Electronic Supplementary Information

Rational design of Sn-based multicomponent anodes for high performance lithium-ion batteries: SnO_2@TiO_2@reduced graphene oxide nanotubes

Jun Young Cheong,‡ Chanhoon Kim,‡ JiSoo Jang, and Il-Doo Kim*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon, 305-701, Republic of Korea.

Experimental

Synthesis of materials

For the electrospinning solution of SnO_2 nanotubes (NTs), 1 g of tin chloride dehydrate ($SnCl_2 \cdot 2H_2O$, Sigma Aldrich), 5 g of ethanol (C_2H_6O, Merck) were mixed first and stirred for 2 h and 1.4 g of polyvinylpyrrolidone (M_w = 1,300,000, PVP, Sigma Aldrich) and 5 g of N, N-dimethylformamide (DMF, Sigma Aldrich) were added and stirred for 4 h. Electrospinning was conducted under the following conditions: distance of 12 cm between the tip of the needle (25 gauge) and current collector, applied voltage of 15 kV, with a flow rate of 20 μl min^{-1}. As-spun Sn precursor/PVP nanofibers (NFs), then, were calcined at 600 °C for 1 h and 700 °C for 1 h at a heating rate of 10 °C min^{-1} in a muffle furnace under air atmosphere, in order that SnO_2 NTs were formed. To carry out the sol-gel process of TiO_2 layer on top of SnO_2 NTs, 0.12 g of titanium butoxide ($Ti[O(CH_2)_3CH_3]_4$, Aldrich) and 0.12 g of de-ionized water (DIW) were mixed in 4.8 g of ethylene glycol (EG, Junsei Chemical) and 1.2 g of ethanol in the presence of 0.3 g of SnO_2 for 6 h at 80 °C. It was cleaned with ethanol two times by centrifugation at 3000 rpm for 15 min each. It was dried overnight (for 12 h) and thermally annealed at 550 °C for 1 h at a heating rate of 10 °C min^{-1} in a muffle furnace under air atmosphere. This sample is denoted as SnO_2@TiO_2. For another sample with higher TiO_2 concentration, 0.4 g of titanium butoxide ($Ti[O(CH_2)_3CH_3]_4$, Aldrich) and 0.4 g of DIW were mixed in 3.2 g of ethylene glycol (EG, Junsei Chemical) and 0.8 g of ethanol in the presence of 0.2 g of SnO_2 for 6 h at 80 °C, under same centrifugation condition and subsequent drying and annealing process. This sample is denoted as SnO_2@TiO_2 (X5). To synthesize SnO_2@TiO_2 NTs wrapped by rGO sheets, 0.3 g of SnO_2@TiO_2 was mixed with 0.1 g of polyallylamine hydrochloride (PAH, M_w = 15,000, Sigma Aldrich) for 2 h and centrifuged three times at 3000 rpm for 15 min each. It was dried for 12 h and stirred with 6 g of graphene oxide in

water solution (2 ml mg^{-1}, Sigma Aldrich) for 24 h. It was then mixed and stirred with 2 g of hydrazine monohydrate (64–65%, Sigma Aldrich) and dried for 12 h. This rGO-wrapped SnO_2@TiO_2 sample is denoted as SnO_2@TiO_2@rGO.

Cell Assembly

To carry out the electrochemical tests, cells were assembled in 2032 coin-type half cells. The anodes (SnO_2, SnO_2@TiO_2, and SnO_2@TiO_2@rGO NTs) were composed of active materials, super P carbon black, poly(acrylic acid)/sodium carboxymethyl cellulose (50/50 wt%/wt%, Aldrich) binder at a weight ratio of 80:10:10. They were slurry-casted on Cu current collector and dried in a vacuum at 150 °C for 2 h. The mass loading of active materials were ~ 2 mg cm^{-2} for SnO_2, SnO_2@TiO_2, and SnO_2@TiO_2@rGO NTs. The 2032 coin-type half cells consisted of lithium metal as a counter electrode, a Celgard 2325 separator, and 1.3 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/diethylene carbonate (EC/DEC, 3/7 v/v) with 10 wt% fluoroethylene carbonate (FEC) (PANAX ETEC.) for electrolytes. They were assembled in an Ar-filled glove box.

