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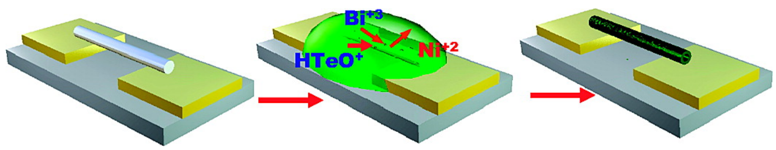

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Synthesis of Bi_2Te_3 Nanotubes by Galvanic Displacement

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Thermoelectric (TE) energy converters are solid-state devices that can generate electricity by harvesting waste thermal energy, thereby improving the efficiency of a system. The many advantages of TE devices include solid-state operation, zero-emissions, vast scalability, no maintenance, and a long operating lifetime. Nonetheless, because of their limited energy conversion efficiencies, thermoelectric devices currently have a rather limited set of applications. However, there is a reinvigorated interest in the field of thermoelectrics by identifying classical and quantum mechanical size effects, which provide additional ways to enhance energy conversion efficiencies in nanostructured materials[1,2] including superlattice thin films[3] and quantum dots.[4] For example, thermoelectric figure of the merit (ZT) up to 2.5 was achieved by synthesizing two-dimensional Sb_2Te_3/Bi_2Te_3 superlattice thin films, exceeding pervious limits of ~1 from bulk counterpart.[5] Even more exciting are the theoretical predictions for one-dimensional nanostructures including nanowires and nanotubes, which are thought to have ZT exceeding 5.[1,6] In the case of nanotubes, theoretical calculation predicts a further reduction in the thermal conductivity, because of a stronger phonon−surface scattering, compared to solid nanowire.[7]

Limited works have been reported on the synthesis of thermoelectric nanotubes including hydrothermally grown Bi, Bi_2Se_3, and Bi_2Te_3 nanotubes[8] and electrodeposited Bi nanotubes.[9] However, these processes have some limitations. For example, the nanotube production yield is very low (<30%).[8] In the template-directed method it is difficult to restrict the proceeding electrodeposition along the walls without filling up the whole pores.[9]

The galvanic displacement reaction is an electrochemical process, which is induced by the difference in redox potentials between materials. Various metallic nanotubes have been synthesized via this reaction (e.g., gold nanotubes from silver nanowires);[10] however, no one to-date has demonstrated the synthesis of semiconducting thermoelectric nanotubes. In this paper, we demonstrate the synthesis of high-aspect ratio Bi_2Te_3 nanotubes with controlled composition by galvanic displacement of nickel nanowires in acidic nitric electrolyte containing Bi^{3+} and $HTeO_2^+$ ions. Bi_2Te_3 nanotubes were synthesized because Bi_2Te_3 and its derivative compounds are considered to be the best materials used in thermoelectric refrigeration at room temperature. In addition to synthesis, we also demonstrate the fabrication method to create individual Bi_2Te_3 nanotube-based devices by combining the magnetic assembly of single nickel nanowire across microfabricated electrodes, followed by a galvanic displacement reaction.

Figure 1A shows the schematic illustration of the galvanic displacement reaction of Ni nanowires to Bi_2Te_3 nanotubes. The detailed experimental conditions are provided in the Supporting Information. When Ni nanowires are immersed into an acidic nitric solution containing Bi^{3+} and $HTeO_2^+$ ions, Ni nanowires are galvanically displaced to form Bi_2Te_3, because of the difference in the reduction potentials (i.e., Ni^{2+}/Ni^0 ($E^o = -0.257$ V vs SHE) and Bi^{+3}, $HTeO_2^+/Bi_2Te_3$ ($E^o = -0.62\ \mathrm{V} - 0.01475\log[HTeO_2^+] = 0.0443\ [\mathrm{pH}]$ vs NHE)).[11,12]

