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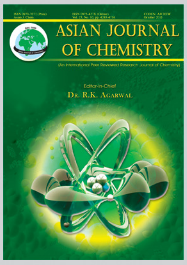

Synthesis, Characterization and Growth Mechanism of PbTe@carbon Core-Shell Nanowires by One-Pot Hydrothermal Approach

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One-dimensional PbTe@carbonaceous thermoelectric core-shell nanowires has been fabricated successfully by a one pot hydrothermal process, which are obtained from reaction with lead acetate and sodium tellurite using glucose as reductive agent and carbon source at 160 ºC for 7 h. The growth mechanism of the PbTe@carbonaceous core-shell nanowires was discussed carefully, which is to some extent similar to the so called synergistic soft-hard template mechanism (SSHM). Furthermore, these PbTe@carbonaceous thermoelectric core-shell nanowires are obviously highly functionalized, which is of great importance to potential application in catalysis, wastewater treatment, infrared detectors, laser diodes and thermoelectric device, *etc*.

Key Words: Crystal growth, Nanocomposites, PbTe nanowires, Hydrothermal synthesis.

INTRODUCTION

In recent years, fabrication of nanomaterials with a controllable size and shape is of great scientific and technological interest[1-3]. Lead telluride (PbTe) is a kind of important thermoelectric semiconductor material with a narrow band gap (*ca.* 0.32 eV at 300 K), which has attracted intense scientific interest owing to potential applications in infrared detectors, laser diodes and thermophotovoltaics and thermoelectric device, *etc.*[4-9]. The lead telluride (PbTe) crystal usually achieved by various methods such as: bridgman method, crystal pulling, sublimation and chemical vapour transport[10-13]. Much efforts have been made to synthesize lead telluride nanomaterials with different morphologies and size, including, nanocrystals[14,15], dendritic structures[16], hollow nanospheres/nanotubes[17,18], nanorods[19,20] and nanowires[21], *etc*. It is well known that one-dimensional semiconductor nanowires have received much attention owing to their potential use as building blocks of miniaturized electrical, nanofluidic and optical devices[22,23]. A variety of techniques have been employed to synthesize PbTe nanowires successfully, such as, chemical vapour transport method[24], hydrothermal process[25,26], electrodeposited method[27]. Most synthetic approaches for the fabrication of lead nanowires rely on hard templates involved in the growth process or harsh condition.

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, 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[21]. A facile and mild solution method has been discovered for the synthesis of complex PbTe hopper crystals in large quantities[28]. Films of nanoparticles of thermoelectric materials has been achieved by polymer film of polyethylene oxide (PEO) or poly(L-lactide) embedded with PbSe or PbTe nanoparticles[29]. 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[30]. Recently, the synthesis of PbTe nanocrystalline networks using weak capping ligands in aqueous media has been demonstrated and more complicated nanostructures including carbohydrate spheres@PbTe core-shell structures and Te@carbohydrate @PbTe multilayered submicron cables have been fabricated[31]. To the best of our knowledge, there are few reports about synthesis of PbTe@carbonaceous core-shell nanowires. Previous study revealed that carbonaceous nanofibers obtained from carbohydrate were excellent platform for application in waste water treatment and filter and separate nanoparticles with different sizes from solution by a simple filtration process[32].

In the present study, one-pot hydrothermal process has been developed to synthesize PbTe@carbonaceous core-shell nanowires successfully. The core-shell nanowires was obtained from lead acetate and sodium tellurite using glucose as reductive agent and carbon source at 160 ºC for 7 h. The detailed reaction, shape evolution process and the growth mechanism of the core shell nanowires have been studied.

EXPERIMENTAL

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

General procedure: Lead acetate [$Pb(OAc)_2 \cdot 3H_2O$] and sodium tellurite (Na_2TeO_3) was used as lead and tellurium sources, respectively. In a typical synthesis, $Pb(OAc)_2 \cdot 3H_2O$ (0.0948 g, 0.25 mmol) and 1.5 g glucose were dissolved in 12 mL of distilled water to form an aqueous solution, 10 mL of PVA (3 wt %) solution were put into the solution and with vigorously stirring and subsequently followed by addition of 0.0553 g (0.25 mmol) of sodium tellurite. It was then transferred to a Teflon-lined stainless steel autoclave (30 mL in total volume), sealed and maintained at 160 ºC for 7 h in a digital-type temperature-controlled oven, then allowed to cool to room temperature naturally. The resulting precipitates in black colour were collected, centrifuged and washed with deionized water and ethanol for three times and dried at 60 ºC for 4 h.

