Efficient Synthesis of PbTe Nanoparticle Networks

Qiangfeng Xiao¹, Ding Weng¹, Zhenglong Yang¹, Javier Garay², Minjuan Zhang³ (✉), and Yunfeng Lu¹ (✉)

¹ Chemical and Biomolecular Engineering Department, University of California, Los Angeles, CA 90095, USA

² Mechanical Engineering Department, University of California, Riverside, CA 92521, USA

³ Materials Research Department, Toyota Motor Engineering and Manufacturing North America, Inc., 1555 Woodridge Ave. Ann Arbor, MI 48105, USA

Received: 23 April 2010 / Revised: 17 July 2010 / Accepted: 6 August 2010

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ABSTRACT

The synthesis of semiconductor nanocrystalline networks using weak capping ligands in aqueous media has been demonstrated. Carbohydrates, including β -cyclodextrin, *D*-(+)-glucose, *D*-glucosamine, lactobionic acid, sucrose, and starch were chosen as weak ligands to facilitate the formation of PbTe nanoparticle networks. The nanoparticle size, ranging from 5 nm to 30 nm, can be tuned by manipulating the temperature and concentration. Through a similar strategy, more complicated nanostructures including carbohydrate spheres@PbTe core-shell structures and Te@carbohydrate@PbTe multilayered submicron cables have been fabricated. This is a general approach which can be easily extended to the fabrication of other semiconductor networks, including PbSe and Bi₂Te₃ using carbohydrates and ethylenediaminetetraacetic acid (EDTA), respectively, as ligands.

KEYWORDS

Lead telluride, nanoparticle, network, core shell structures, thermoelectric, carbohydrate

1. Introduction

Compared to the bulk materials, nanocrystals possess unique size-dependent chemical and physical properties due to their quantum confinement effect [1]. Great success in the synthesis of colloidal nanocrystals with controlled morphology and composition has been achieved in the last two decades [2–5]. More advanced one-, two-, and three-dimensional superstructures have been constructed for practical device applications using nanocrystals as building blocks. For example, oriented attachment of preformed nanocrystals allows the formation of one-dimensional nanostructures of various materials, such as Ag [6], ZnO [7], ZnS [8], PbSe [9], PbTe [10], and CdTe [11]. Two-dimensional

nematic and smectic liquid-crystalline phases [12] have been obtained by Langmuir–Blodgett assembly of BaCr₂O₄ nanorods, whilst a water-droplet assisted self-assembly of nanocrystals generated various combinatorial hierarchically ordered two-dimensional architectures [13]. Three-dimensional ordered superlattices can be obtained using mixed solvents [14], programmable deoxyribonucleic acid (DNA) ligands [15, 16], or external magnetic fields [17]. Furthermore, the combination of binary monodisperse nanocrystals of different sizes and interactions can yield a wide range of three-dimensional superlattices with tunable structures and properties [18, 19].

Nanocrystalline networks facilitate charge transport and possess large surface area. Such materials may

Address correspondence to Minjuan Zhang, mindy.zhang@tema.toyota.com; Yunfeng Lu, luucla@ucla.edu

