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Design and Synthesis of One and Two Dimensional Thermoelectric Nanomaterials Composed of Bismuth, Antimony, and Tellurium.

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ABSTRACT

With the advent of nanotechnology, the field of thermoelectric (TE) materials has been re-invigorated with many recent advances towards materials with high thermoelectric efficiency (dimensionless figure of merit, ZT). The realization of such materials opens up new avenues to the creation of devices that can be used in freon-less refrigeration, micro-electronic cooling, or for harnessing lost heat energy from sources such as car engines. In our own research work, we have successfully synthesized thermoelectric nanoscale materials composed of bismuth, antimony, and tellurium. By using a wet chemical thermal reduction procedure, we were able to create bismuth, antimony, and tellurium composite particles. What's more, by employing different molecular encapsulating agents in the synthesis, we were able to control the resulting shapes of the nanomaterials, resulting in both one and two dimensional bismuth, antimony, and tellurium nanoparticles. The one dimensional nanowires exhibit a micron scale length and ~20-50nm diameter, while the two dimensional nanodiscs exhibit a diameter of ~100nm and a thickness of ~25nm. The unique morphology of these materials make them ideal candidates for processing into functional thermoelectric devices. This paper focuses on our recent study of the synthesis of bismuth, antimony, and tellurium composite nanomaterials of a nanowire and nanodisc morphology, which was directed by the capping agents used in the synthesis. Part of our preliminary study includes analysis of the thermoelectric efficiency of the materials. The resulting nanomaterials are characterized using techniques such as HR-TEM, XPS, XRD, and SEM the results of which provide insight into the design and synthesis of nanoscale materials with enhanced thermoelectric properties.

INTRODUCTION

With the realization that nanotechnology can be an effective rout to developing a new generation of efficient TE devices, there has been renewed interest in research seeking to create novel nanoscale TE materials [1]. The difficulties associated with creating efficient TE materials stem from the challenges in significantly enhancing the materials electrical conductivity while simultaneously suppressing its thermal conductivity, two very closely related physical properties [2]. Bulk materials applied in this area of technology have relied on composition-structure control and/or alloying to achieve significant TE activity, which ultimately has not lead to highly efficient TE materials. Nanoscale materials on the other had offer an intriguing method for tuning the electrical and thermal conductivities through manipulation of the nanoscale morphology [3]. The creation of TE materials with a nanoscale structure increases the phonon scattering along grain boundaries, ultimately suppressing the thermal conductivity, which increases the thermoelectric efficiency (ZT value) of the material [4]. In addition to shape, nanoscale materials offer a plethora of additional beneficial properties such as unique composition or enhanced conductivity. Some of the most TE efficient bulk materials today are composed of Bi_2Te_3 or $(Bi_xSb_y)Te_{100-x-y}$ [1,2,5]. The creation of TE materials with sphere, wire,

disc, or other nanoscale shapes composed of bismuth, antimony and tellurium are a promising avenue towards new and highly efficient TE materials. In our own study we focus on the synthesis of these nanomaterials using a one pot wet chemical reaction using a variety of different organic capping molecules. The nanoparticle growth is mediated by the capping ligands, which directs the morphology. The TE activity of the resulting nanowires and nanodiscs is studied and gives insight in the design and fabrication of new and promising TE materials.

EXPERIMENT

Chemicals: bismuth trichloride, antimony trichloride, tellurium tetrachloride, oleic acid, oleylamine, 1,2-hexadecanediol, 1-decanethiol and di-octylether as well as other common solvents were obtained from Aldrich.

