

EXPERIMENTAL SECTION

Electrochemical deposition of ZnSb:

The electrochemical depositions were carried out in a three-electrode cell by using a potentiostat/galvanostat Ch 1200A instrument. The working electrodes were ITO glass (Kintec Co.) with 10 ohm/sq conductivity. Before electrodeposition, the ITO substrates were rinsed with ethanol to remove any impurities and then left to dry. A platinum wire with a diameter of 0.5 mm was used as a counter electrode and an Ag/AgCl electrode was used as the reference. The distance between the working and counter electrodes was fixed at 2.0 cm. The bath was filled with ethylene glycol (99.5 purity, Sigma-Aldrich) containing ZnCl₂ (99.5 purity, Sigma-Aldrich) and SbCl₃ (99.95 purity, Sigma-Aldrich).

Constant potentials in the range of 3-9 V were applied for electrochemical deposition. Electrochemical deposition process was performed at room temperature without any stirring or inert-gas bubbling. After deposition, the electrodes were rinsed with ethanol several times and then dried in vacuum oven for 6 hours.

Characterization:

The sample morphology was examined using a transmission electron microscopy (TEM; JEOL, JEM-2100) and a field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The elemental compositions of the samples were analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to the TEM. Crystallographic information for the samples was collected using a powder X-ray diffractometer (Bruker AXS: D8 advance, Cu K α radiation with $\lambda = 1.5406 \text{ \AA}$).

Electrochemical Measurements:

To prepare the composite, Zn-Sb crystals deposited on ITO substrates were ultrasonicated in ethanol and the dispersed powders were centrifuged and washed with ethanol and water twice. The powder was then dried in 70°C in a vacuum oven for 16 hours. The prepared Zn-Sb powder was physically mixed with 20 wt % SWCNT which was added as a conducting agent. The CNT was the single walled, purified, highly functioned P3 type purchased from Carbon Solutions, Inc.

Anode electrodes were prepared by coating slurries containing the active material Zn-Sb mixed with SWCNT, carbon black (10 wt %) as a conductor, and polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP) as a binder (10 wt %) on copper foil substrates.

Assembly of the coin-type battery cells was performed in an Ar-filled glove box with moisture and oxygen lower than 1.00 ppm. Li foil was used both as the counter and reference electrodes, while 1M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) was used as the electrolyte. All the coin cells were tested using a NEWWARE battery tester galvanostatically between 0.0 V and 2.0 V (vs. Li/Li⁺) at a current density of 100 mA/g (0.18 C).