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find applications in catalysis, sensors, solar cells, and other fields. Generally, nanocrystalline networks can be prepared by either template or template-free methods. Of these methods, construction of nanocrystalline networks from preformed nanocrystals is attracting increasing interest. For instance, Au networks were prepared from Au particles by hydrothermally detaching surfactants [20], and CdS, ZnS, PbS, CdSe, and CdTe semiconductor networks (aerogels) were fabricated by partial oxidative ligand removal from nanoparticles synthesized in either aqueous or organic solution [21, 22]. PbSe nanocrystal networks have also been formed by the displacement of oleic acid ligands with pyridine [23]. In order to circumvent the necessity of removing the template or the synthesis of preformed nanocrystals, we have devised a one-step strategy for the synthesis of nanocrystalline networks using weak ligands. Various carbohydrates, such as β -cyclodextrin, *D*-(+)-glucose, *D*-glucosamine, lactobionic acid, sucrose, and starch were chosen as weak ligands. Compared to anchoring points such as $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, $-\text{SH}$, $-\text{NH}_2$, and $\equiv\text{P}=\text{O}$ in commonly used ligands, the binding capacity of $-\text{OH}$ on the carbohydrates is relatively weak. The weak ligands lack strong the steric repulsion and binding capability required to produce isolated nanoparticles. Therefore the growing nanoparticles tend to form continuous networks in order to reduce their surface energy. Among various semiconductors, lead telluride (PbTe) is of particular interest owing to its unique combination of properties including large excitonic Bohr radius, high carrier mobility, efficient multiexciton generation, large dielectric constant, high melting point, low vapor pressure, and relatively high thermoelectric figure of merit [24–27]. Although PbTe nanoparticles, nanorods, and nanowires have previously been produced, this work represents the first synthesis of nanocrystalline networks of this material.

2. Experimental

2.1 Reagents

Lead(II) nitrate (99.999%), sodium hydroxide (beads, 20–40 mesh), potassium hydroxide ($\geq 85\%$), tellurium

(powder), sodium borohydride ($\sim 98\%$), hydrazine (anhydrous), polyvinylpyrrolidone (average $M_w \sim 55,000$), β -cyclodextrin (powder), *D*-(+)-glucose ($\geq 99.5\%$), sucrose ($\geq 99.5\%$), starch (soluble, ACS reagent), α -lactose monohydrate (reagent grade), *D*-(+)-glucosamine hydrochloride ($\geq 99\%$), lactobionic acid (97%), poly(ethyleneimine) solution (PEI, average $M_n \sim 1,200$), ethylenediaminetetraacetic acid (99%), and 3-mercaptopropionic acid ($\geq 99\%$) were purchased from Aldrich.

2.2 Synthesis of PbTe networks

NaHTe was prepared [28] by reacting sodium borohydride with tellurium in water at 0°C for 8 h using a molar ratio of sodium borohydride:tellurium:water = 2:1:56. The lead precursors were prepared by consecutively dissolving 2 g of KOH, 1 g of carbohydrate, and 1.655 g of $\text{Pb}(\text{NO}_3)_2$ in 10 mL of distilled (DI) water under sonication. After purging the carbohydrate–Pb solution with nitrogen, an equimolar amount of freshly prepared NaHTe solution was added dropwise at room temperature under stirring, resulting in the immediate formation of black PbTe nanoparticles. The nanoparticles were separated by centrifugation, washed with ethanol and water, and finally dried under vacuum. This synthesis protocol is highly effective. For example, 10 g or more of PbTe nanoparticles can be prepared in less than 20 min starting with 12 g of $\text{Pb}(\text{NO}_3)_2$ in a 250 mL flask with a high yield of 80%.

2.3 Synthesis of carbohydrate sphere @PbTe core-shell structures

Carbohydrate spheres were prepared [29–32] by dissolving 4 g of *D*-(+)-glucose in 100 mL of distilled water and treating the resulting solution hydrothermally at 190°C for 4 h. The resulting dark brown precipitate was isolated by centrifugation and purified by three cycles of centrifugation/washing/redispersion in water and then in alcohol. Then 0.1 g of the as synthesized carbohydrate spheres, 0.02 g of NaOH, and 0.8275 g of $\text{Pb}(\text{NO}_3)_2$ were added to 30 mL of distilled water and the mixture ultrasonicated for 20 min. The resulting suspension was separated by centrifugation/washing/redispersion in water and

then in alcohol, and redispersed in 30 mL of distilled water. Under a flow of N_2 , 1 mL of 0.5 mol/L NaHTe solution was added dropwise at room temperature over 10 min. The carbohydrate composite spheres were obtained by another three cycles of centrifugation/washing/redispersion in water and alcohol.

