A Simple Chemical Approach for PbTe Nanowires with Enhanced Thermoelectric Properties

Qingyu Yan,* Hao Chen, Wenwen Zhou,
Huey Hoon Hng, Freddy Yin Chiang Boey, and Jan Ma

*School of Materials Science and Engineering,
Nanyang Technological University, 50 Nanyang Avenue,
Singapore 639798*

Thermoelectric semiconductors have attracted much attention for their applications in power generation from waste heat and solid state cooling.[1,2] Because of their high seebeck coefficient, S, low thermal conductivity, k, and high electric conductivity, σ, bulk PbTe[3] and its alloy[4] are of particular interest and shows very high figure of merit ZT, defined as $S^2\sigma/k$, in the temperature range of 400−700 K. Reducing the dimension of the thermoelectric semiconductor has been predicted as a successful strategy[5,6] to gain further enhancements in ZT because of the quantum size effect and the enhanced interface scattering of phonons. One dimensional (1D) structures, e.g., nanowires (NWs), are of particular interest because they are suitable for building device circuit, which allows the study of thermal and electrical properties of individual nanostructure through contact formation.

Currently, the synthesis of PbTe-based 1D structure still largely depends on electrochemical deposition into hard templates,[7,8] which gives polycrystalline products and requires a tedious process to remove the hard template for further device integration. Although chemical vapor deposition also has been applied to produce PbTe NWs, the diameter of the NWs is relatively large in the range of 100−200 nm and is away from the quantum size region. Limited success has been demonstrated in PbTe NWs growth by solution-based soft-templating approaches, which normally yield spherical or cubic nanoparticles[9−13] possibly because of the cubic crystal structure favoring isotropic growth. Previous attempt on using pre-synthesized Te nanotube as the template to react with Pb(Cl)$_2$ yields large sized PbTe nanorods with diameter 75−100 nm and with impurity phase of unreacted Te.[14]

Here, we introduce a new approach in a simple one-step solvothermal polyol process to prepare PbTe nanowires with tunable sizes, e.g., with diameters varying from 10 to 30 nm and lengths varying from 600 nm to 3 μm. The diameter of the PbTe nanowires is smaller than those previous reported by other preparation methods and is close to the quantum size regions. The 1D growth of PbTe is directed because of the interaction between the Pb element in the PbTe and the hydroxyl groups in the sucrose molecule, which are proposed to form stacking templates in the solution because of $\pi-\pi$ electron interaction. The growth mechanism is studied by changing synthesis conditions to produce various nanostructures and discussed. The film samples made from the PbTe nanowires yield very high seebeck coefficients >470 μV/K in the temperature range of 375−425 K, which is about 80% higher than that of bulk pure PbTe.[15]

In a typical synthesis procedure, telluric acid and lead acetate were dissolved separately into small amounts of pentanediol. They were then mixed and injected into hot sucrose containing pentanediol at 180−210 °C in a three-neck round flask under Ar protection. The whole solution turned black within 30 s. The reaction was stopped after 1−2 min by quenching in an ice water bath. The precipitates were washed with ethanol and centrifuged out.

Scanning electron microscopy (SEM) image in Figure 1a reveals the PbTe nanowires obtained from samples prepared at 180 °C and quenched after 90 s. The nanowires are straight and have uniform lengths spanning 2−3 μm. Although the side wall of the wires is jagged, the nanowire width has a narrow distribution in the range of 15−25 nm (see Figure 1a−c). Energy-dispersive X-ray (EDX) analysis of the as-prepared sample revealed a Pb:Te ratio of close to 50:50, independent of the ratio between the precursors, lead acetate and telluric acid. Phase contrast atomic resolution TEM and the selected area electron diffraction (SAED) pattern indicate that each nanowire is a single crystal (see c and d in Figure 1). The long axis of the nanowires is parallel to $(\bar{2}11)$ planes and the short axis is parallel to $(0\bar{1}1)$ planes. X-ray diffraction (XRD) pattern from the as-prepared nanowires reveals the cubic crystal structure (see Figure 1d), which is consistent with the HRTEM and SAED results. No impurity phases were detected in the XRD result.

The size and morphology of the PbTe nanowires are sensitive to the reaction temperature, reaction time, the

* Corresponding author. E-mail: alexyan@ntu.edu.sg.