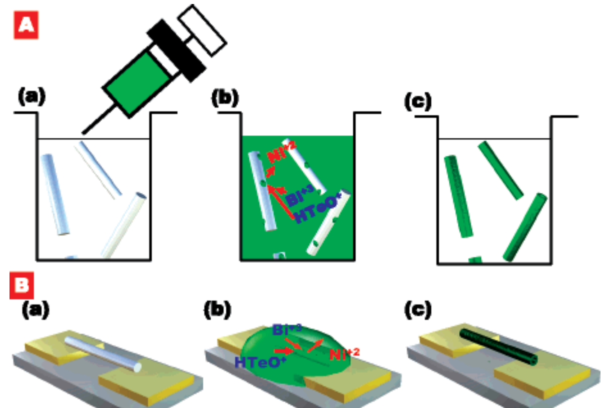

Figure 1. Schematic illustrations of Bi_2Te_3 nanotube synthesis (A) and individual Bi_2Te_3 nanotube laid across electrodes (B).

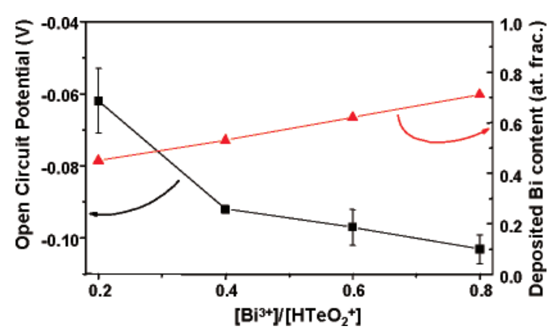

Figure 2. Dependence of the steady-state OCP and the deposited Bi content in nanotubes on the ratio of $[Bi^{3+}]/[HTeO_2^+]$.

To monitor the reaction, the open-circuit potential (OCP) of nickel thin films deposited on platinum was first measured continuously, while immersed in an acidic nitric solution (1 M HNO_3) containing 0.002−0.008 M Bi^{3+} and 0.01 M $HTeO_2^+$ (Figure S.1 in Supporting Information). In general, the OCP sharply decreased to a steady-state value. When nickel thin films were completely displaced by Bi_2Te_3 films, the OCP was increased to >0 V versus SCE. The deposition time was ~60 min at $[Bi^{3+}] = 0.002$ M and reduced to ~30 min when $[Bi^{3+}] = 0.008$ M. Figure 2 shows the dependence of steady-state OCP and the deposited Bi content in nanotubes on the $[Bi^{3+}]/[HTeO_2^+]$ ratio. As expected, the OCP of nickel films decreased with an increase in the ratio of $[Bi^{3+}]/[HTeO_2^+]$.

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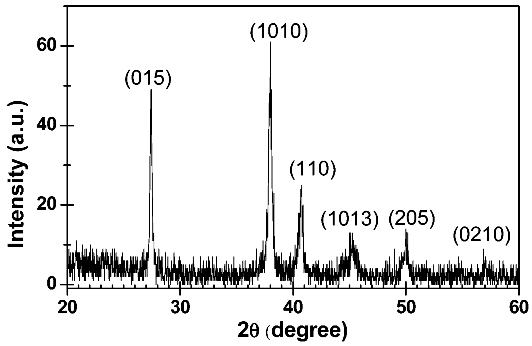

Figure 3. XRD pattern of galvanically displaced Bi_2Te_3 from Ni (3 μm)/Si in the solution of 0.01 M $HTeO_2^+$, 0.006 M Bi^{3+}, and 1 M HNO_3.

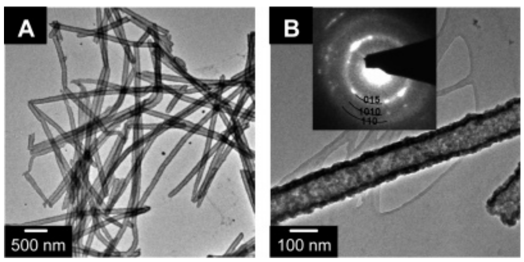

Figure 4. TEM images and SAED pattern of high aspect ratio Bi_2Te_3 nanotubes (A) synthesized from nickel nanowire (∼100 nm in diameter). Tube thickness was approximately 20 nm (B).