Characterization

As-spun Sn precursor/PVP NFs, SnO_2, SnO_2@TiO_2, and SnO_2@TiO_2@rGO NTs were characterized by a field emission scanning electron microscopy (FE-SEM, Nova 230, FEI) operating at 10 kV. Surface area of SnO_2@TiO_2 was measured using BET (Brunauer–Emmett–Teller) device (Tristar II 3020, Micromeritics). To characterize the morphologies of the SnO_2@TiO_2, SnO_2@TiO_2 (X5), and SnO_2@TiO_2@rGO, field emission electron microscopy (FE-TEM, Tecnai TF30 ST, FEI) operating at 300 kV was employed. The crystalline structure of SnO_2 and SnO_2@TiO_2 (X5) was analyzed with a powder

X-ray diffractometer (XRD, D/MAX-2500, Rigaku) using Cu Kα radiation (λ=1.54 Å) between 20° and 80° at a scan rate of 0.066 ° s^{-1}. The weight percentage of rGO in SnO_2@TiO_2@rGO was confirmed by thermogravimetry analyzer (TGA, TG 209 F3, NETZSCH). Raman spectra were obtained from dispersive Raman spectrometer (ARAMIS, Horiba Jobin Yvon) to investigate the characteristics of wrapped rGO layer in SnO_2@TiO_2@rGO using a He-Ne laser operating at λ = 633 nm. Surface state of SnO_2@TiO_2 and SnO_2@TiO_2@rGO was analyzed using X-ray photoelectron spectroscopy (XPS) (K-alpha, Thermo VG Scientific). The 2032 coin-type half cells were cycled at a current density of 100-5000 mA g^{-1} between 0.01 and 3 V using battery testing device (Maccor Series 4000, KOREA THERMO-TECH). Cyclic voltammetry (CV) was conducted at 0.1 mV s^{-1} within a range of 0.01 to 3.0 V using battery testing device (WBCS4000, Wonatech). Conductivity of SnO_2, SnO_2@TiO_2, and SnO_2@TiO_2@rGO NTs was examined by an AC impedance analyzer (ZIVE SP1, Wonatech).

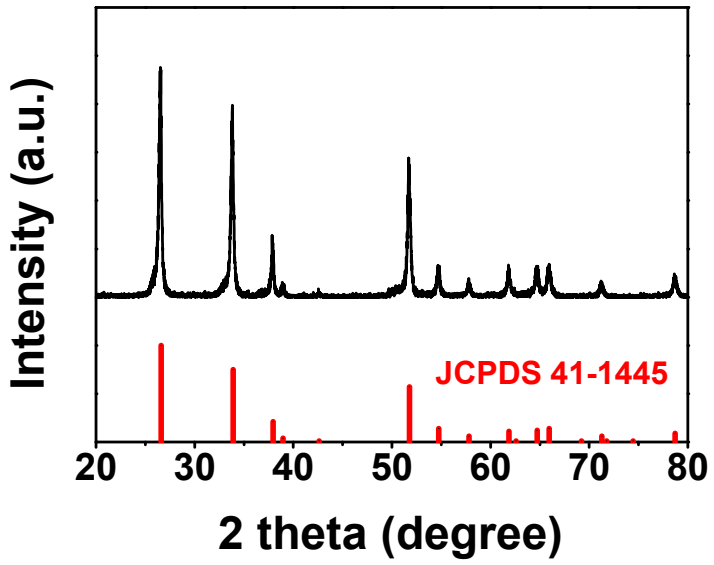

Fig. S1 XRD patterns of SnO_2 NTs.

