Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Materials

Synthesis of Ultra-long Hollow Chalcogenide Nanofibers

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Experimental

Polyvinylpyrrolidone (PVP, MW=360,000) was purchased from Sigma Aldrich as polymer matrix. Nickel acetate tetrahydrate (Ni-acetate, $Ni(CH_3COO)_2 \cdot 4H_2O$) was purchased from Acros Organics to be utilized as the Ni precursor. Bismuth nitrate pentahydrate (Bi-nitrate, $Bi(NO_3)_3 \cdot 5H_2O$) and Tellurium oxide (TeO_2) were obtained from Fisher Scientific and Alfa Aesar, respectively, for galvanic displacement deposition. All chemicals were used as received.

Ni nanowirers were synthesized based on electrospinning process. PVP and Ni solutions were prepared separately. The PVP solution was prepared to 10 g using PVP and anhydrous ethanol with a weight ratio of 1:9. The Ni solution was prepared with the controlled concentration of nickel acetate from 5 to 12 mmol in 3 g of DI-water. Once the solutions were prepared, the PVP and Ni solutions were mixed under continuous stirring at 60^{o}C for 30 min to create a homogenous solution. The mixed solution was loaded into a plastic syringe connected to a nozzle connector with a capillary tip (0.31 mm diameter) placed at the end of it. At this time, the nozzle connector was also connected to a high voltage power supply (High voltage AC-DC, Acopian). After assembling electrospinning setup, the solution was fed at a constant rate of 0.5 ml/hr using syringe pump (Perfusor compact S, B.Braun). Applied voltage of 10 to 16 kV was applied between the capillary tip and the collectors (two half of 4" highly doped Si wafers with controlled gap of 25 mm) which was grounded to protect the setup from electrostatic discharge. A SiO_2/Si substrate (1.5×1.5 cm) was positioned between the collectors. Upon applying voltage, a fluid jet was drawn from the capillary tip and the solvent evaporated rapidly. Highly aligned Ni acetate/PVP nanowires were deposited on Si/SiO_2

substrate for 5 sec. The calcination of aligned Ni acetate/PVP nanowires was achieved by thermal treatment at 500^{o}C for 3 hours in air, with a heating rate of 3 ^{o}C/min to form NiO nanofibers. Finally, ultra long and aligned Ni nanofibers were reduced by annealing in forming gas (5%H_2 + 95 %N_2) for 3 hours at 400°C.

Aligned Ni nanowires were employed in galvanic displacement reaction to synthesize ultra high long with highly aligned Bi_xTe_y nanotubes. The electrolyte utilized to make Bi_xTe_y nanotubes by galvanic displacement reaction was prepared by dissolving TeO_2 in concentrated nitric acid, followed by addition of $Bi(NO_3)_3$. After uniform mixing, the resulting solution was diluted with DI water. The final concentration of the electrolyte was 1 mM $HTeO_2^+$, 20 mM Bi^{3+} and 1 M HNO_3. To perform galvanic displacement reaction, highly aligned Ni nanofibers on oxidized Si substrates were immersed into the electrolyte solution for 1 hour and rinsed with DI water. The effect of Bi^{3+} concentration on Bi_xTe_y nanofibers composition was performed by altering the [Bi^{3+}] from 1 mM to 100 mM.

Characterization: The morphology of the Ni acetate/PVP nanowires, NiO nanowires, Ni nanowires and Bi_xTe_y nanotubes were investigated by FE-SEM. The average diameter and distribution were calculated from high magnification images of FE-SEM, collected from at least 200 samples. The composition of the Bi_xTe_y nanotubes was analyzed by electron dispersive X-ray spectroscopy (EDS). X-ray differaction (XRD) and selected area diffraction pattern (SAED) were used to determine crystal structure of synthesized nanofibers. A Keithley source meter with Janis cryostat were used to characterize temperature dependent electrical properties.