The X-ray diffraction pattern of the deposited film confirmed the formation of highly crystalline rhombohedral Bi_2Te_3 crystals without obvious preferential orientation (Figure 3).

On the bais of the thin film results, continuous Bi_2Te_3 nanotubes were synthesized by displacing electrodeposited nickel nanowires (100 nm in diameter) in solution containing 0.002−0.008 M Bi^{3+} and 0.01 M $HTeO_2^+$. The deposited Bi content in the nanotubes varied linearly with the ratio (Figure 2), which are in good agreement with those observed by Stacy et al.[12] They observed that nearly stoichiometric Bi_2Te_3 thin films were electrodeposited when the applied potentials were more negative than ca. −0.08 V versus SCE. They concluded that the direct deposition of Bi_2Te_3 is thermodynamically favorable over co-deposition of elemental Bi^0 and Te^0 metals because of negative Gibbs free energy of Bi_2Te_3 formation ($\Delta G_f^0 = -899.088$ kJ/mol).[12] Thus, the galvanic displacement reaction of nickel nanowires to Bi_2Te_3 nanotubes can be represented as follows:

$$2Bi^{3+}(aq) + 3HTeO_2^{+}(aq) + 9Ni^0(s) + 9H^+(aq) \rightarrow Bi_2Te_3(s) + 9Ni^{2+}(aq) + 6H_2O(aq) \quad (1)$$

Figures S.2 and 4 show the SEM and TEM images of synthesized Bi_2Te_3 nanotubes from a solution containing 0.006 M Bi^{3+}. Evidence for Bi_2Te_3 nanotube formation is also confirmed with the selected-area electron diffraction (SAED) pattern (inset image of Figure 4B). Ni trace was not observed by both EDAX (Figure S.3) and atomic absorption spectroscopy (AAS) analysis. The surface of nanotubes was rough which might be caused by rough Ni nanowires. Homogeneous Bi_2Te_3 nanotubes with well-defined void spaces were formed, probably because the displacement reaction occurred initially at the spots with highest surface energy and then proceed to those with lower energies. As a result, an incomplete thin sheath formed at the early stage allowing both reactants and products to diffuse across the sheath until a homogeneous Bi_2Te_3 nanotube is formed.

To fabricate nanodevices, nanotubes must be integrated with micro- or macroelectrodes. We achieved this goal by first magnetically assembling an individual nickel nanowire on gold electrodes (Figure 1Ba), followed by postannealing in a reducing environment (5% H_2 + 95% N_2) at 500 °C for 2 h to create interconnect with minimum contact resistance.[13] Once a good electrical contact was made between nanowire and electrodes, the nickel nanowire was displaced to form Bi_2Te_3 nanotubes (Figure 1Bb,c). Finally, the electrodes and nanotubes were rinsed thoroughly with DI water. Using this device, temperature-dependent electrical properties of Bi_2Te_3 nanotubes were measured. Figure S.4, parts a and b show the temperature-dependent current−voltage ($I-V$) curves and resistances. Ohmic contacts were formed between the nanotube and electrodes as indicated by the linear characteristic of the $I-V$ curves. Figure S.4b shows that the nanotube was a semiconductor.

In summary, we synthesized stoichiometric Bi_2Te_3 nanotubes by a galvanic displacement reaction of Ni nanowires. The composition of Bi_2Te_3 nanotubes was precisely tuned by adjusting the $[Bi^{3+}]$/$[HTeO_2^+]$ ratio. The ability to adjust the composition is critical since optimum n-type (Bi-doped Bi_2Te_3) and p-type (Te-doped Bi_2Te_3) nanotube can be synthesize by altering the ratio. By combining the premagnetically assembled nickel nanowire and galvanic displacement reaction, individual Bi_2Te_3 nanotube-based devices were fabricated and their temperature-dependent electrical properties were measured.

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Supporting Information Available: Experimental details, SEM, EDS, and temperature-dependent $I-V$ characteristics of nanotubes are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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