S*ynthetic Technique:* 1.67×10^{-4} moles each of bismuth, antimony and tellurium precursors was mixed with 25 ml di-octylether, then 1.5×10^{-3} moles of 1,2-hexadecanediol was added along with the capping species, the identity of which was used to manipulate the morphology of the resulting nanostructures. For the synthesis of nanowires, 0.16ml of oleic acid and 0.17ml of oleylamine were used. For the synthesis of nanodiscs, 1.5ml of 1-decanethiol was used as capping agent. The mixture was purged with argon under vigorous stirring. At this point the mixture temperature was raised to 105 ^{0}C for 10 minutes to remove water, which also caused the reactants to completely dissolve in the solvent (a light grey color in the solution). After this, the temperature was increased to 200 ^{0}C and was held for 1 hour. The formation of particles within this time was evidenced by the solution color change from light grey to dark grey or black depending on the capping species used. After reaction, the nanoparticle solution was cooled to room temperature and the particles were purified by precipitation in ethanol. The materials could be briefly re-suspended (precipitation occurs in about 1 day) in hexane with additional OAM/OAC or DT. The resulting nanomaterials were then analyzed.

Instrumentation and Measurements: An array of techniques including Transmission Electron Microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS), Raman Scattering Spectroscopy and X-ray Diffraction (XRD) were used to characterize the size, shape, composition, structure and other properties of the materials. TEM analysis was performed on an Hitachi H-7100 transmission electron microscope operated at 100kV. TEM samples were prepared by dropping the suspended particles onto a carbon coated copper grid and drying in air overnight. Samples for XPS, Raman Scattering Spectroscopy and XRD measurements were prepared in powder form after cleaning the reaction product with ethanol and drying in a vacuum evaporator.

DISCUSSION

The discussion section covers two main areas. First we illustrate and discuss our synthesis of the nanoscale materials with two different capping species systems towards nanoparticles with wire and disc morphology. Then we characterize the materials in terms of morphology, composition, and structure. Scheme 1 shows our general approach to the TE materials with well defined shape. In this synthesis we begin with bismuth, antimony, and tellurium chloride precursors in a wet chemical synthesis scheme. The technique allows us to take advantage of organic capping ligands to control the morphology of the resulting nanostructures. We found that when oleic acid/oleylamine capping species were used the nanoparticles were of a wire morphology, while decanethiol capping species led to the formation of nanodiscs. Such an ability is highly exciting for the creation of nanostructured TE materials

with enhanced efficiency as it is the nanoscale structure (i.e. wires, discs, etc) that serve to minimize the thermal conductivity (most often accomplished through increased phonon scattering at crystal boundaries in the material [2,4]).

Scheme1: Synthetic rout towards TE materials composed of bismuth, antimony and tellurium with nanowire and nanodisc shape.

