Flexible Thermoelectric Textiles Made from Shape-controlled Bi$_2$Te$_3$ Nanowires

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Abstract
We developed a series of flexible nonwoven textile materials made from n-type Bi$_2$Te$_3$ nanowires exceeding 0.1 of thermoelectric figure of merit ZT. We revealed that crystallinity of Te nanowire precursors in the Bi$_2$Te$_3$ nanostructure synthesis affected the transformation into filled nanowire and hollow nanotubes, and consequently, their thermoelectric properties. We explored the strong correlation between crystallinity and Seebeck coefficient of Bi$_2$Te$_3$ nanowires. The present methodology could be extended to other nanowire materials, which contributes to engineering and improvement of nanowire-based flexible thermoelectrics.

1. Introduction
Thermoelectrics are materials capable of the solid-state conversion between thermal and electrical energy.$^{[1]}$ Heat is three-dimensionally dispersed, and the shape of heat source is not limited in plane. So far, recent progress on nanostructured thermoelectric materials from nanowires to nanocrystals show the comparable or superior performance to the bulk crystals possessing the same chemical compositions because of the dramatically reduced thermal conductivity due to phonon scattering at nanoscale surface and interface.$^{[2]}$ Most thermoelectric devices made from inorganic nanostructures are, however, fabricated into rigid configuration to focus on their thermoelectric performance. Few materials have demonstrated truly flexible and high performance thermoelectric devices, where flexibility in principle could significantly benefit the collection and conversion of waste heat into electricity or the solid-state cooling by applying the devices to any kind of objects with any kind of shapes. Better adhesion helps thermal transport efficiency to approach Carnot efficiency, which could improve the total thermoelectric conversion efficiency, that is defined as thermal efficiency and material efficiency.

We here report flexible thermoelectric textiles made from shape-controlled Bi$_2$Te$_3$ nanowires. We show a key role of Te nanowire on the final form of Bi$_2$Te$_3$ nanowires in similar batches but with a small difference in the feedstocks, and realized both Bi$_2$Te$_3$ filled nanowires and hollow nanotubes. Furthermore the Bi$_2$Te$_3$ nanowire and nanotube can be assembled into nonwoven fabrics (textiles) from dispersions by simple vacuum filtration. Both textiles were bendable, and we also pointed out the difference of Seebeck coefficient between Bi$_2$Te$_3$ nanowire and nanotube textiles and better n-type thermoelectrics exceeding 0.1 of ZT with Bi$_2$Te$_3$ nanowires. Such high performance flexible thermoelectrics would be useful for fabricating the thermoelectric device arrays on any surface.

2. Results and Discussion
Selective Transformation
We first emphasize an importance of tellurium sources in the selective transformation into Bi$_2$Te$_3$ nanowires and nanotubes. Our approach involved a clear trend that, in the syntheses, a subtle difference of Na$_2$TeO$_3$ and TeO$_2$ feedstocks with a common solvent (ethylene glycol) and a common surfactant (polyvinylpyrrolidone) resulted in apparently similar as-grown Te nanowire intermediates, and we then succeeded in selective synthesis of Bi$_2$Te$_3$ nanowires and nanotubes from the specific Te nanowires. (Fig. 1a-d) Unlike one-pot autoclaves, two-pot synthesis under relatively mild conditions such as ambient pressure and temperature below 160 °C, which is below a boiling point of an ethylene glycol solvent, would help to control each steps of Te nanowire growth and subsequent transformation of Bi$_2$Te$_3$ nanostructures. Diameter, and crystallinity dependence of Te nanowire precursors on the final form of Bi$_2$Te$_3$ nanostructures explained that Te nanowires made from small crystallites gave filled Bi$_2$Te$_3$ nanowires.

NW Growth from Na$_2$TeO$_3$  NT Growth from TeO$_2$

![Fig.1 Bi$_2$Te$_3$ nanowire and nanotube growth depending on growth time of tellurium nanowire templates. SEM and TEM images of Bi$_2$Te$_3$ nanowires (a, b), and nanotubes (c, d) from Te nanowires derived from Na$_2$TeO$_3$, and TeO$_2$.](image-url)
Flexible Textiles

From a viewpoint of fabrication, softness and processability is helpful for developing flexible thermoelectrics. Bendability was thus realized by fabricating nonwoven papers from as-obtained Bi$_2$Te$_3$ nanowires and nanotubes with small diameter. As discussed above, small-diameter nanowires are ultralong (> 10 µm), whereas thick nanowires were short and plump. Such nanowires with a high aspect ratio can form self-standing monolith. The nonwoven Bi$_2$Te$_3$ fabric textiles were fabricated by filtering their ethanol dispersion onto 0.2 um-pore filters. These filtered films were washed with ethanol and hydrazine (10 v/v%), and dried under vacuum at 80 °C. Note that the Bi$_2$Te$_3$ textiles were spontaneously peeled off from filter substrates during a washing period, and they formed flexible films (Fig. 2a). The films had networking and porous structures (Fig. 2b), which could contribute to fabrication of light and robust materials. The films, when they were dried on round surface, were set bending and showed shape memory effect (Fig. 2c).

Thermoelectric Properties

Textiles made from Bi$_2$Te$_3$ nanowires and nanotubes showed n-type thermoelectric properties, and the nanowires possessed higher Seebeck coefficients, leading to better figure of merit, ZT (Fig. 3). These difference will be discussed from a viewpoint of their crystallinity.

3. Conclusions

We developed a series of flexible nonwoven textile materials made from n-type Bi$_2$Te$_3$ nanowires exceeding 0.2 of thermoelectric figure of merit ZT. We revealed that crystallinity of Te nanowire precursors in the Bi$_2$Te$_3$ nanostructure synthesis affected the transformation into filled nanowire and hollow nanotubes, and consequently, their thermoelectric properties. The present method thus provided a route to flexible thermoelectric materials.

Acknowledgements

We thank Prof. M. Nakamura (NAIST) for valuable discussion, and help with the thermal conductivity measurements.

References