Thermoelectric Nanocrystals

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Large-Scale Synthesis and Characterization of the Size-Dependent Thermoelectric Properties of Uniformly Sized Bismuth Nanocrystals**

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Highly efficient thermoelectric materials have attracted tremendous attention because of various technological applications such as power generation from waste heat and environmentally friendly refrigeration.[1] The efficiency of thermoelectric materials is generally evaluated in terms of thermoelectric figure of merit $ZT = (\sigma S^2/k)T$, where σ is the electrical conductivity, S is the Seebeck coefficient, k is the thermal conductivity, and T is the absolute temperature. Recently, various nanostructured thermoelectric materials have been reported to exhibit high ZT values. This increase in thermoelectric efficiency was attributed to the decrease of thermal conductivity caused by the increased interfaces to scatter phonons or the enhancement of power factor (σS^2) by quantum confinement effects.[2] However, most of the high-ZT nanostructured materials were prepared by costly and complicated processes, making it very difficult to inexpensively synthesize a large quantity of nanostructured materials. More recently, several kinds of nanostructured bulk materials with high ZT values were fabricated in large quantity by a ball-milling process and subsequent hot-press process.[3] Recently, colloidal chemical methods have been used to synthesize large quantities of uniform-sized nanocrystals.[4] These chemical methods can synthesize uniform-sized nanocrystals in a size-controlled manner, allowing the characterization of size-dependent properties,[5] which is very difficult to perform using top-down physical methods, such as the ball-milling process.

Over the past few decades, intensive research has attempted to characterize the electrical properties of bulk bismuth (Bi), because it is semimetallic with a small band overlap and has high carrier mobility and extremely small carrier effective mass. Furthermore, thermoelectric properties of Bi nanocrystals were intensively studied,[6] because theoretical calculations predicted that Bi nanocrystals can exhibit a ZT value as high as 10 at 77 K. Moreover, Bi costs around one tenth of the price of bismuth telluride, which is one of the most popular thermoelectric materials.[7] However, a high ZT value has not yet been realized experimentally for Bi nanostructured materials. Although several chemical syntheses of Bi nanocrystals have been reported,[8] the thermoelectric properties of spherical Bi nanocrystals have rarely been studied. Herein, we report a simple and large-scale synthetic method to produce uniform-sized Bi nanocrystals with controlled sizes and characterized their size-dependent thermoelectric properties. The size-dependant electrical and thermal properties were clearly demonstrated using uniform Bi nanocrystals with controlled particle sizes. Interestingly, the ratio of electrical to thermal conductivity increased with decreasing particle size, which leads to the enhancement of the ZT values.

Bi nanocrystals were synthesized by reducing bismuth dodecanethiolate, which was generated by the reaction of dodecanethiol and bismuth neodecanoate in octadecene. Bismuth thiolate was so reactive that Bi nanocrystals could be readily produced by injecting the mild reducing agent tri-*n*-octylphosphine (TOP) into bismuth dodecanethiolate solution at a temperature as low as 80 °C. The sizes of Bi nanocrystals could be easily tuned by varying the aging temperature and time. Transmission electron microscopy (TEM) images (Figure 1 a–f) show uniform-sized Bi nanocrystals with sizes ranging from 6 to 27 nm. All of the nanocrystals exhibited narrow size distribution with standard deviation of less than 10 %. The electron diffraction patterns (Figure 1 a–f, insets) revealed the highly crystalline nature of the Bi nanocrystals. The X-ray diffraction (XRD) patterns (Figure 1 g) showed that all of the nanocrystals had a rhombohedral Bi structure (JCPDS 85-1331), while the peaks became broader as the size decreases. To demonstrate large-scale production, we performed the reaction with 20 mmol of bismuth precursor and obtained as much as

