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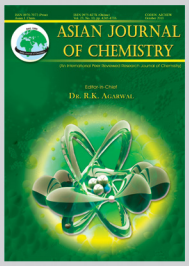

Template-Free Synthesis of Lead Telluride Nanowires by a Hydrothermal Process

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One-pot template-free approach was developed to synthesize lead telluride nanowires by reaction of lead acetate and sodium tellurite at 180 ºC, in which sodium hypophosphite ($NaH_2PO_2·H_2O$) was used as reducing agent. The product was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscope (HRTEM). During this process, the pH value and reducing agent have great influence on the morphology of the final products. This method provides the advantage of synthesizing PbTe nanowires without employing surfactants, templates and the experiments were carried out in an easy and mild way, which is of great importance to potential application in IR detection, photoconductivity and thermoelectric materials for thermoelectric power generation field, *etc*.

Key Words: PbTe Nanowires, Crystal growth, Hydrothermal process, Characterization.

INTRODUCTION

In recent years, fabrication of nanomaterials with a controllable size and shape is of great scientific and technological interest[1,2]. As one of the most important types of semiconductor, lead telluride (PbTe) has been extensively studied because of its wide applications in IR detection, photoconductivity and thermoelectric materials for thermoelectric power generation[3-5].

Lead telluride crystal usually achieved by various methods such as: bridgman method, crystal pulling, sublimation and chemical vapour transport[6,7]. In contrast to these preparation methods, solution approaches are usually carried out in an easy and mild way. Many efforts have been made to synthesize different nanostructures of PbTe by solution methods. For examples, Li *et al.*[7,8] have reported a new hydrothermal path to synthesize PbTe nanoparticles and nanorods by reaction of lead acetate and tellurium powder in sodium hydroxide solution in the presence of hydrazine hydrate as reducing agent and have developed a co-reduction method to synthesize CoTe and NiTe nanowires successfully. Lead telluride hollow nanoscale spheres and single crystal tubular have been successfully synthesized in a homogeneous ethanol/glycerol system[9]. Lu and his co-workers have synthesized high-quality spherical PbTe nanocubes by injecting lead acetate trihydrate and trioctylphosphine telluride (TOP-Te) into vigorously stirring hot phenyl ether in the presence of oleic acid at 200 ºC. A facile and mild solution method has been discovered for the synthesis of complex PbTe hopper crystals in large quantities[10].

Recently, uniform single-crystalline pearl-necklace-shaped PbTe nanowires were successfully synthesized by a hydrothermal process using tellurium nanowires as templates and $Pb(NO_3)_2$ as a precursor at a molar ratio of 1:1[11]. Highly uniform CdTe and PbTe nanowires with a very high aspect ratio of 1000 and an average diameter of 12 nm can be conveniently synthesized using ultrathin Te nanowires as templates *via* a low-temperature hydrothermal process[12]. Hydrothermal rolling-up formation was proposed to synthesize one-dimensional, single-crystalline lead telluride nanostructures by a hydrothermal reaction between lead foil and tellurium powder[13]. To the best of our knowledge, there is few report about synthesis of one-dimension nanostructures of PbTe in the absence of hard templates.

Herein, a template-free approach was developed to synthesize lead telluride nanowires successfully by reaction of lead acetate and sodium tellurite in the presence of sodium hypophosphite ($NaH_2PO_2·H_2O$) using as reducing agent by a simple hydrothermal process. The growth mechanism has been considered and investigated carefully.

EXPERIMENTAL

All chemicals are analytical grade and were used without further purification.

General procedure: Lead acetate ($Pb(OAc)_2·3H_2O$) and sodium tellurite (Na_2TeO_3) was used as lead and tellurium sources, respectively. In a typical synthesis, $Pb(OAc)_2·3H_2O$

(0.0948 g, 0.25 mmol) was dissolved in 23 mL of distilled water to form an aqueous solution, 0.0553 g (0.25 mmol) of sodium tellurite and 1.0 mL 1.0M NaOH solution and 0.1059 g (1.0 mmol) sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) added into the previous solution, respectively; which was then transferred to a Teflon-lined stainless steel autoclave (30 mL in total volume), sealed and maintained at 180 ºC for 24 h in a digital-type temperature-controlled oven, then allowed to cool to room temperature naturally. The resulting precipitates in black-blue colour were collected, centrifuged and washed with deionized water and ethanol for three times and dried at 60 ºC for 4 h. In another synthesis, sodium hypophosphite was replaced by hydrazine hydrate and sodium borohydride ($NaBH_4$) while other experimental conditions were kept the same.

Detection method: The as-prepared product was characterized by X-ray diffraction, TEM and HRTEM. X-ray power diffraction (XRD) analysis was carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized CuK_α radiation (λ = 1.54056 Å) and the operation voltage and current were maintained at 40 kV and 40 mA, respectively. The morphology and size of the samples were investigated by field-emission scanning electron microscopy (FESEM, Jeol-6700F) and transmission electron microscopy (TEM, Jeol 3010). Selected area electron diffraction (SAED) pattern was obtained on Jeol JEM 2010F.