2.4 Synthesis of Te@carbohydrate@PbTe multilayer cable structures

Te nanowires were obtained [33] by dissolving 0.6 g of polyvinylpyrrolidone (PVP), 0.1107 g of Na_2TeO_3 , 1 mL of hydrazine hydrate (85% w/w), and 2 mL of an aqueous ammonia solution (25%–28% w/w) in 22 mL of distilled water and hydrothermally treating the mixture at 180 °C for 4 h. The Te@carbohydrate cables were prepared by dissolving 2 g of *D*-(+)-glucose in 100 mL of distilled water with 0.1 mmol of Te nanowires as the template and hydrothermally treating the mixture at 180 °C for 8 h. The precipitate was isolated by centrifugation and purified by three cycles of centrifugation/washing/redispersion in water and then in alcohol. Then 0.1 g of as synthesized Te@carbohydrate cable, 0.02 g of NaOH, and 0.8275 g of $Pb(NO_3)_2$ were added to 30 mL of distilled water and the mixture stirred magnetically for 20 min. The resulting suspension was separated by centrifugation/washing/redispersion in water and then in alcohol, and redispersed in 30 mL of distilled water. Under a flow of N_2 , 1 mL of 0.5 mol/L NaHTe solution was added dropwise at room temperature over 10 min. Finally the carbohydrate composite spheres were obtained by three cycles of centrifugation/washing/redispersion in water and then in alcohol.

2.5 Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert PRO X-ray diffractometer. Transmission electron microscope (TEM) images and energy dispersive spectra (EDS) were obtained using a JEOL 2011 FasTEM microscope. For X-ray photoelectron spectroscopy (XPS) measurements the samples were coated on carbon tape and the data were collected with a PHI 3057 spectrometer. Fourier transform infrared (FTIR) spectra were obtained using a JASCO FTIR spectrometer.

3. Results and discussion

Figure 1(a) shows a representative TEM micrograph of the sample synthesized using 1 mol/L NaHTe and 0.5 mol/L Pb- β -cyclodextrin complex at room temperature which clearly shows that the product consists of an interconnected network of nanoparticles with diameters around 20 nm. A high-resolution TEM (HRTEM) image of a constituent particle (Fig. 1(b)) shows the material has a crystalline structure with an adjacent lattice-fringe distance of ca. 3.2 Å, which is consistent with the (200) interplanar distance (3.23 Å) of the face centered cubic (FCC) PbTe. EDS (Fig. S-1 in the Electronic Supplementary Material (ESM)) indicates a Pb/Te atomic ratio of 1:1, further confirming the formation of PbTe. Reducing the precursor concentration leads to the formation of networks composed of smaller particles. For example, Fig. 1(c) shows a TEM image of the nanoparticle network prepared using 0.1 mol/L NaHTe and 0.05 mol/L Pb- β -cyclodextrin complex solutions. Networks of nanoparticles with an average diameter of 5 nm are clearly observed. It is worth mentioning that although the particle diameters are so small, these networks are crystalline (see the HRTEM image in Fig. 1(e)). Moreover, the diameter of the component particles can be further tuned by varying the reaction temperature. Figure 1(d) shows a TEM image of the nanoparticle networks prepared by the addition of 1 mol/L NaHTe to a refluxing solution of 0.5 mol/L Pb- β -cyclodextrin complex. Networks of particles with an average diameter of 30 nm were formed. In general, the particle size increases with increasing concentration of the precursors as more material is available for growth, and also with increasing temperature as the growth rate increases. The ability to tune the size of the component particles potentially provides the possibility of tuning the quantum effect, which is critical to achieve an enhanced thermoelectric figure of merit. The FTIR spectra (Fig. S-2 in the ESM) indicate that β -cyclodextrin acts as a capping ligand and endows the networks with high dispersibility in water. Due to the weak binding interactions, most of the β -cyclodextrin can be removed by copious washing with water as shown by the Infrared (IR) spectra in Fig. S-2 (in the ESM). It is interesting to note that similar network structures can be formed by replacing