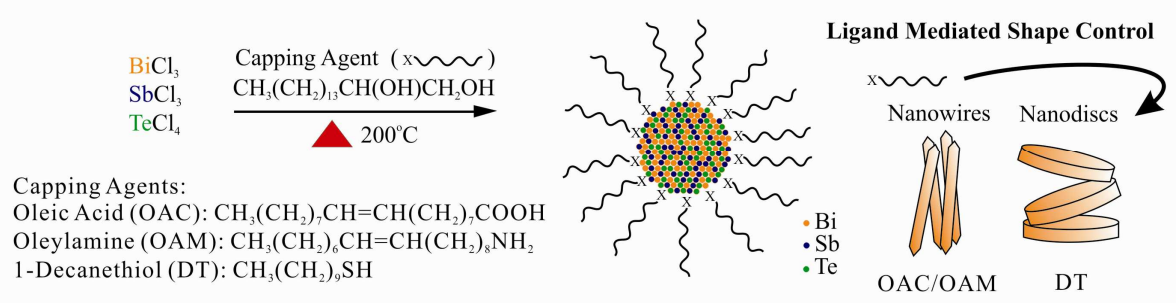

Figure 1 shows the TEM images collected for the two different types of nanomaterials synthesized. Figure 1A is a TEM image for nanowires synthesized using OAM/OAC capping species. The nanowires have a micron length (~3-5microns) scale and the diameter ranges from about 20 to 50nm. The aspect ratio of these nanowires is quite high (~100x) as well as the shape monodispersity with only nanowires observed. Figure 1B shows a magnified view of the nanowires. In this TEM image some of the fine structure of the nanowires can be observed. Some nanowires seem to have darker areas along the wire with striations across the diameter of the structure. These observations may arise as a result of imperfections in the nanoparticle crystal or inhomogeneity in the composition of a single nanowire. Finally Figure 1C shows a TEM image of nanodiscs synthesized using decanethiol capping species. The particles have disc morphology with a diameter of about 100nm and thickness of about 25nm. In the TEM image several particles can be observed lying on the wide face of the crystal while others are sitting on edge of the disc. In addition a few particles lying on face are slightly overlapping each other, further illustrating the disc morphology.

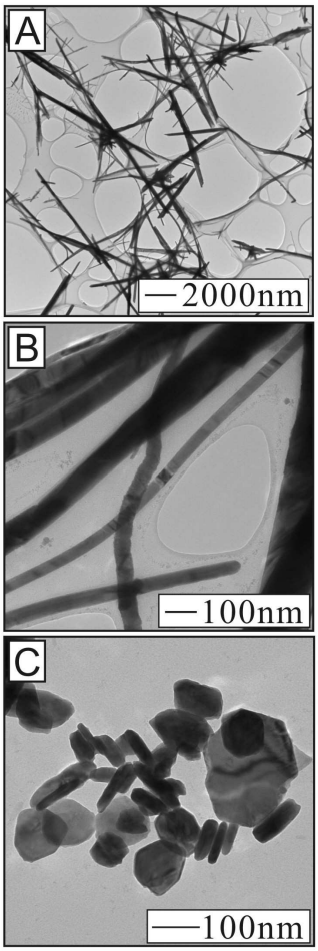

Figure 1: TEM images of nanowires synthesized with OAM/OAC (A), a magnified view of the nanowires (B) and nanodiscs synthesized with DT (C).

In terms of addressing the composition of the nanomaterials, we performed X-Ray Photoelectron Spectroscopy (XPS). This technique afforded us a sensitive means for determining the composition of the nanomaterials as well as addressing the oxidation properties. Table 1 lists the composition of the two synthesized materials as determined by XPS. The compositional results are quite interesting and reveal that composition as well as nanoscale shape can be modified by the organic capping ligands. In the case of the nanowires synthesized by OAM/OAC the material was found be bismuth deficient, but in the case of the nanodiscs it was antimony that was found to be mostly absent. The amount of the other two metals in the material was about 50%, which does not conform to the expected stoicheometry of current known bulk materials for bismuth, antimony or tellurium such as Bi_2Te_3. This observation may be attributed to a unique structure for the nanomaterials whose composition is dependent on the nanoscale properties, or could be due to inhomogeneity in the composition of individual nanocrystals. In terms of addressing the surface properties of the nanomaterials, we did not detect any oxides or oxidation in the XPS peaks for any of the samples studied. This observation will be discussed and is further supported in both the Raman and XRD analysis.

Table 1: XPS determined composition of the different TE materials.

Sample ID	Bismuth %	Antimony %	Tellurium %
Nanowires	0.6	52.1	47.3
Nanodiscs	50.3	1.7	48.0

Raman spectroscopy was used to study the structure-composition properties of the nanomaterials. Figure 2 shows the Raman spectra taken for the nanowires synthesized with OAM/OAC (spectrum A) and for the nanodiscs synthesized with DT (spectrum B). There are several peaks identified in the spectra. For the nanowires, the identification of the E^1_g and A^1_{1g} peaks identify the presence of a Bi_2Te_3 type structure [6], however from the composition analysis we know there is only a small amount of bismuth present in the sample. We attribute the observation of these peaks to an antimony-tellurium structure, which could display similar peaks in the Raman spectrum to that of Bi_2Te_3. For the nanodiscs the strong E^2_g and A^1_{2g} peaks indicate the presence of tellurium structure in the nanomaterials, which indicates the complex structure of the as-synthesized nanomaterials.