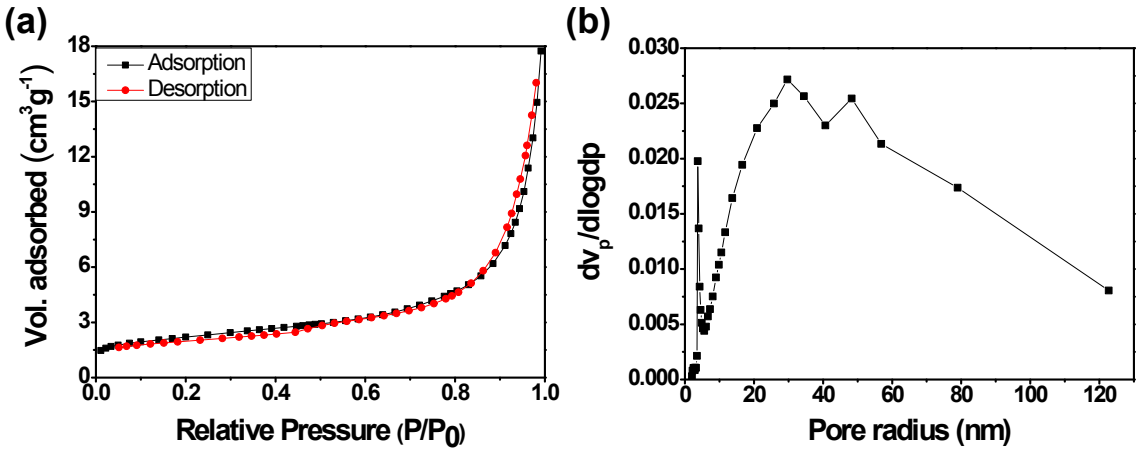

Fig. S2 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of SnO_2@TiO_2 NTs.

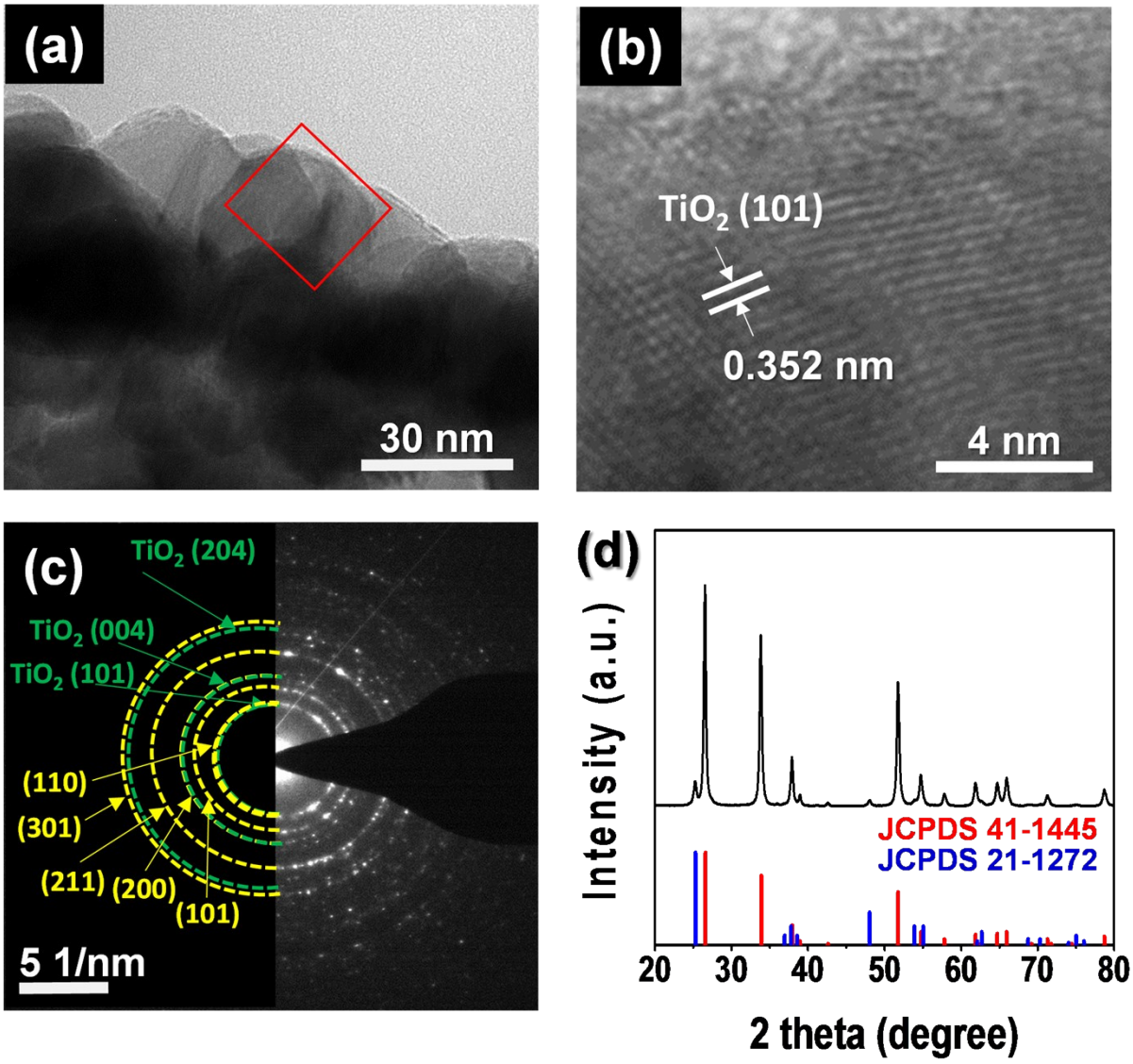

Fig. S3 (a) TEM image of SnO_2@TiO_2 (X5) NTs in low magnification, (b) TEM image magnified from the red box seen in (a) confirming the crystal structure of TiO_2, (c) SAED pattern of SnO_2@TiO_2 (X5) NTs showing both the crystal structure of SnO_2 (yellow) and TiO_2 (green), and (d) XRD patterns of SnO_2@TiO_2 (X5) NTs.