Figure 1 TEM images of the PbTe nanoparticle network prepared by reacting 1 mol/L NaHTe with 0.5 mol/L Pb- β -cyclodextrin complex precursor solution at room temperature (a, b) and under reflux (d), and of that prepared by reacting 0.1 mol/L NaHTe solution with 0.05 mol/L Pb- β -cyclodextrin complex precursor solution at room temperature (c, e)

β -cyclodextrin with other low-cost carbohydrates, such as *D*-(+)-glucose (Fig. S-3 in the ESM), sucrose (Fig. S-4 in the ESM), *D*-glucosamine (Fig. S-5 in the ESM), lactobionic acid, and starch.

Figures 2(a) and 2(b), respectively, show the XRD patterns of the nanoparticle networks prepared from 1 mol/L NaHTe and 0.5 mol/L Pb- β -cyclodextrin complex solutions and 0.1 mol/L NaHTe and 0.05 mol/L Pb- β -cyclodextrin complex solutions. Both patterns

can be indexed to an FCC structure (*Fm*3*m* with a unit cell parameter of 6.459 Å), which is consistent with the standard pattern of bulk PbTe. The diffraction peaks are broader than those of the bulk sample, in accordance with their smaller crystalline domains. Consistent with the TEM observations, decreasing the precursor concentration results in broader diffraction peaks, indicating smaller crystalline domain sizes. The crystallite size estimated from the Scherrer equation,

Figure 2 Powder X-ray diffraction (XRD) patterns of PbTe nanoparticle networks prepared from (a) 1 mol/L NaHTe and 0.5 mol/L Pb- β -cyclodextrin complex solution and (b) 0.1 mol/L NaHTe and 0.05 mol/L Pb- β -cyclodextrin complex solution at room temperature

based on Gaussian fitting of the (200) peak, is around 20 nm and 8 nm for the particles prepared from the

concentrated (Fig. 2(a)) and dilute (Fig. 2(b)) solutions, respectively. It is interesting to note that the peaks shift toward higher angles with the decrease of crystallite size, which can be ascribed to surface stress; a similar effect has been observed for gold and ionic crystals [34]. XPS (Fig. S-6 in the ESM) further confirms the formation of PbTe. XPS also shows that, on exposure to air, the surface of the PbTe networks can be easily oxidized to PbTeO₃ (Fig. S-7 in the ESM).

This simple synthesis process can be extended to the construction of nanostructured materials with more complicated structures. For example, as shown in Fig. 3(a), we first prepared carbohydrate spheres with an average diameter around 100 nm by hydrothermally reacting an aqueous solution of *D*-(+)-glucose at 190 °C for 4 h. We then complexed Pb²⁺ with these carbohydrate spheres, using a similar technique to that described above. Subsequent reaction of the complexed spheres with NaHTe afforded composite spheres containing the nanoparticle shells (Fig. 3(b)).

Figure 3 TEM images of (a) carbohydrate spheres, (b) carbohydrate spheres coated with PbTe nanoparticle shells, (c) Te@carbohydrate cables, and (d) Te@carbohydrate cable@PbTe multilayered submicron cables

The formation of the PbTe shell was validated by EDS (Fig. S-8 in the ESM) and XRD (Fig. S-9 in the ESM). Using a similar strategy, Te@carbohydrate submicrocables and Te@carbohydrate tubes@PbTe multilayer submicrocables were obtained, as shown by the TEM images in Figs. 3(c) and 3(d) and the XRD patterns in Figs. S-10 and S-11 (in the ESM).