(1) Goldsmid, H. J. *Thermoelectric Refrigeration*' Plenum: New York, 1964.
(2) Venkatasubramanian, R.; Siivola, E.; Colpitts, T.; O'Quinn, B. *Nature* **2001**, *413* (6856), 597–602.
(3) Rowe, D. M. *CRC Handbook of Thermoelectrics*; CRC press: Boca Raton, FL, 1995.
(4) Hsu, K. F.; Loo, S.; Guo, F.; Chen, W.; Dyck, J. S.; Uher, C.; Hogan, T.; Polychroniadis, E. K.; Kanatzidis, M. G. *Science* **2004**, *303* (5659), 818–821.
(5) Dresselhaus, M. S.; Dresselhaus, G.; Sun, X.; Zhang, Z.; Cronin, S. B.; Koga, T.; Ying, J. Y.; Chen, G. *Microscale Thermophys. Eng.* **1999**, *3* (2), 89–100.
(6) Dresselhaus, M. S.; Dresselhaus, G.; Sun, X.; Zhang, Z.; Cronin, S. B.; Koga, T. *Phys. Solid State* **1999**, *41* (5), 679–682.
(7) Liu, W. F.; Cai, W. L.; Yao, L. Z. *Chem. Lett.* **2007**, *36*, 1362–1363.
(8) Sima, M.; Enculescu, I.; Sima, M.; Vasile, E. *J. Optoelectron. Adv. Mater.* **2007**, *9* (5), 1551–1554.
(9) Wang, W. Z.; Poudel, B.; Wang, D. Z.; Ren, Z. F. *Adv. Mater.* **2005**, *17* (17), 2110.
(10) Mokari, T. L.; Zhang, M. J.; Yang, P. D. *J. Am. Chem. Soc.* **2007**, *129* (32), 9864.
(11) Urban, J. J.; Talapin, D. V.; Shevchenko, E. V.; Kagan, C. R.; Murray, C. B. *Nat. Mater.* **2007**, *6* (2), 115–121.
(12) Murphy, J. E.; Beard, M. C.; Norman, A. G.; Ahrenkiel, S. P.; Johnson, J. C.; Yu, P. R.; Micic, O. I.; Ellingson, R. J.; Nozik, A. J. *J. Am. Chem. Soc.* **2006**, *128* (10), 3241–3247.
(13) Lu, W. G.; Fang, J. Y.; Stokes, K. L.; Lin, J. *J. Am. Chem. Soc.* **2004**, *126* (38), 11798–11799.
(14) Purkayastha, A.; Yan, Q.; Gandhi, D.; Li, H.; Pattanaik, P. G.; Borca, T.; Ramanath, G. *Chem. Mater.* **2008**, *20* (15), 4791–4793.
(15) Heremans, J. P.; Thrush, C. M.; Morelli, D. T. *J. Appl. Phys.* **2005**, *98* (6), 063703-1–6.

Communications

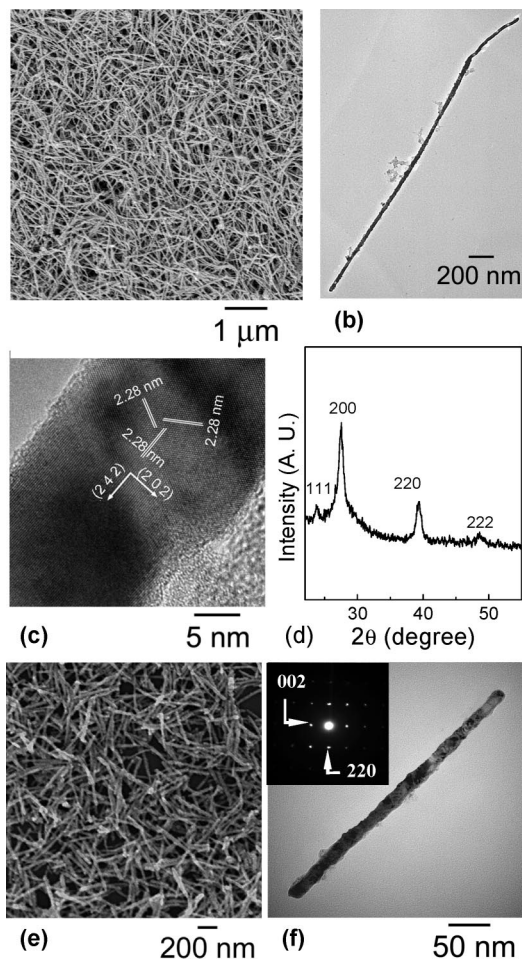*Chem. Mater., Vol. 20, No. 20, 2008* 6299

Figure 1. (a) A SEM image of PbTe nanowires prepared at 180 °C. Representative (b) TEM and (c) HRTEM images of a PbTe NW in the same batch as (a). (a−c). (d) X-ray diffractogram of PbTe NWs as shown in (a−c). (e) SEM image of PbTe NWs prepared at 210 °C. (f) Typical TEM image of a PbTe NW in the same batch as (e). Inset in (f) is the corresponding SAED pattern.