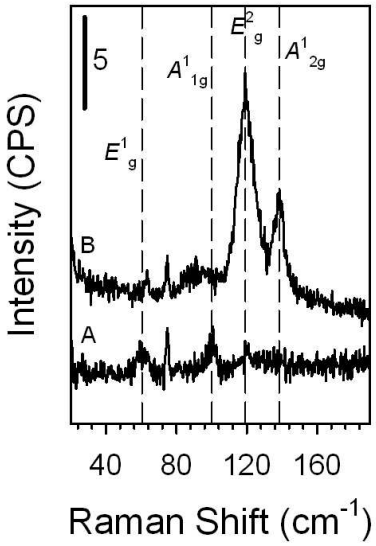

Figure 2: Raman spectra of the nanowires synthesized with OAM/OAC (A) and the nanodiscs synthesized with DT (B) capping species.

Figure 3 shows the XRD patterns collected for the nanowires synthesized with OAM/OAC (pattern A) and nanodiscs synthesized with DT (pattern B). There are several peaks found in the XRD spectra, the primary peaks labeled correspond to the 015 (~27.6°), 1010 (38.7°), 110 (40.8°), and 205 (50.5°) planes of symmetry with rhombohedral structure for a BiSbTe alloy [2]. The additional unlabelled peaks correspond to other lattice planes in the crystal with lower intensity. In addition, some peaks are split such as the 015 peak for the nanodiscs, or the 1010 and 110 planes for the nanowires. We attribute this observation to non-uniform composition in the nanocrystals, which could exist in single crystals, or the composition could deviate from crystal to crystal in the samples. One important observation in the XRD patterns is the complete lack of any oxide peaks (located at ~32°), which illustrates that our samples are composed of only bismuth, antimony and tellurium and have no indication of oxides.

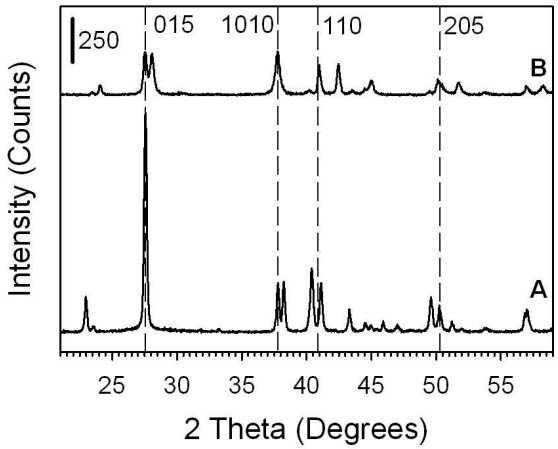

Figure 3: XRD patterns for nanowires capped in OAM/OAC (A) and nanodiscs capped in DT (B). The primary peak positions are indexed as the 015, 1010, 110, and 205 planes of symmetry with rhombohedral structure for a BiSbTe alloy [2].

CONCLUSIONS

In conclusion we have developed a straightforward one pot wet chemical synthetic technique for the creation of nanomaterials composed of bismuth, antimony and tellurium with wire and disc shapes. The nanoscale shape was found to arise as a result of the capping species identity. Oleic acid/oleylamine was found to lead to nanomaterials with wire morphology while decanethiol was found to lead to disc shaped nanoparticles. The formation of such highly monodispersed wires and discs improves our understanding of how to synthesize a new class of thermoelectric materials as it is the nanoscale shape that gives rise to heightened TE efficiency. Part of the ongoing work in this study is the optimization of the reaction parameters to study the control of the composition of the nanomaterials as well as the characterization of the TE characteristics and efficiency of the shaped particles composed of bismuth, antimony and tellurium.

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