Detection method: The phase and morphology of the as-prepared product was characterized by X-ray diffraction, transmission electron microscopy and high resolution transmission electron microscopy (HRTEM); respectively. X-Ray 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); transmission electron microscopy and high resolution transmission electron microscopy (HRTEM) was obtained on Jeol 3010.

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) $NaTeO_3$, 1.5 g glucose at 160 ºC for 7 h. All the peaks can be indexed as face-centered cubic PbTe with cell constants a = 6.457 Å, which is in good agreement with the literature value (JCPDS card No. 38-1435) and without impurity peaks were detected.

Fig. 2a-b shows field-emission scanning electron microscopy (FESEM) images of the as-prepared product obtained at 160 ºC for 7 h, which indicates that the product consist of nanowires with *ca*. 50 nm in diameters and tens of micrometers in length as FESEM images shown. Fig. 2c shows a low magnified TEM image of the as-prepared sample. This indicates that the product is consisted of core-shell nanostructures of a core with about 15 nm in diameters and a surrounding sheath about 15 nm in thickness (Fig. 2d). Fig. 2e shows the high-resolution TEM image taken from the core nanowires in the rectangle portion as shown in Fig. 2d; which indicates that the nanowire is single crystalline and the fringe spacing of 0.31 nm corresponds to the interplanar distance of {200} planes implying that the growth direction of this nanowire was <100>.

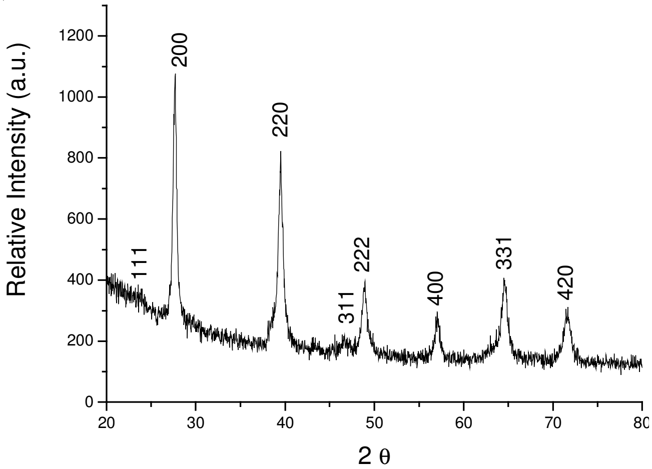
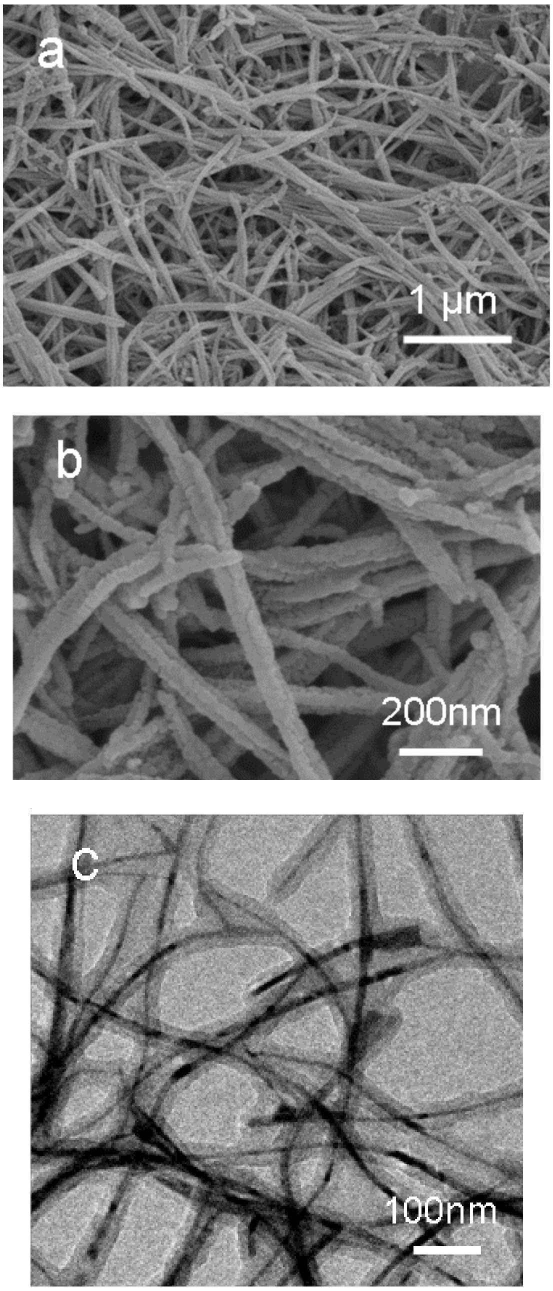