Besides carbohydrates, ethylenediaminetetraacetic acid (EDTA), thioglycolic acid (TGA), and 3-mercaptopropionic acid (MPA) were used as ligands to produce PbTe using the same concentration as for β -cyclodextrin. XRD and TEM (Figs. S-12 and S-13 in the ESM) showed that PbTe nanoparticle networks were also obtained. As indicated by the formation of $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COO-Pb-OH}$ in the reaction of Pb^{2+} and cysteine under weakly basic conditions, Pb^{2+} ions have a stronger interaction with $-\text{COO}^-$ than with $-\text{SH}$ groups [35], in contrast to the case for Cd^{2+} . We believe that solvation of Pb^{2+} in aqueous media

attenuates the binding capability of $-\text{COO}^-$ with Pb^{2+} , and consequently leads to the formation of networks. In addition to the steric repulsions caused by the capping ligands, electrostatic repulsions resulting from charged species at the surface have frequently been employed for nanoparticle stabilization. When positively charged polymeric PEI was employed as a ligand, we obtained isolated PbTe nanoparticles, as shown by XRD and TEM (Fig. S-14 in the ESM).

Based on the above results, a reaction mechanism can be proposed as illustrated in Fig. 4. The formation of PbTe nanoparticles, their subsequent aggregation, and growth into a continuous network structure are all involved. It is known that Pb^{2+} is precipitated from basic aqueous solution as $\text{Pb}(\text{OH})_2$. Adding carbohydrates—which can be deprotonated in a strongly basic environment—results in the formation of stable polyolato complexes [36]. Such complexes are present as a clear solution (Step I). Rapid reaction

Figure 4 Schematic illustration of the formation of PbTe nanoparticle networks in aqueous media containing carbohydrates (a), carbohydrate spheres@PbTe core shell structures (b), and Te@carbohydrate tubes@PbTe multilayer cable structures (c)

(Step II) of the lead polyolato complexes with NaHTe produces PbTe clusters or nanoparticles stabilized by the deprotonated carbohydrates. This is consistent with the TEM image (Fig. S-15 in the ESM) of the sample produced in an extremely dilute solution. However, unlike trioctylphosphine oxide (TOPO), oleic acid, and other commonly used organic capping agents, carbohydrates have a much weaker stabilization capability, which prevents the formation of highly dispersed nanoparticles. This allows the clusters or nanoparticles to form more stable continuous nanoparticle networks (Step III), leading to a reduction in the surface energy. Since PbTe has the highly symmetric cubic rocksalt crystal structure, the absence of dipole–dipole interactions leads to a random orientation of nanoparticles in the networks, as shown by the TEM image in Fig. 1(e).

In addition to PbTe, other semiconductor networks including PbSe and Bi_2Te_3 can be produced using a

similar strategy. Representative TEM images and XRD patterns shown in Fig. 5 confirm the successful synthesis of PbSe and Bi_2Te_3 networks when β -cyclodextrin and EDTA, respectively, were employed as ligands.

4. Conclusions

We have developed a novel one-step approach for the synthesis of nanocrystalline semiconductor networks using weak ligands. As illustrated for PbTe networks, a variety of carbohydrates can act as weak ligands which facilitate the formation of continuous nanoparticle networks. The nanoparticle size can be tuned by changing the temperature and concentration. Through a similar strategy, more complicated structures including spherical core–shell structures and multilayered submicron cables have been fabricated. This approach is general and can be readily extended to the

Figure 5 (a) TEM image and (c) XRD pattern of a nanocrystalline PbSe network prepared using β -cyclodextrin as a ligand. (b) TEM image and (d) XRD pattern of a nanocrystalline Bi_2Te_3 network prepared using EDTA as a ligand

fabrication of other semiconductor networks, including PbSe and Bi₂Te₃.

Acknowledgements

This work was supported by Toyota Motor Engineering and Manufacturing North America.

Electronic Supplementary Material: EDS spectra, FTIR spectra, XPS spectra, and TEM images of PbTe nanoparticle networks using a variety of ligands under different conditions and EDS spectra and XRD patterns of carbohydrate spheres@PbTe core-shell composites and Te@carbohydrate tubes@PbTe multilayer submicrocables are available in the online version of this article at <http://dx.doi.org/10.1007/s12274-010-0030-8> and accessible free of charge.

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