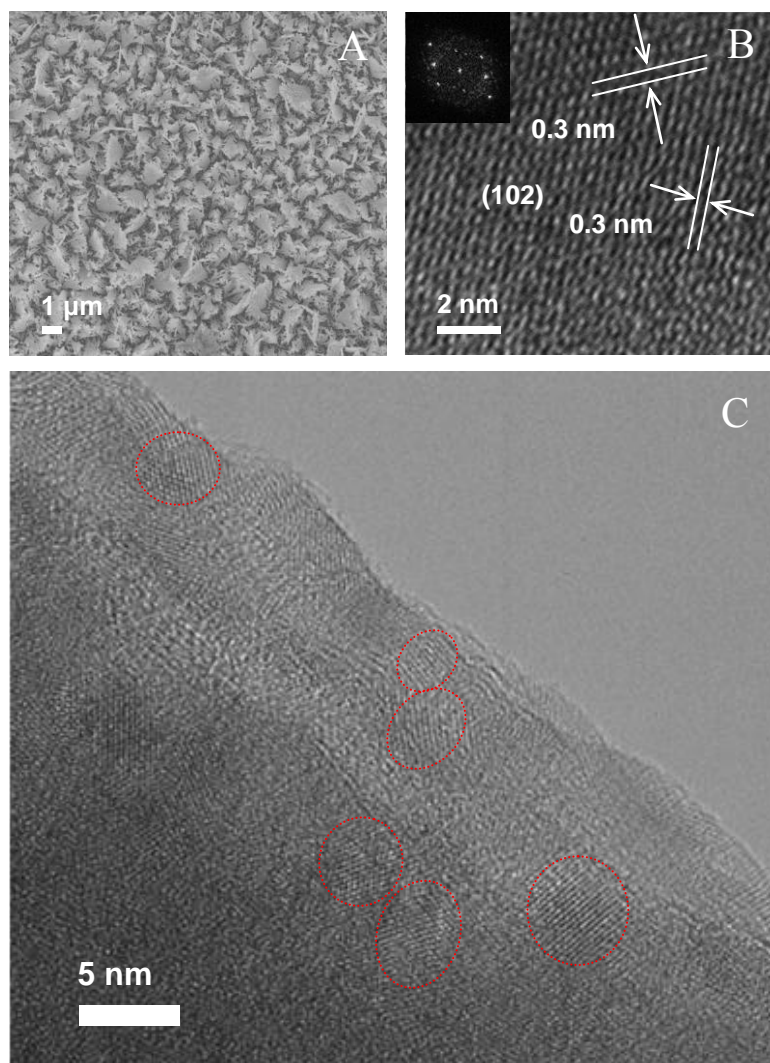


Figure 1 (A) SEM images, (B, C) HRTEM images of Zn-Sb nanotubes electrodeposited in ethylene glycol solution with a precursor molar ratio $I_{\text{ZnCl}_2\text{-SbCl}_3} = 1.6$ and an applied voltage $V_d = -7$ V for 200 s on ITO glass. The inset in (B) is the fast Fourier transform pattern of the lattice structure.

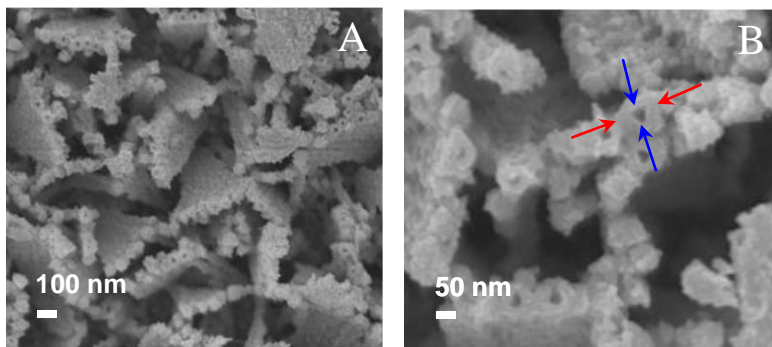


Figure S2 SEM of Zn-Sb nanotubes deposited in ethylene glycol solution with precursor ratio $I_{\text{ZnCl}_2\text{-SbCl}_3} = 1.6$ and $V_d = -9\text{V}$ for 200 s on ITO glass.

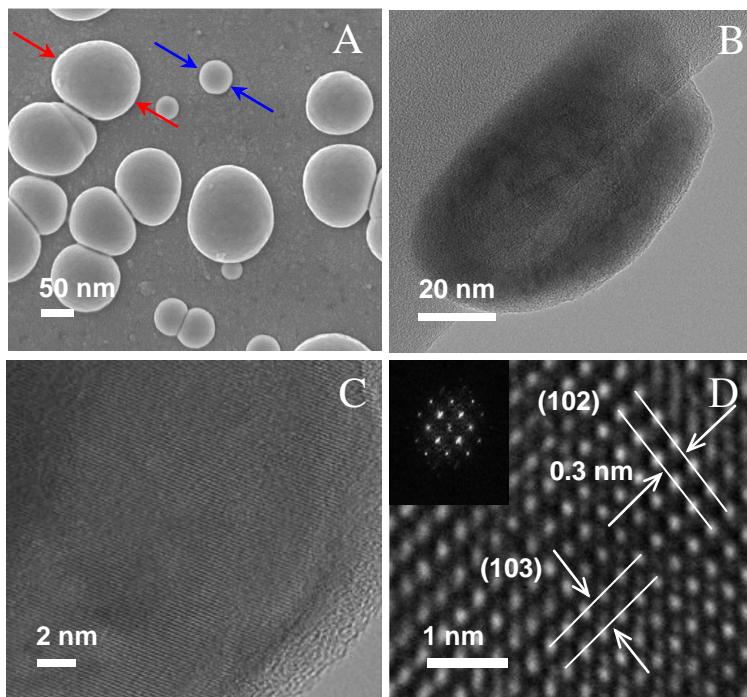


Figure S3 (A) SEM, (B) TEM, (D,E) HRTEM of ZnSb nanoparticles deposited in ethylene glycol solution with precursor ratio $I_{\text{ZnCl}_2\text{-SbCl}_3} = 2$ and $V_d = -2\text{V}$ for 200 s.

