Electronic Supplementary Information

Formation of Porous SnO$_2$ Microboxes via Selective Leaching for Highly Reversible Lithium Storage

Lei Zhang, Hao Bin Wu, Bin Liu,* and Xiong Wen (David) Lou*

School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459. Email: liubin@ntu.edu.sg; xwlou@ntu.edu.sg; Webpage: http://www.ntu.edu.sg/home/xwlou/
Experimental details

Materials Synthesis. The single-crystalline ZnSn(OH)$_6$ microboxes are synthesized through a modified self-templating co-precipitation method. In a typical synthesis, 20 mL of ethanol solution of SnCl$_4$ (4 mmol, Sigma-Aldrich) was added into 140 mL of a mixture aqueous solution containing ZnCl$_2$ (4 mmol, Sigma-Aldrich) and citric acid (4 mmol, Sigma-Aldrich) under stirring, followed by quick addition of 20 mL of aqueous solution of NaOH (2 M) at room temperature. After 1 h, 60 mL of aqueous solution of NaOH (2 M) was poured into the suspension and the reaction was lasted for 30 min. The resulting white precipitate was harvested by several rinse-centrifugation cycles with deionized water and ethanol, and dried at 60 °C. Then the as-prepared single-crystalline ZnSn(OH)$_6$ microboxes were annealed at 650 °C in air for 6 h with a heating rate of 1 °C min$^{-1}$, resulting in a white product of Zn$_2$SnO$_4$/SnO$_2$ microboxes.

To obtain porous SnO$_2$ microboxes, 50 mg of Zn$_2$SnO$_4$/SnO$_2$ microboxes was dispersed in 40 mL of 1.0 M HCl for 30 min at room temperature under stirring. The white product was rinsed with deionized water until the solution became neutral, and finally dried at 60 °C. Afterwards, porous SnO$_2$ microboxes were coated by glucose-derived carbon-rich polysaccharide by a simple hydrothermal process. In a typical synthesis, 50 mg of the porous SnO$_2$ microboxes was dispersed by ultrasonication in 30 mL of 0.2 M aqueous glucose solution. The suspension was transferred to a 60 mL Teflon-lined autoclave, which was then heated in an air-flow electric oven at 170 °C for 10 h. The product was harvested by centrifugation and washed with deionized water and ethanol for at least five times, and dried at 60 °C. Finally, the resulting brown powder was carbonized at 500 °C for 4 h under nitrogen atmosphere to obtain the final product of SnO$_2$@C microboxes.

Materials Characterization. X-ray diffraction (XRD) patterns were collected on a Bruker D8
Advanced X-Ray Diffractometer with Ni filtered Cu Kα radiation ($\lambda=1.5406$ Å) at a voltage of 40 kV and a current of 40 mA. Field-emission scanning electron microscope (FESEM) images were acquired on a JEOL JSM-6700F microscope operated at 5 kV. Transmission electron microscope (TEM) images were taken on JEOL JEM-2010 and JEOL JEM-2100F microscopes. Elemental mapping were performed using the energy-dispersive X-ray spectroscopy attached to the JEM-2100F. Thermogravimetric analysis (TGA) was carried out under air flow with a temperature ramp of 10 °C min$^{-1}$. Nitrogen sorption measurement was performed on Autosorb 6B at liquid N$_2$ temperature.

*Electrochemical Measurements.* The electrochemical tests were carried out in two-electrode Swagelok cells. The working electrode consists of 70 wt% of active material, 20 wt% of conductive carbon black (Super-P-Li), and 10 wt% of polymer binder (polyvinylidene fluoride, PVDF). The electrolyte is 1M LiPF$_6$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by weight). Lithium disc was used as both the counter and reference electrode. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. The charge-discharge tests were performed on a NEWARE battery tester. Cyclic voltammograms (CV) were obtained on a CHI 660D electrochemical workstation. The specific capacity of the SnO$_2$@C microboxes is based on the total mass of SnO$_2$ and C.
**Figure S1.** XRD pattern of single-crystalline ZnSn(OH)$_6$ microboxes.

**Figure S2.** Selected-area electron diffraction (SAED) pattern of a single-crystalline ZnSn(OH)$_6$ microbox.
Figure S3. XRD pattern of Zn$_2$SnO$_4$/SnO$_2$ microboxes.

Figure S4. FESEM (a, b, c) and TEM (d) images of Zn$_2$SnO$_4$/SnO$_2$ microboxes.
Figure S5. N₂ adsorption-desorption isotherm of Zn₂SnO₄/SnO₂ microboxes.

Figure S6. XRD pattern of porous SnO₂ microboxes.
Figure S7. FESEM images of cracked porous SnO$_2$ microboxes.
Figure S8. TEM image of porous SnO$_2$ microboxes.

Figure S9. N$_2$ adsorption-desorption isotherm of porous SnO$_2$ microboxes.
Figure S10. TGA curve of SnO$_2$@C microboxes in air.

Figure S11. XRD pattern of SnO$_2$@C microboxes.
Figure S12. N₂ adsorption-desorption isotherm of SnO₂@C microboxes.

Figure S13. Discharge-charge voltage profiles of porous SnO₂ microboxes over the voltage range of 0.05−1.5 V vs. Li/Li⁺ at the current density of 200 mA g⁻¹.
Figure S14. Rate capability of SnO$_2$@C microboxes between 0.05 and 1.5 V.
Figure S15. (a) Discharge-charge voltage profiles and (b) cycling performance of SnO$_2$@C microboxes over the voltage range of 0.05–2.5 V vs. Li/Li$^+$ at the current density of 200 mA g$^{-1}$. 
Figure S16. (a) Discharge-charge voltage profiles and (b) cycling performance of SnO$_2$@C microboxes over the voltage range of 0.05–3.0 V vs. Li/Li$^+$ at the current density of 200 mA g$^{-1}$. 