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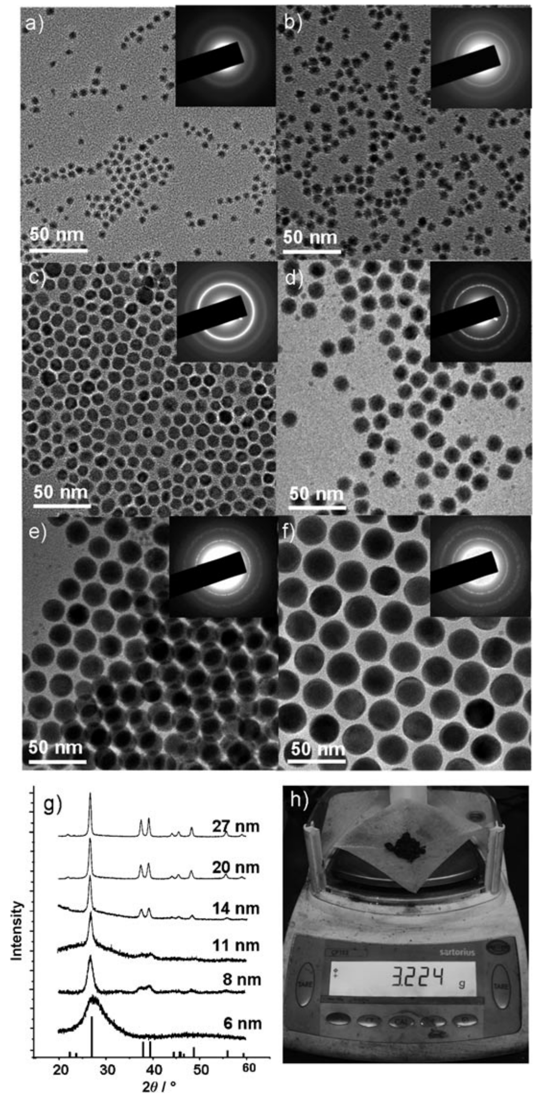

Figure 1. Characterization of Bi nanocrystals. TEM images and ED patterns (insets) of the Bi nanocrystals with sizes of a) 6 nm, b) 8 nm, c) 11 nm, d) 14 nm, e) 20 nm, and f) 27 nm. g) XRD patterns (the vertical lines are the peaks of bulk rhombohedral Bi). h) Photograph showing 3.224 g of the 11 nm sized Bi nanocrystals synthesized on a large scale.

3.2 g of 11 nm Bi nanocrystals in a single batch (Figure 1 h and Figure S1 in the Supporting Information).

The thermoelectric properties were characterized on the Bi nanocrystals with sizes of 8, 11, 14, 20, and 27 nm. More than three sets of samples were prepared for the characterization. To characterize the thermoelectric properties of the Bi nanocrystals, we made pressed nanocrystals in a disk-shaped pellet (Figure S2). Before the pellets were made, dodecanethiol was exchanged with short-chain alkylthiols to shorten the interparticle distance to improve electrical properties. The pellets were made by pressing the alkylthiol-capped nanocrystals powder at room temperature. The TEM and SEM images (Figure S3) showed that the size and shape of Bi nanocrystals were almost unchanged after the surfactant exchange reaction and the pressing process. However, the particle sizes estimated using Debye–Scherrer formula of the XRD patterns (Figure S4) revealed that the size of 8 nm (measured by TEM) sized nanocrystals was increased from 6.7 to 9.5 nm during the surfactant exchange process, and that the particle size did not change during the pelleting process. To achieve highest electrical conductivity, we screened alkanethiols of various chain length and found that the propanethiol capped Bi nanocrystals exhibited the highest electrical conductivity (Figure S5).

The electrical conductivities and Seebeck coefficients of the pressed Bi nanocrystals were measured at room temperature. The size-dependent electrical conductivities of the pressed Bi nanocrystals are shown in Figure 2 a. As nanocrystal size increases from 8 to 27 nm, the electrical conductivity increases from 2.1×10^4 to $8.4 \times 10^4\,\mathrm{S\,m^{-1}}$, which is comparable to that of nanostructured BiSbTe alloys.[3a] Such a significant enhancement of electrical conductivity demonstrates that exchange coupling in the pressed Bi nanocrystals is strong enough to overcome the charging energy, and this is attributed to the extremely small electron effective mass of Bi[9] (detailed explanation in the Supporting Information). The Seebeck coefficients of the pressed Bi nanocrystals ranged from −70 to −80 of $\mu\mathrm{V\,K^{-1}}$ and were nearly constant regardless of the particle size (Figure 2 b). The negative sign of the Seebeck coefficients indicated the n-type character of the nanocrystals.