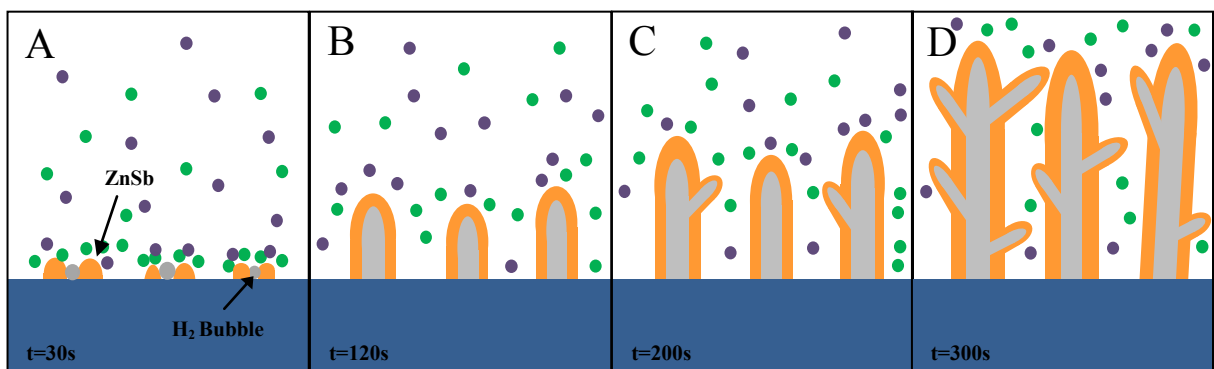


Figure S4 Schematic drawing of ZnSb nanotubes depositing on ITO glass in ethylene glycol solution with precursor molar ratios of $I_{\text{ZnCl}_2\text{-SbCl}_3} = 1.6$ and $V_d = -7$ V for different times, (A) 30 s, (B) 120 s, (C) 200 s, (D) 300 s.

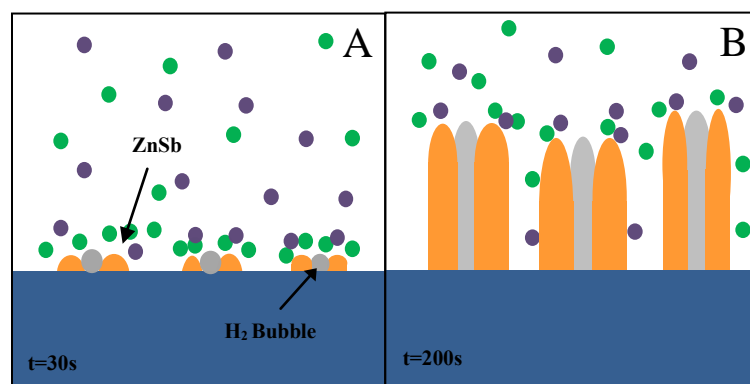


Figure S5 Schematic drawing of ZnSb nanotubes depositing on ITO glass in ethylene glycol solution with precursor molar ratios of $I_{\text{ZnCl}_2\text{-SbCl}_3} = 1.6$ and $V_d = -9$ V for different times, (A) 30 s, (B) 200 s.

