Electronic Supplementary Information

Branched Tellurium Hollow Nanofibers by Galvanic Displacement Reaction and Their Sensing Performance toward Nitrogen Dioxide

Hosik Park^{*a*}, Hyunsung Jung^{*a*}, Miluo Zhang^{*a*}, Chonghyun Chang^{*a*}, Yongho Choa^{**b*}, and Nosang V. Myung $*^{a}$

^a Department of Chemical and Environmental Engineering, University of California-Riverside, Riverside, CA 92521, USA. E-mail: <u>myung@engr.ucr.edu</u>

^b Department of Bionanotechnology, Hanyang University, Ansan 426-791, Republic of Korea. E-mail: <u>ychoa15@hanyang.ac.kr</u>

Experimental details:

Synthesis of Ni Nanofibers: Ni nanofibers were synthesized via an electrospinning process. The precursor solutions were prepared separately using Polyvinylpyrrolidine (PVP, MW=360,000; Sigma Aldrich) and nickel acetate tetrahydrate (Ni-acetate, Ni(CH₃COO₂)·4H₂O; Acros Organic). In general, a PVP solution was prepared by dissolving 1 g of PVP in 9 g of anhydrous ethanol, and a Ni solution was prepared by dissolving 3 g of Ni-acetate in 3 g of DI water. The PVP and Ni solutions were mixed and magnetically stirred at 60 °C for 45 min and 70 °C for 15 min to form a homogeneous solution. The obtained solution was loaded into the plastic syringe equipped with a nozzle connector with a capillary tip (0.31 mm diameter). For the electrospinning, the nozzle connector was connected to a high-voltage supply, and a piece of aluminum foil was placed 10 cm below the tip of the nozzle connector to collect the nanofibers. The applied voltage was 10 kV, and the feeding rate for the precursor solution was 0.5 ml h^{-1} . This process was carried out in air at room temperature. The electrospun Ni acetate/PVP nanofibers were calcined at 500 °C for 3 h in air, with a heating rate of 3 ^oC min⁻¹ to obtain the NiO nanofibers. Finally, Ni nanofibers were obtained by reducing the NiO nanofibers under forming gas (5 % H₂ + 95 % N₂) at 400 °C for 3 h, with a heating rate of 5 °C min⁻¹. Before performing the GDR, Ni nanofibers were sonicated at 40 kHz for 10 min for dispersion.

Galvanic Displacement Reaction: The electrolytes for galvanic displacement reaction were prepared by dissolving TeO₂ (99.99%; Alfa Aesar Inc.) in 1 M HNO₃. The concnetration of $HTeO_2^+$ was varied

from 0.5 mM to 10 mM to observe the effect of the electrolyte concentration on the morphology of synthesized Te hollow nanofibers. To perform the GDR, dispersed Ni nanofibers were immersed into the electrolyte solution for 1 h at 25 °C. After the GDR, nanofibers were rinsed with DI water and kept in isopropyl alcohol.

Material Characterization: Morphology and crystallinity of synthesized materials were analyzed by SEM (XLG-30FEG, Philips) and TEM (JEM-2100, JEOL) with high resolution-TEM, selected area electron diffraction (SAED), and Fast Fourier Transform analyses (FFT). The average wall thickness of hollow Te nanofibers synthesized by GDR using different electrolyte concentrations were calculated from TEM images.

Sensor Fabrication and Characterization: A piece of SiO₂/Si (3×3 cm) substrate instead of an aluminum foil was utilized during the electrospinning process for sensor fabrication. After GDR using Ni nanofibers on the SiO₂/Si substrate, Pt electrodes with a 3 µm gap were fabricated by an e-beam lithography process. After photolithographically defining the electrode area, a 3000 Å-thick Pt layer was e-beam evaporated, and Pt electrodes were defined using lift-off techniques. For gas sensing, Pt electrodes with aligned Te nanofibers were connected to a chip holder by wire bonding. The sensing chip was installed in a 3.6 cm³ sealed glass chamber with gas inlet and outlet ports for gas flow and connected to a Keithley 236 source measurement to obtained the electrical connection. The gas sensing was carried out at a constant applied voltage (1V) at room temperatuer, and the change of sensor resistance under various gas concentrations was monitored by a LabView program every 0.2 seconds. A constant flow rate of 200 ccm with the desired analyte gas (purity: 99.998 %) diluted in dry synthetic air (purity: 99.998 %) was applied using mass-flow controllers (Alicat Scientific Inc., USA). Dry synthetic air was used as a carrier and reference gas for the sensing of NO₂, NH₃, H₂S, and H₂O vapor.



Figure S1. Wall thickness of Te hollow nanofibers with/without branched nanostructures synthesized by GDR depending on the concentration of $HTeO_2^+$: (a) 0.5 mM, (b) 1.0 mM and (c) 10 mM ((a), (b), and (c) represent the responses acquired from Te hollow nanofibers shown in Figures 2(B), (C), and (D), respectively).



Figure S2. (A, C) TEM, and (B, D) HR-TEM of Te branched hollow nanofibers synthesized by GDR with varying the concentration of $HTeO_2^+$: (A, B) 1.0 mM and (C, D) 10 mM.



Figure S3. Real-time sensing performance and calibration curve of Te hollow nanofibers with/without branched nanostructures towards (A, B) NH_3 , (C, D) H_2S and (E, F) H_2O , respectively ((a), (b), and (c) represent the responses acquired from Te hollow nanofibers shown in Figures 2(B), (C), and (D), respectively).