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction (XRD) pattern of the as-prepared product from 0.0948 g (0.25 mmol) $Pb(OAc)_2 \cdot 3H_2O$ and 0.0553 g (0.25 mmol) $NaTeO_3$ at 180 ºC using sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) as reducing agent. All the peaks can be indexed as face-centered cubic PbTe with cell constants a = 6.459 Å, which is in good agreement with the literature value (JCPDS card No. 38-1435).

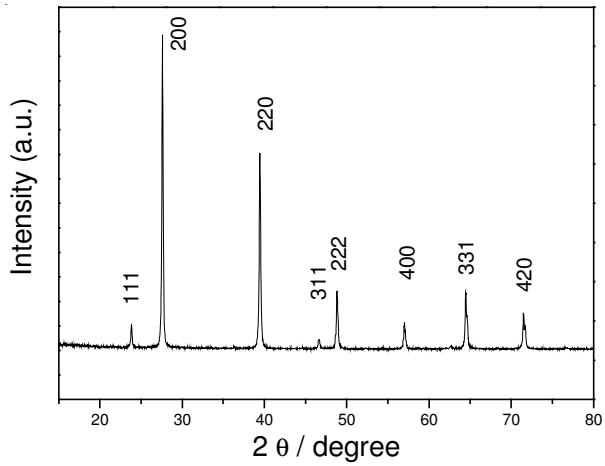

Fig. 1. XRD patterns of the as-prepared product obtained from 0.0948 g (0.25 mmol) $Pb(Ac)_2 \cdot 3H_2O$ and 0.0553 g (0.25 mmol) $NaTeO_3$ at 180 ºC for 24 h

The morphology and size of the product were investigated by transmission electron microscope (TEM) and field emission scanning electron microscopy (FESEM). Fig. 2a shows a low magnification TEM image of the as-prepared product obtained at 180 ºC, which indicates that the product consist of nanowires with *ca.* 30-100 nm in diameters and tens of micrometers in length as FESEM images shown (Fig. 3a). Fig. 2b shows an individual nanowire with 40 nm in diameters and tens of micrometers in length. Fig. 2b shows electron diffraction (ED) pattern of the single nanowires taken from the middle portion of the nanowires, which indicates that the nanowire is single crystalline and can also be confirmed by high-resolution TEM image obtained from an individual nanowire (Fig. 2c). The fringe spacing of 0.32 nm corresponds to the interplanar distance of {200} planes, implying that the growth direction of this nanowire was < 100 >.

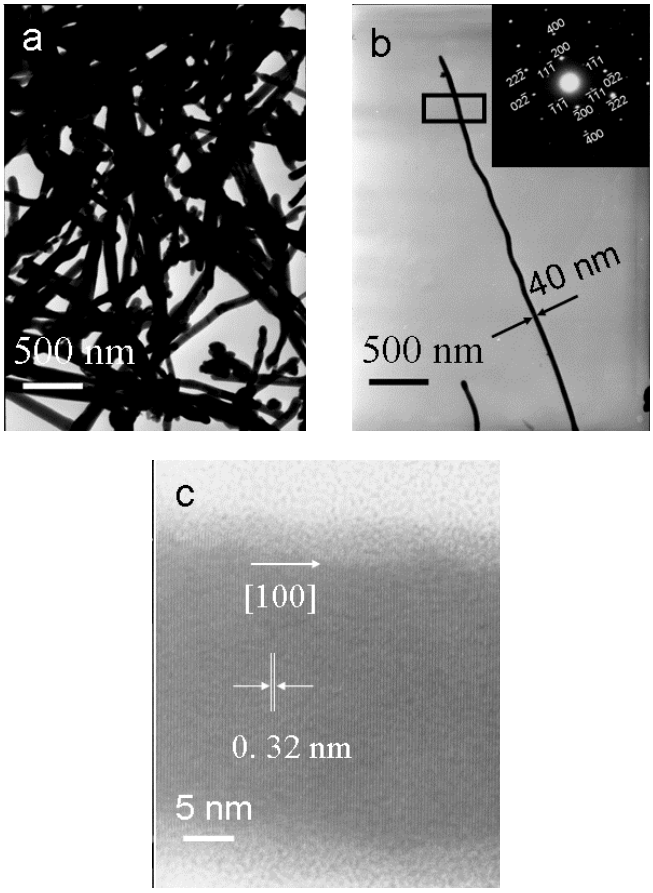

Fig. 2. TEM and HRTEM images of as-prepared PbTe nanowires (inset: ED pattern)