Figure 2. SEM images of (a) PbTe cubes precipitate in the synthesis without sucrose, (b) PbTe clusters formed in the synthesis by replacing sucrose with TOPO. (c) Typical TEM image of the PbTe clusters in the same batch as (b) indicates the cluster is formed as folded thin film (see details in the Supporting Information, Figure S2). (d) SAED pattern on the sample in (c) indicates that the film is crystallized with normal direction of ($\bar{1}11$).

Scheme 1. Proposed Growth Mechanism of the PbTe NWs[a]

[a] The sucrose molecules form stacking templates. The hydroxide groups in the sucrose preferentially interacted with Pb atom.

thermal history, as well as the surfactant template. Nanowires of 10−16 nm in width and 400−600 nm in length were obtained (see e and f in Figure 1) by injecting precursors into pentanediol heated at 210 °C and quenched after 60 s. We noted that the width of the PbTe nanowires is smaller than those reported to date. Nanowires with smaller width hold more promise because the increased interface phonon scattering decreases the thermal conductivity and the quantum size effect can enhance the seebeck coefficient.[6] Extending the reaction time will leads to formation of PbTe nanoparticles (see the Supporting Information, Figure S3). However, dissolving lead acetate and telluric acid into pentanediol at room temperature and then heating the mixture gradually with a heating rate of 5 K/min to 180−210 °C to allow the reaction to take place led to the formation of a non-uniform-shaped mixture (see the Supporting Information, a and b in Figure S1). We also noted that sucrose is the key to direct 1D growth[16] in this particular reaction. Precipitation of PbTe under the same condition without sucrose led to the formation of cubes with an average size of ∼100 nm
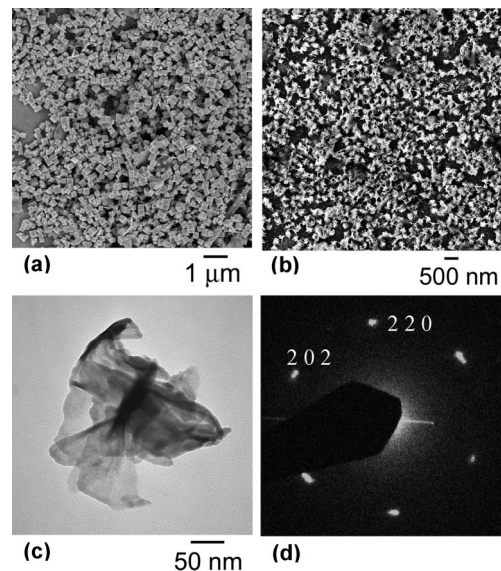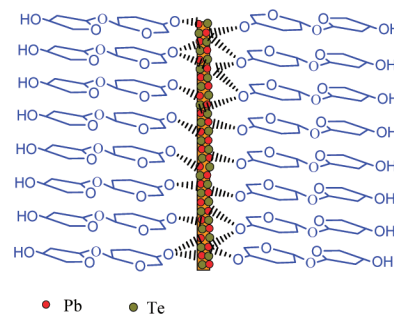
(see Figure 2a). By replacing sucrose with trioctylphosphine oxide (TOPO) under the same reaction conditions, we observed flower shaped nanocluster forming from folded thin film (see b and c in Figure 2 and the Supporting Information, Figure S2a−d). The normal of the film is ($\bar{1}11$) as indicated by the SAED (see Figure 2d). The required reaction times for the above two cases without sucrose were prolonged to ∼30 min as judged by the appearance of black precipitation. The reaction time for synthesis without sucrose is much longer as compared to with sucrose, indicating that sucrose facilitates the reduction of the precursors as well as providing the soft templates to direct 1D growth.

On the basis of the above observation, we propose the phenomenological description that describes the key aspect of the PbTe nanowire formation. Although sucrose has been proven to assist 1D growth[16] by forming stacking template due to the π−π electron interaction as illustrated in Scheme 1, the hydroxyl groups of sucrose interact only effectively with Pb but not Te. For example, replacing Pb with Pt in the same synthesis process led to the formation of highly