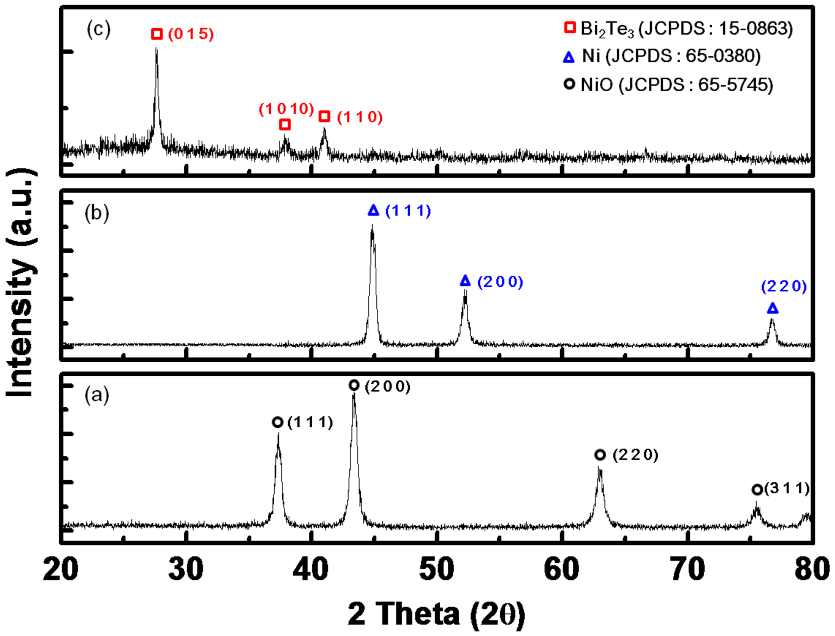

Figure S.1 XRD patterns of synthesized nanofibers: (a) NiO nanofibers synthesized by calcinating PVP/Ni acetate nanofibers at 500°C in air, (b) Ni nanofibers after thermal reduction of NiO nanofibers at 400°C in 5% H_2/N_2 and (c) Bi_2Te_3 nanotubes fibers after galvanic displacement reactions.

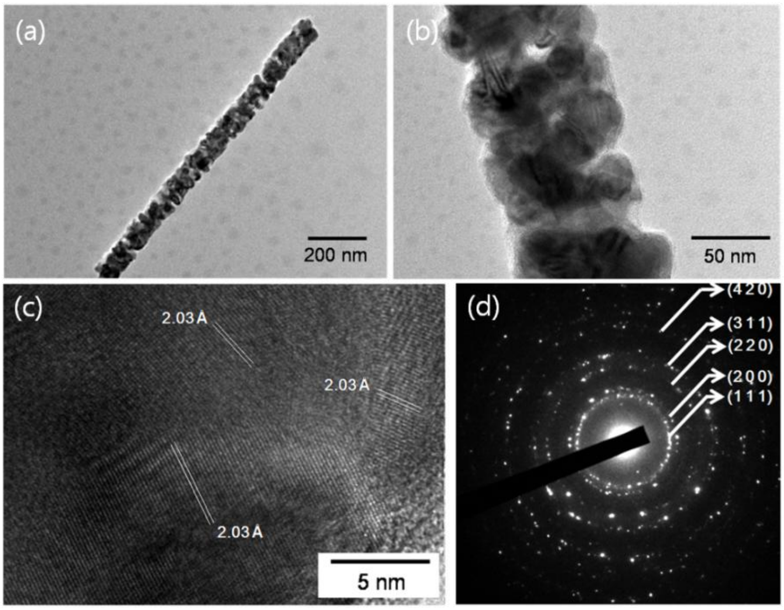

Figure S.2. HR-TEM images (a, b, c) and corresponding SAED pattern (d) of the nickel nanofibers.

Table S.1. The average diameter of the electrospun nanofibers as a function of Ni acetate concentration and applied voltage.

Synthesis condition (Ni acetate/Applied voltage)	Average diameter (nm)		
	Ni acetate/PVP NW	NiO NW	Ni NW
5 mmol/10kV	138 ± 38	70 ± 14	63 ± 20
5 mmol/16kV	170 ± 68	102 ± 27	89 ± 25
6 mmol/10kV	157 ± 37	74 ± 18	62 ± 19
6 mmol/16kV	170 ± 54	66 ± 22	69 ± 21
12 mmol/10kV	269 ± 40	128 ± 25	80 ± 16
12 mmol/16kV	531 ± 84	210 ± 76	149 ± 32

