proved the formation of the Schiff base compound derived from 1,8-diamino-3,6-dioxaoctane and 2-hydroxybenzophenone. FT-IR spectrum of the as-prepared (2-HBP)-(DaDo) was

presented in figure 1(b). The strong peak marked at 1607 cm^{-1} is attributed to $\nu(\text{C}=\text{N})$ as a characteristic band for the Schiff base compound. The ring skeletal vibrations ($\text{C}=\text{C}$) of the Schiff base compound were observed at 1494 and 1448 cm^{-1} . The phenolic $\text{C}-\text{O}$ stretching vibration appeared at 1258 cm^{-1} in this compound. All

Figure 2. SEM images of products synthesized at 160 (a), 180 (b) and 200 °C (c) for 12 h.

Figure 3. XRD patterns of products synthesized at 160 (a), 180 (b) and 200 °C (c) for 12 h.

the absorption bands in FT-IR spectrum of (2-HBP)-(DaDo) were attributed to the Schiff base compounds (Kazemi-Babaheydari *et al* 2012). ^1H NMR and FT-IR spectra proved the formation and purity of the as-synthesized Schiff base compound.

3.2 Characterization of PbTe micro/nanostructures

To investigate effect of temperature on the morphology of the final products, the starting reagents were heated at 160 (sample 1), 180 (sample 2) and 200 °C (sample 3) at the same conditions. SEM images of the samples 1–3 are seen in figures 2(a–c), respectively. As shown in figure 2(a), morphology of the sample 1 consists of irregular shapes including a small amount of cubic-like micro/nanostructures. By increasing the temperature from 160 to 180 °C, the formation of cubic-like nanostructures was observed in SEM image of sample 2 (figure 2b). On further increasing the temperature to 200 °C, particle-like nanostructures were obtained (figure 2(c)). Based on SEM images presented in figure 2, it was found that self-assembly of PbTe crystals to produce cubic-like micro/nanostructures increased at 180 °C.

XRD patterns of the samples synthesized at 160, 180 and 200 °C are shown in figures 3(a–c), respectively. All the reflection peaks in figures 3(a–c) can be indexed to the cubic PbTe with cell constants $a = b = c = 6.4610 \text{ \AA}$ (JCPDS card no. 77-0246). XRD results proved high crystallinity and purity of the products synthesized by

Figure 4. SEM images of products synthesized at 180°C after heating for 3 (a), 6 (b), 9 (c) and 24 h (d).

hydrothermal method. The crystalline size of the as-synthesized products was calculated from the major diffraction peak (2 0 0) using the Scherrer formula ($D_c = K\lambda/\beta \cos \theta$) (Jenkins and Snyder 1996). The crystal diameters of samples 1, 2 and 3 estimated by the Debye–Scherrer formula were about 95, 83 and 90 nm, respectively.

To study effect of the reaction time on the morphology of the final products, experiment was carried out at 180 °C for 3 (sample 4), 6 (sample 5), 9 (sample 6) and 24 h (sample 7) at the same conditions, respectively. SEM images of samples 4–7 are seen in figures 4(a–d), respectively. When the reaction time was 3 h, morphology of products was composed of rod-like, cubic-like and particle-like micro/nanostructures (figure 4a). When the reaction time was 6 h, although the presence of nanorods disappeared, formation of the nanocubes is also seen in the morphology of sample 5 (figure 4b). In addition, agglomeration of the nanoparticles in sample 5 is very high. As shown in figure 4(c and d), the formation of cubic-like nanostructures are increased by increasing the reaction time to 9 and 24 h. According to SEM image presented in figure 4(d), it is observed that rod-like nanostructures were produced by self-assembly of cubic-like nanostructures. Therefore, it can be found that by increasing the reaction time at the same conditions, the production of uniform nanocubes increased.

To further study the purity and chemical composition of the products, EDS spectrum of the sample 3 formed at 200 °C for 12 h was taken and shown in figure 5. Figure 5 indicates that the elements in sample 3 are Pb and Te only (Si signal was from the substrate). EDS results gave a rough atomic ratio of Pb:Te as nearly 1:1 (Pb: 46.84; Te: 53.16), confirming purity of products synthesized through this route.

3.3 Possible formation mechanism of PbTe micro/nanostructures

Based on the available reports, it was found that PbTe can be formed by two independent pathways, involving ionic and atomic processes. It was found that in the ionic process, Pb^{2+} ions can react with Te^{2-} ions to generate PbTe nuclei. Besides, in the atomic process, the metal Pb reduced from Pb^{2+} by reducing agent and it combined with metal Te to generate PbTe nuclei (Zhu *et al* 2008; Wan *et al* 2009; Cao *et al* 2010). It must be remembered that the formation of PbTe through both ionic and atomic processes results from red-ox reactions. The main steps for the formation of PbTe nanostructures by hydrothermal method are as follows:

Figure 5. EDS spectrum of PbTe micro/nanostructures.

According to the proposed formation mechanism of PbTe, addition of NaOH accelerated the dissolution process of Te powder. The disproportional reaction of Te can produce TeO_3^{2-} ions, which can reduce to Te_{a+1}^{2-} ions by hydrazine hydrate. Te_{a+1}^{2-} ions with purple-black colour consist of Te and Te^{2-} ions (Lisiecki *et al* 1996). By reaction between Te^{2-} and Pb^{2+} ions, PbTe was formed via an ionic process (1, 2, 3, 5). In addition, Te powder can react with the metal Pb reduced from Pb^{2+} by hydrazine hydrate through an atomic process to produce PbTe. Because of the presence of hydrazine hydrate as a reductant in the reaction vessel, the formation of PbTe nuclei through the atomic mechanism was possible (3, 4, 6). When the presence of the metal Pb and Te was not observed in XRD patterns of the products, we could propose an atomic formation mechanism for the synthesis of PbTe nanostructures. In addition, the experimental observations such as the formation of the purple solution including Te^{2-} ions proved the ionic formation mechanism.

4. Conclusions

In summary, cubic-like PbTe micro/nanostructures were successfully fabricated by hydrothermal routes. A new Schiff base compound derived from 1,8-diamino-3,6-dioxaoctane and 2-hydroxybenzophenone was synthesized and then used as capping agent instead of the current surfactant molecules for the preparation of PbTe nanostructures. Pure cubic phased PbTe nanostructures

without any impurities like Pb and Te have been obtained by hydrothermal approach. It was found that by increasing reaction time from 3 to 24 h, the formation of PbTe nanocubes increased. We hope that the synthesis and application of new Schiff base compounds for the preparation of nano-sized materials can be useful to control crystal growth and morphology of nanomaterials.

Acknowledgement

Authors are grateful to the council of University of Kashan for providing financial support to undertake this work.

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