(16) Yan, Q.; Rahuveer, M. S.; Li, H. F.; Singh, B.; Kim, T.; Shima, M.; Bose, A.; Ramanath, G. *Adv. Mater.* **2007**, *19* (24), 4358.
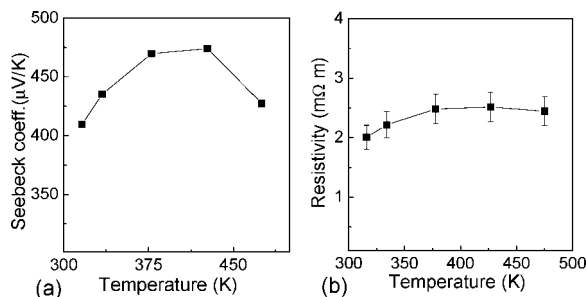
Figure 3. (a) Seebeck coefficients measured on the film sample of PbTe NW film in the temperature range of 315−525 K. (b) The corresponding resistivity of film sample at $T = 315−475$ K.

agglomerated random-shaped PtTe crystals (see the Supporting Information, Figure S4), which indicates the lack of effective interaction between sucrose and both elements of Te and Pt. Thus, the precipitation sequence of Te and Pb is the key to allow anisotropic growth. During the process of gradually heating to grow PbTe, Te precipitates faster than that of Pb (see the Supporting Information, Figure S5). This is because of the higher reduction potential of Te^{6+} as compared to that of Pb^{2+}, which forms large non-uniform-shaped mixtures because of the absence of passivation by sucrose during the initial Te nucleation stage. Injecting the precursors into the solvent at high temperature accelerates the precipitation of Pb that mixes with Te. The Pb interacts effectively with sucrose to passivate the nanostructure and translate the templating effect from the sucrose to direct the 1D growth. The oriented attachment process[17] may also be involved in the growth process, though we still lack of experimental proof.

To assess the thermoelectric properties of the PbTe NWs, we sprayed the NWs onto glass substrates after hydrazine washing and then annealed them at 300 °C in a vacuum. The NW film is porous while the NWs are randomly aligned without noticeable coalescence (see the Supporting Information, a and b in Figure S6). Seebeck coefficient S measurement on the annealed NW film in the temperature range 315−475 K revealed p-type semiconductor behavior (see Figure 3a). The S values are >470 μV/K at $T = 375$ and 425 K. These values are is about 80% higher than that of bulk pure PbTe.[15] While postulating that the quantum size achieved by the small diameter (10–20 nm) has enhanced the seebeck effect due to an induced modification of the density of state (DOS),[18] we also noted other possibility of

the phonon drag[19] caused by the increased scattering between phonon and charge carrier,[20] as the length (1−3 μm) of the NWs are higher than the mean free path of phonons in PbTe, and interface electron temperature gradient in the interfaces of the NWs.[21] Further investigation is currently undergoing to verify this. The film exhibits a linear current−voltage (I−V) curve (see the Supporting Information, Figure S6c) indicating the Ohmic contact response. The resistivities of the annealed film are plotted at different temperatures as shown in Figure 3b. Here, the variation of the film thickness contributes to the error of the resistivity values. The resistivity of the NWs films at room temperature is about 3−4 times higher than that[15] of bulk PbTe with a charge carrier concentration of 2×10^{17} cm^{-3}. This is possibly due to the un-optimized interconnection in the NW network. Here, we also noticed that the resistivity is highly dependent on the charge carrier concentration in the PbTe. The measurement of resistivity of individual NW is currently ongoing to check whether higher conductivity can be achieved in the PbTe NW.

In summary, we have demonstrated a simple solvothermal approach to synthesize PbTe NWs with tunable size. Sucrose passivation is the key to induce the 1D growth of PbTe. The size and morphology of the NWs are highly dependent on the reaction temperature, heating rates and type of surfactants used. Enhanced seebeck coefficient has been observed, which could possibly be due to either quantum size effect or phonon drag effect or both. The mechanism is under further investigation. Although the resistivity measured in the NW films are still high because of the unoptimized interconnections, we expect the resistivity of individual NW to be lower. Further optimizations of the thermoelectric properties of PbTe NW-based devices through interconnect alignment and doping may lead to energy conversion application of high efficiency.

(17) Penn, R. L.; Banfield, J. F. *Science* **1998**, *281* (5379), 969–971.
(18) Dresselhaus, M. S.; Chen, G.; Tang, M. Y.; Yang, R. G.; Lee, H.; Wang, D. Z.; Ren, Z. F.; Fleurial, J. P.; Gogna, P. *Adv. Mater.* **2007**, *19* (8), 1043–1053.
(19) Boukai, A. I.; Bunimovich, Y.; Tahir-Kheli, J.; Yu, J. K.; Goddard, W. A.; Heath, J. R. *Nature* **2008**, *451*, 168–171.
(20) Heremans, J. P.; Thrush, C. M.; Morelli, D. T. *Phys. Rev. B* **2004**, *70* (11), 115334-1–5.
(21) Chen, G. *J. Appl. Phys.* **2005**, *97* (8), 083707-1–8.