To gain a better understanding on the growth mechanism of the PbTe nanowires, products obtained from the experiments under different condition were collected for SEM analysis. It is found that only part of nanowires formed when the experiments was carried out at 100 ºC for 24 h (Fig. 3b); when the temperature raised to 200 ºC for 24 h, PbTe nanowires become shorter and some nanoparticles of PbTe were also formed. The product shown in Fig. 3d exhibits nanoparticles of PbTe aggregation together formed at a higher pH value. Previous study revealed that reducing agent also play important role in formation of PbTe nanowires[13,17]. For comparison, sodium hypophosphite was replaced by hydrazine hydrate and sodium borohydride ($NaBH_4$) while other experimental conditions were kept the same. Fig. 4 show TEM images of the pearl-necklace-like PbTe nanostructues and irregular nanoparticles obtained using hydrazine hydrate and $NaBH_4$ as reducing agent,

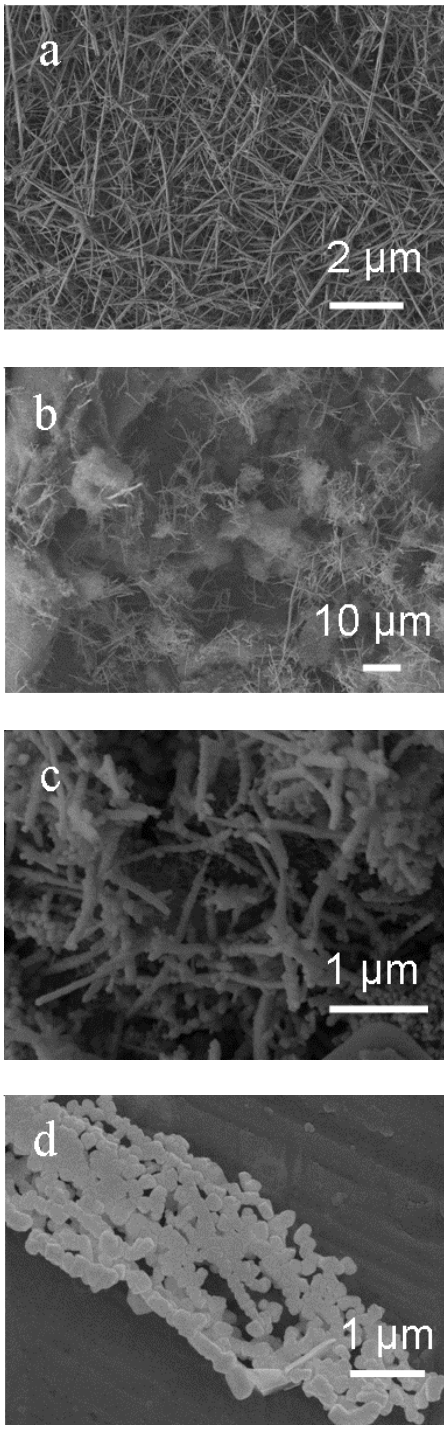

Fig. 3. SEM images of the samples obtained under different temperatures for 24 h (a) 180 ºC; (b) 100 ºC; (c) 200 ºC; (d) at 180 ºC and 5mL 1.0M NaOH used

respectively; while other experimental conditions were kept the same. The results demonstrated that the choice of different temperature and pH value and reducing agents will result in the PbTe nanostructures with different shapes. The synthesis of PbTe nanowires was kinetically controlled and the detailed formation process of the nanowires is complicated and needs to be investigated further.

Conclusion

We have demonstrated a simple hydrothermal synthesis of unique PbTe nanowires by reaction of lead acetate and sodium

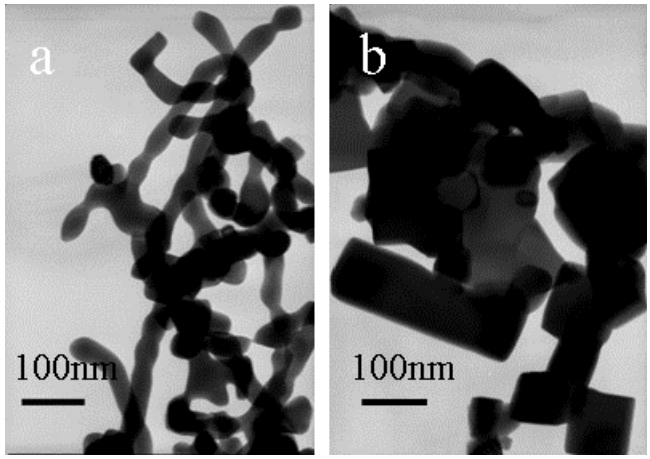

Fig. 4. TEM images of as-prepared PbTe at 180 ºC for 24 h (a) 1 mmol hydrazine hydrate; (b) 1 mmol sodium borohydride ($NaBH_4$)

tellurite in large quantities in the presence of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) using as reducing agent and without using any surfactants or capping agents. High resolution transmission electron microscope analysis reveals that the growth direction of PbTe nanowires was along < 100 >. Temperature and pH value and reducing agent play important roles in formation of PbTe nanowires and one-pot synthesis of PbTe nanowires are carried out in an easy and mild way, which is of great importance to potential application in IR detection, photoconductivity and thermoelectric materials for thermoelectric power generation field, *etc*.

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