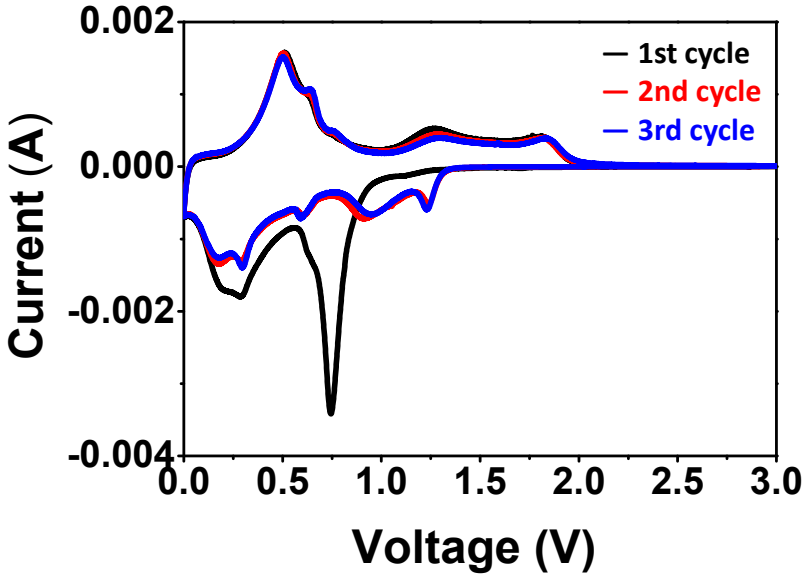

Fig. S4 Cyclic voltammetry (CV) curve of SnO_2@TiO_2 NTs, from 1st to 3rd cycle, at a scan rate of 0.1 mV s^{-1} between 0.01 and 3 V.

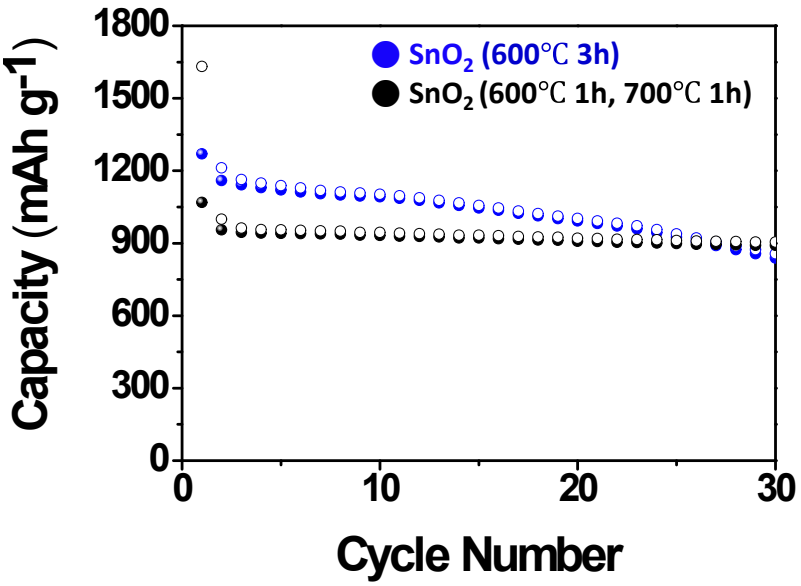

Fig. S5 Cycle retention of SnO_2 NTs under different calcination conditions at a current density 500 mA g^{-1} between 0.01 and 3 V.