Fig. 1. XRD patterns of the as-prepared samples obtained from $Pb(OAc)_2 \cdot 3H_2O$, sodium tellurite and glucose in presence of 10 mL of PVA (3 wt %) solution at 160 ºC for 7 h



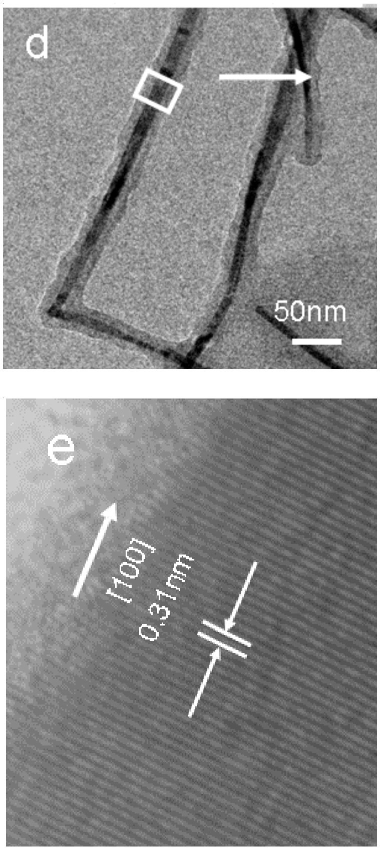


Fig. 2. (a-b) FESEM; (c-e) TEM images of the PbTe@carbon core-shell nanowires obtained from sodium tellurite, lead acetate and glucose in presence of PVA at 160 ºC for 7 h

Fig. 3 shows X-ray photoelectron spectrum (XPS) of the core-shell nanowires, which indicates that peak values at 284.58 and 531.47 eV can be assigned readily to the binding energies of C_{1s} and O_{1s}, respectively. The peak with binding energy at 138.0 eV for $Pb_{4f7/2}$ and 574.2 eV for Te_{3d5} were very weak and can be hardly detected, indicating that all of the tellurium and lead in these product are confined within shells of the carbonaceous layers. Fig. 4 shows FTIR spectrum of the as-prepared sample, in which the peaks around at 1300-1000 cm^{-1} are indicative for the C-OH stretching and OH bending vibrations and the peaks value around 1653 cm^{-1} are attributed to C=O vibration[30-32].

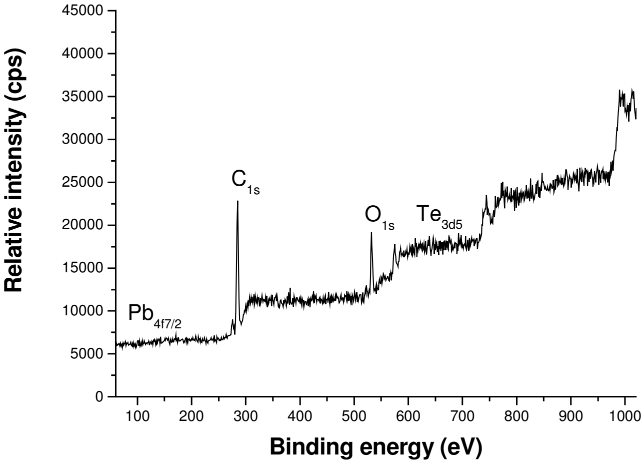


Fig. 3. XPS of the PbTe@carbon core-shell nanowires

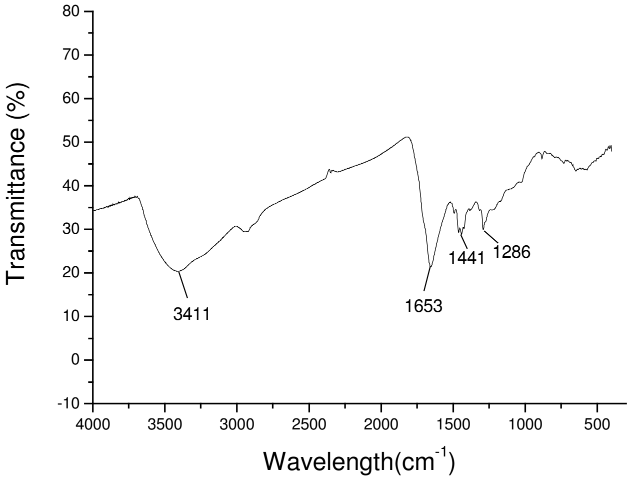


Fig. 4. FTIR spectrum of the PbTe@carbon core-shell nanowires

According to the possible formation mechanism of the PbTe/carbonaceous core-shell nanowires, it's to some extent similar to the synthesis of Ag_2Te fibers by a disproportional process of Te^0 into Te^{2-} and Te^{4+} in the presence of silver ions by a self-sacrificing template process[33]. The previous study revealed that Te^{4+} reduced by hydrogen atom of methylidyne of PVA due to the strongly interaction between Te^{4+} and PVA which leads to the dehydrogen process and makes the PVA cross-linked to form the Te@crosslinked PVA nanocables[34]. Based on above analysis and our previous results, there should be new species produced during the formation of PbTe/carbonaceous core-shell nanowires. The reactions occurred could be formulated as:

$$Pb^{2+} + TeO_3^{2-} \Rightarrow PbTeO_3 \quad (1)$$

$$PbTeO_3 + C_6H_{12}O_6 \Rightarrow Te + Pb^{2+} \quad (2)$$

$$3Te \Leftrightarrow 2Te^{2-} + Te^{4+} \quad (3)$$

$$Te^{4+} + C_6H_{12}O_6 \Rightarrow Te \quad (4)$$

$$Te^{2+} + Pb^{2+} \Rightarrow PbTe \quad (5)$$

In present study, TeO_3^{2-} should be reduced to Te quickly by glucose under hydrothermal condition and subsequently, disproportional process of Te^0 into Te^{2-} and Te^{4+} was followed. Finally, Pb^{2+} and Te^{2-} reacted with each other to form PbTe. All these reactions was carried out and completed in short time, which was confirmed by the experiments. Fig. 5 shows the X-ray diffraction of the sample prepared at 160 ºC for 4 h, which shows similar diffraction patterns as shown in Fig. 1 and without impurity peaks were detected.

A schematic drawing is given in Fig. 6 to illustrate how to synthesize the PbTe@carbonaceous core shell nanowires. Amorphous precipitation of $PbTeO_3$ was formed at the initial stage of the reaction. And then, PbTe nanowires was synthesize in short time under hydrothermal condition. As time increasing, a carbonaceous layer from carbonization of glucose was coated on the backbone of the pre-existed PbTe nanowires to form PbTe@carbonaceous core shell nanowires. The growth mechanism of the PbTe@carbonaceous core-shell nanowires, which is to some extent similar to the so called synergistic soft-hard template mechanism (SSHM) proposed previously[34].

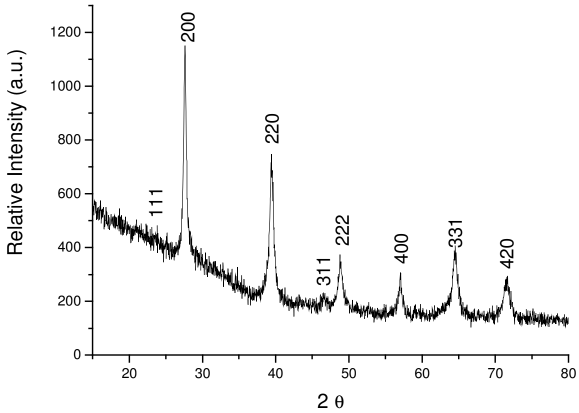


Fig. 5. XRD patterns of the as-prepared samples obtained from $Pb(OAc)_2·3H_2O$ (0.0948 g, 0.25 mmol), 0.0553 g (0.25 mmol) of sodium tellurite and 1.5 g glucose in presence of 10 mL of PVA (3 wt %) solution at 160 °C for 4 h

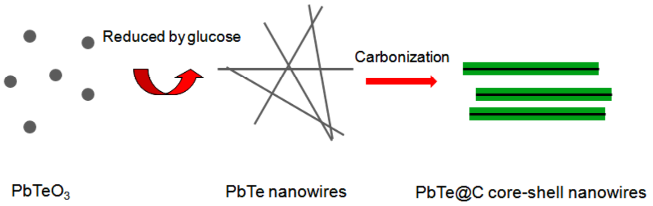


Fig. 6. Schematic illustration of formation of PbTe@carbon core-shell nanowires

Conclusion

In summary, PbTe@carbonaceous core-shell nanowires have been fabricated successfully by a one pot hydrothermal process. FESEM and TEM characterization revealed that the core-shell nanowires with *ca.* 50 nm in diameters and tens of micrometers in length, a core with about 15 nm in diameters and a surrounding sheath with about 15 nm in thickness. The surface of these PbTe@carbonaceous thermoelectric core-shell nanowires are obviously highly functionalized, which is of great importance to potential application in catalysis, wasted water treatment, infrared detectors, laser diodes and thermoelectric device.

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