Interestingly, the Seebeck coefficient was nearly constant regardless of the particle size, whereas the electrical con-

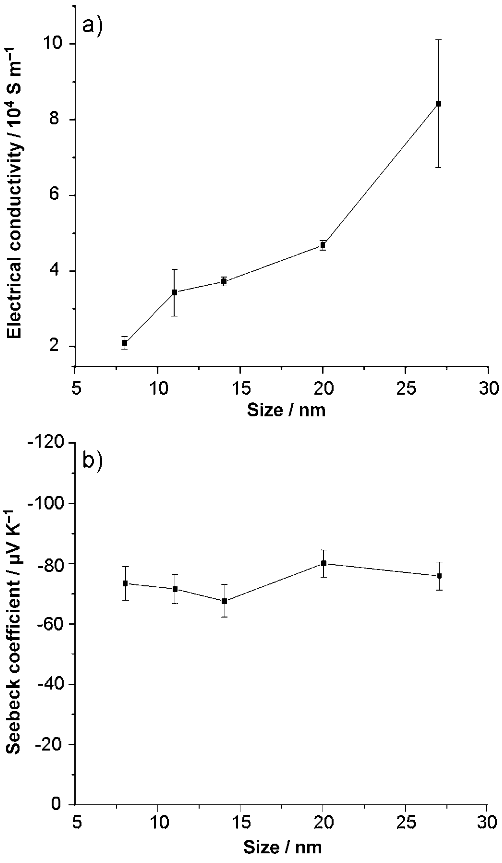

Figure 2. Size dependence of a) electrical conductivities and b) Seebeck coefficients of the pressed Bi nanocrystals.

ductivity increased as the particle size increased. To understand these experimental results, we investigated the electron concentration using a Hall measurement system and calculated the electron mobility from electron concentration and electrical conductivity. The electron concentration of the pressed Bi nanocrystals (Figure S6a) was nearly constant regardless of the particle size, confirming the size-independent Seebeck coefficient that is strongly dependent on carrier concentration.[2a] Furthermore, this nearly size-independent Seebeck coefficient and electron concentration seems to demonstrate semimetallic or degenerate semiconducting characteristics of the pressed Bi nanocrystals. The Seebeck coefficient of semiconductor nanocrystals generally increases with decreasing particle size because of the quantum confinement effect.[5,6] When the nanocrystal size increased from 8 to 27 nm, the calculated mobility increased from 30.6 to 127.5 $\mathrm{cm^2 V^{-1} s^{-1}}$. These results clearly demonstrate that the size dependence of electrical conductivities is due mostly to the size dependence of electron mobility (Figure S6b). This size-dependent electrical behavior can be explained by the carrier scattering process.[10] Similar size dependence of mobility and conductivity was reported in Bi nanowires and Bi films.[11]

The thermal transport was characterized by laser flash analysis (LFA) and differential scanning calorimetry (DSC) at room temperature. The thermal conductivity (k) was calculated using the equation $k = \alpha c_p \rho$, where α is the thermal diffusivity that was measured by LFA, c_p is the specific heat capacity that was measured by DSC, and ρ is the density. Extremely low thermal conductivity of 0.35 $\mathrm{W m^{-1} K^{-1}}$ was observed for 8 nm nanocrystals (Figure 3a and Figure S7), which is about 15 times lower than that of bulk polycrystalline Bi (5.4 $\mathrm{W m^{-1} K^{-1}}$; detailed data in the Supporting Information), is comparable to the insulating limit of solids,[12] and is one of the lowest values among all reported nanostructured thermoelectric materials. As the size increases from 8 to 27 nm, the thermal conductivity dramatically increases from 0.35 to 2.13 $\mathrm{W m^{-1} K^{-1}}$. The clear size dependence and significantly reduced thermal conductivity demonstrate that the phonons were effectively scattered at the interfaces within the pressed nanocrystals and phonon transport was strongly affected by the size of the nanocrystals. In particular, this ultralow thermal conductivity seems to be attributed to organic surfactant coating on the surface of the nanocrystals, which impedes phonon propagation because of the huge mismatch in vibrational spectra (detailed explanation in the Supporting Information).