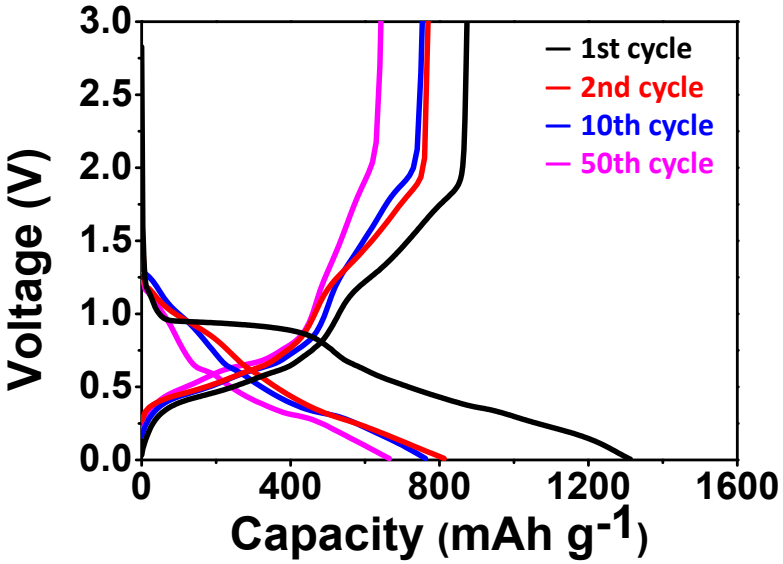

Fig. S6 Charge/discharge profile of SnO_2@TiO_2 NTs at a current density of 500 mA g^{-1} between 0.01 and 3 V.

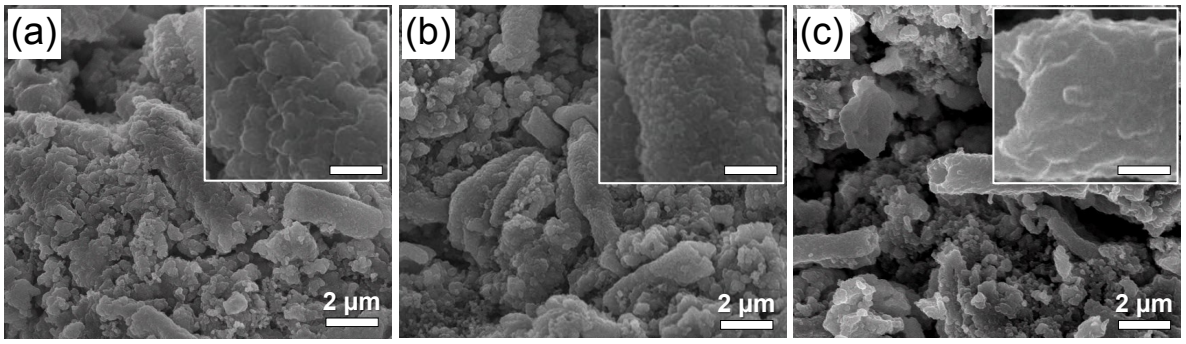

Fig. S7 SEM image of (a) SnO_2, (b) SnO_2@TiO_2, and (c) SnO_2@TiO_2@rGO electrodes after 50 cycles at 500 mA g^{-1}. Insets are magnified SEM images showing the surface of SnO_2, SnO_2@TiO_2, and SnO_2@TiO_2@rGO. Scale bars in the insets are 500 nm.

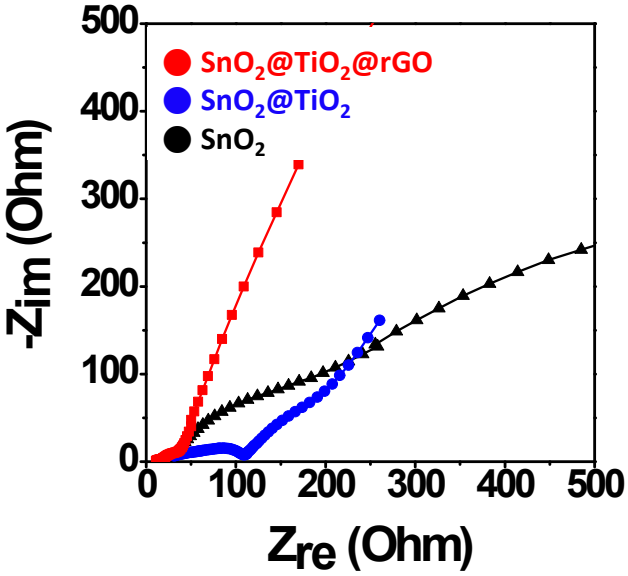

Fig. S8 Nyquist plots of three different samples (SnO_2@TiO_2@rGO, SnO_2@TiO_2, and SnO_2 NTs) after 50th cycle at a current density of 500 mA g^{-1}.