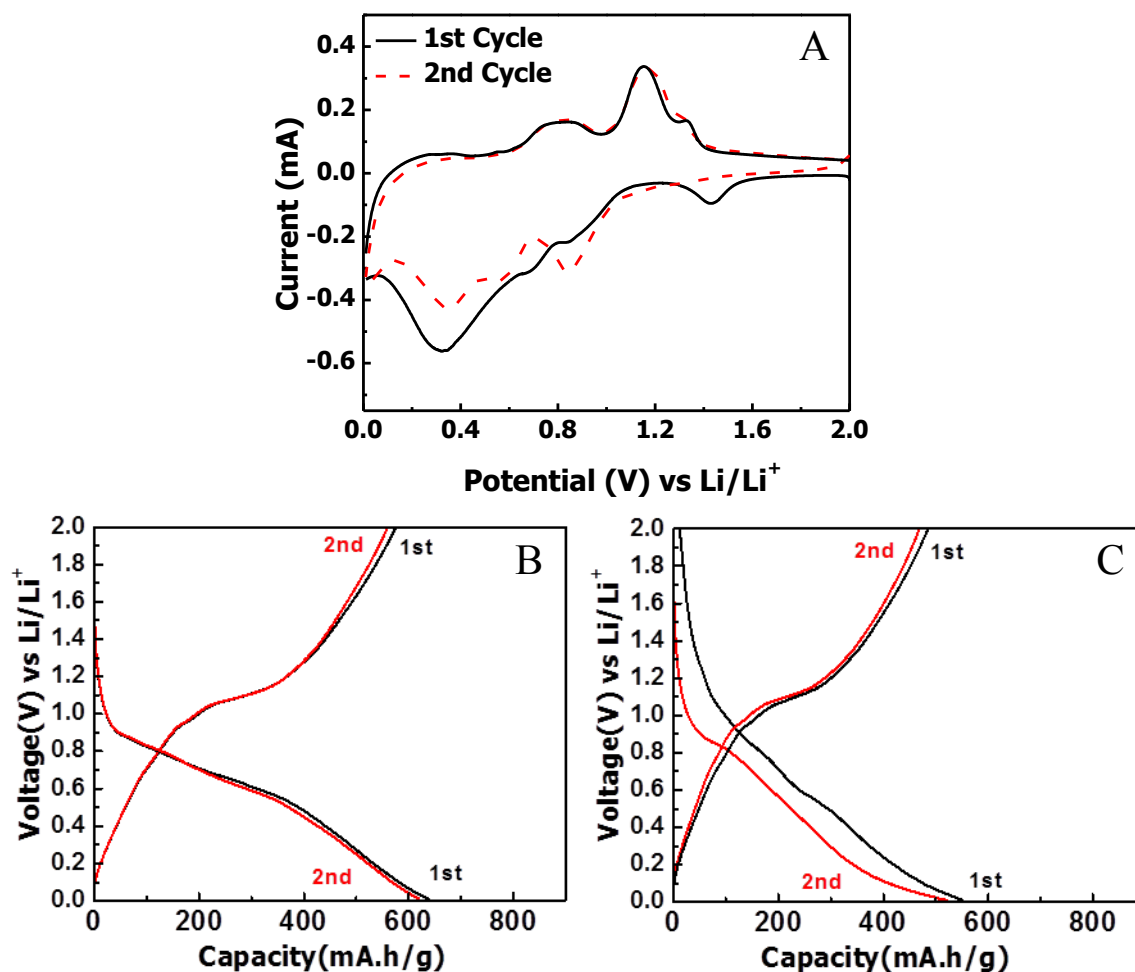


Figure S6 (A) Cyclic voltammograms (CVs) of the first and second cycles of ZnSb nanotubes obtained with $I_{\text{ZnCl}_2\text{-SbCl}_3} = 1.6$ and $V_d = -7$ V at a scan rate of 0.5 mV/s, (B) Charge/discharge voltage profiles of ZnSb nanotubes between 0-2 V (vs Li/Li⁺) at a current density of 100 mA/g (0.18 C), (C) Charge/discharge voltage profiles of ZnSb nanoparticles between 0-2 V (vs Li/Li⁺) at a current density of 100 mA/g (0.18 C).

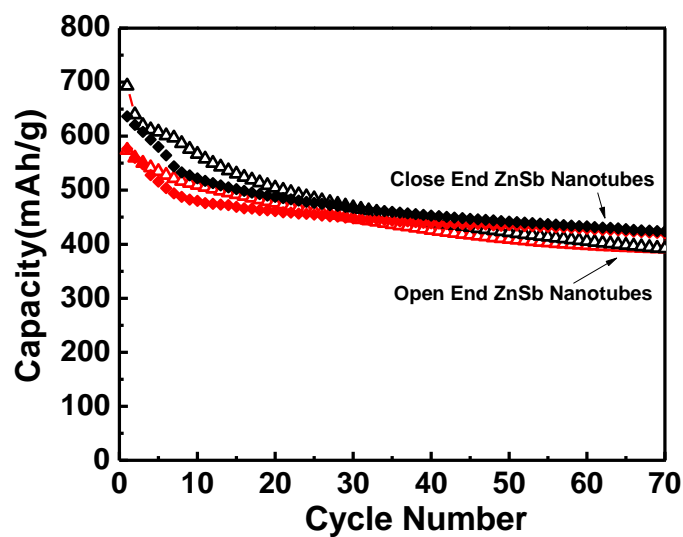


Figure S7 Charge/discharge cycling performance of open and close end ZnSb nanotubes between 0-2 V (vs Li/Li⁺) at a current density of 100 mA/g (0.18 C).

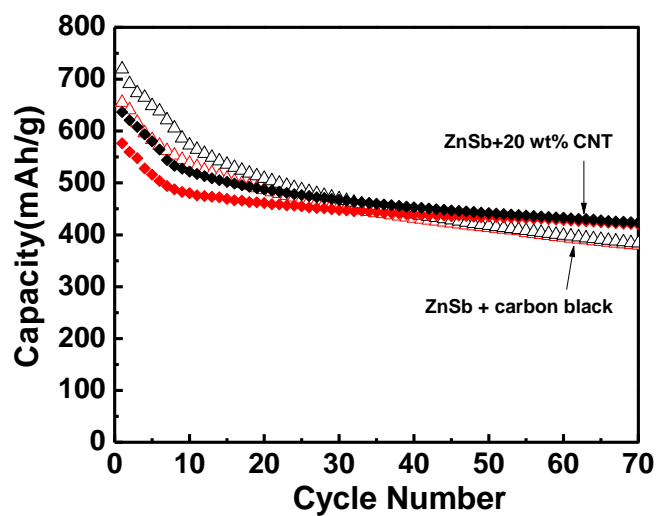


Figure S8 Charge/discharge cycling performance of ZnSb nanotube electrodes with and without addition of 20 wt% CNT between 0-2 V (vs Li/Li⁺) at a current density of 100 mA/g (0.18 C).