The dimensionless figure of merit ZT of the pressed Bi nanocrystals was calculated using electrical conductivity, the Seebeck coefficient, and thermal conductivity at room temperature. Because the Seebeck coefficients are almost constant regardless of the particle size, the ZT values of the pressed nanocrystals depend directly on the ratio of electrical to thermal conductivity (Figure 3b). As the nanocrystal size decreases, these ratios increase, demonstrating that particle size has more influence on the thermal conductivity than on the electrical conductivity.[13] Because the mean free path of phonons is much longer than that of electrons, the interfaces disturb phonon transport more than electron transport, resulting in the increased ratio of electrical to thermal conductivity. Similar size dependence of the ratio of electrical to thermal conductivity was reported in Bi thin films.[14] As a result, the ZT value roughly increases as the size decreases (Figure 3c). The highest ZT value of 0.1 was achieved for the 8 nm sized Bi nanocrystals, which is comparable to that of the polycrystalline bulk Bi (detailed data in the Supporting Information). This high ZT value can be attributed to the high electrical conductivity as a result of strong coupling, and extremely low thermal conductivity as a result of phonon scattering at the interface of the organic surfactant and Bi

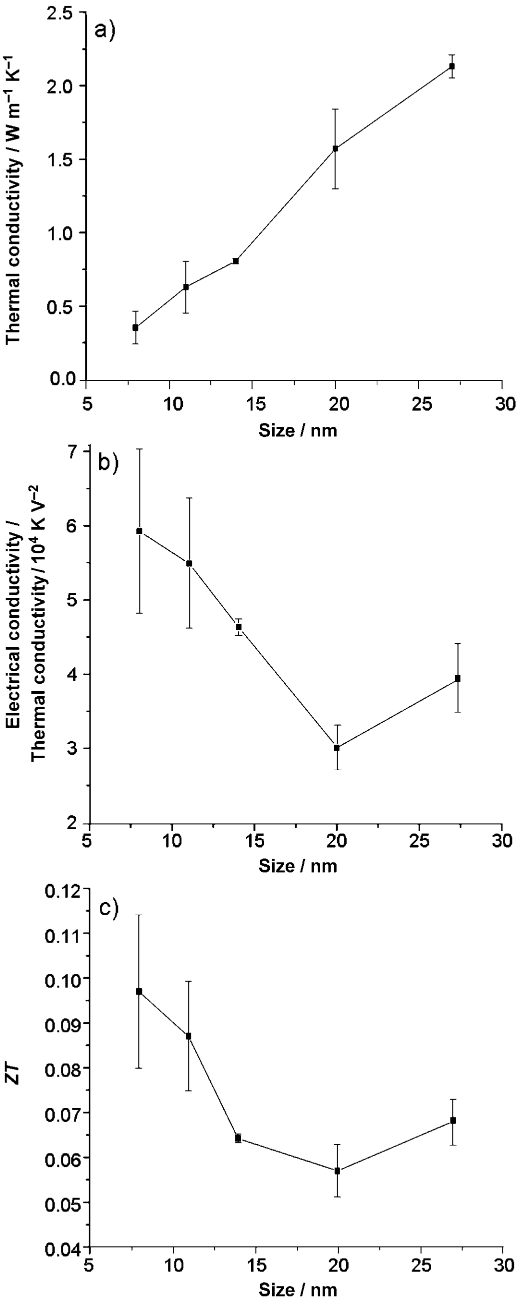

Figure 3. Size dependence of a) thermal conductivities, b) the ratio of electrical to thermal conductivity, and c) ZT values of the pressed Bi nanocrystals.

nanocrystal core. Furthermore, the size dependence of the ratio of electrical to thermal conductivity shows the possibility of independent control of these correlated properties.

In summary, we have developed a simple and large-scale synthetic route for uniform-sized Bi nanocrystals with controlled particle sizes ranging from 6 to 27 nm. Reduction of bismuth thiolate with TOP generated uniform Bi nanocrystals, and the synthetic procedure is easy to scale up to produce gram quantities of nanocrystals. The electrical and thermal conductivities of the pressed Bi nanocrystals were strongly size-dependent. Interestingly, we found that the ratio of electrical to thermal conductivity increased with decreasing particle size, resulting in the increased *ZT* value. Herein, we clearly demonstrated that a colloidal synthetic method can be used for the inexpensive preparation of highly efficient thermoelectric materials by engineering the size of nanocrystals.

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