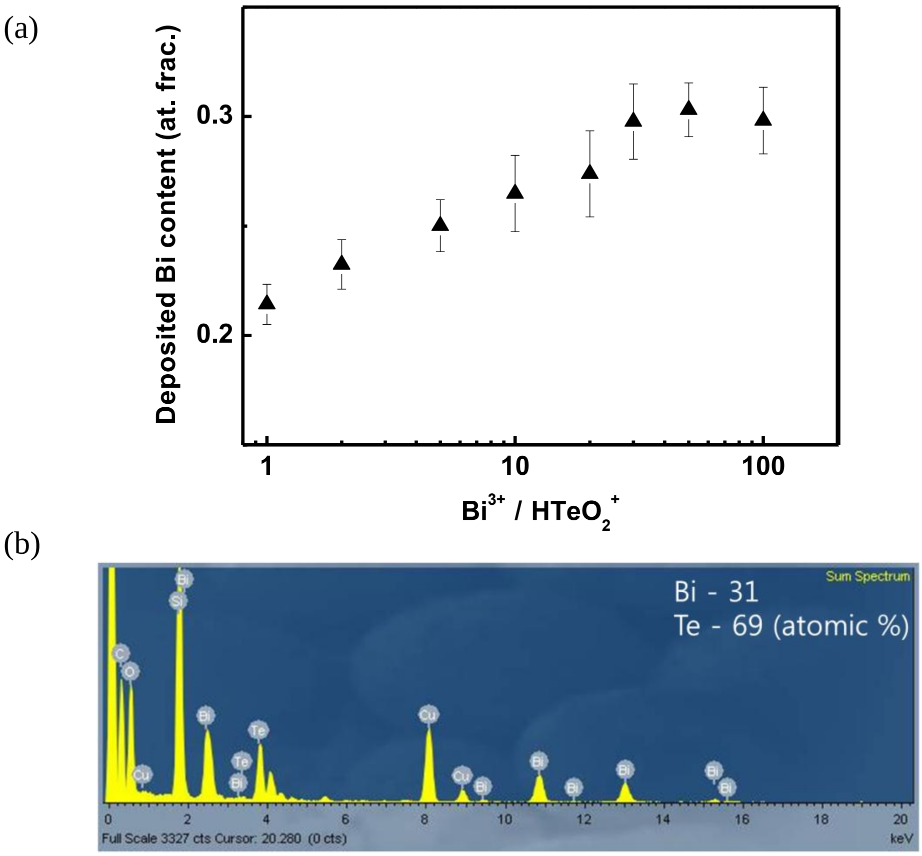

Figure S.3. (a) Dependence of the deposited Bi content of Bi_xTe_y nanofibers as a function of $[Bi^{+3}]/[HTeO_2^+]$ ratio. $[Bi^{+3}]$ was varied from 1 mM to 100 mM while fixing the $[HTeO^+]$ and $[HNO_3]$ at 1 mM and 1 M, respectively at room temperature. (b) Typical EDS spectra of synthesized Bi_xTe_{1-x} nanofibers.

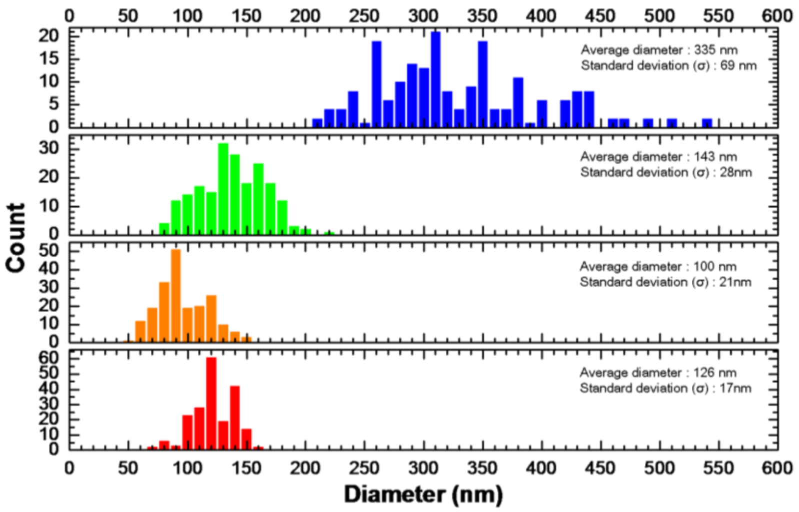

Figure S.4 Diameter distribution of the synthesized nanofibers: (a) PVP/Ni acetate, (b) NiO, (c) Ni, and (d) Bi_2Te_3 nanofibers.

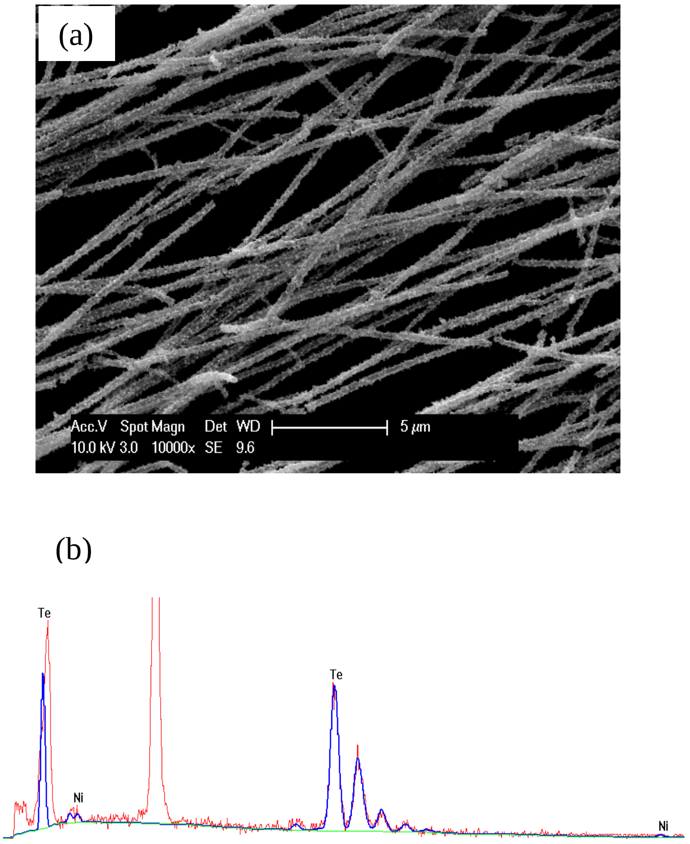

Figure S.5 SEM image of (a) hollow Te nanofibers synthesized by galvanic displacement of Ni nanofibers with corresponding (b) EDS spectra.

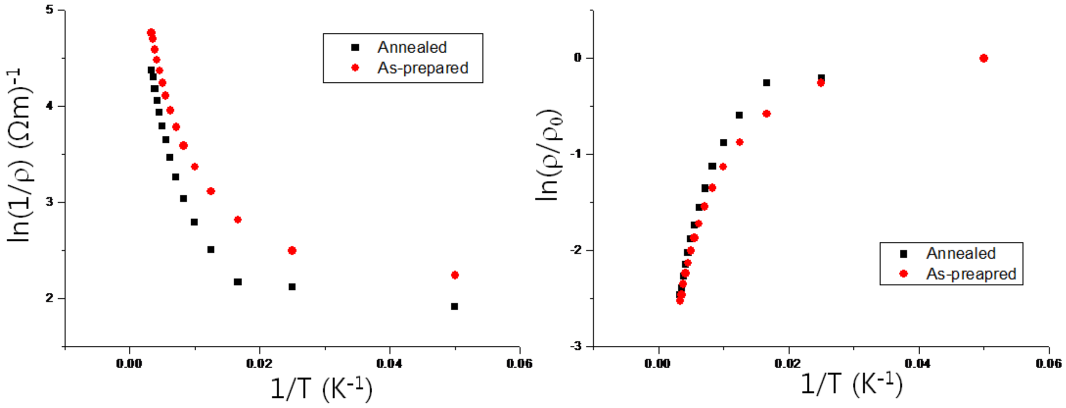

Fig. S.6. TCR analysis of Bi_xTe_y nantubes before and after the annealing process in a reducing environment (5%H_2 + 95 %N_2) at 473 K for 2 hours.