Electronic Supplementary Information

Amorphous CoSnO₃@C Nanoboxes with Superior Lithium Storage Capability

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Experimental details

Synthesis of $CoSn(OH)_6$ *nanocubes*. In a typical synthesis, 5 mL of ethanol solution of SnCl₄ (1 mmol) was added into 30 mL of a mixture solution containing CoCl₂ (1 mmol) and sodium citrate (1 mmol) under stirring, followed by dropwise addition of 5 mL of aqueous solution of NaOH (2 M) at ambient conditions. After 1 h, 20 mL of aqueous solution of NaOH (8 M) was added into the suspension and the reaction was lasted for 15 min at ambient conditions. The resulting product was harvested by several rinse-centrifugation cycles with deionized (DI) water and ethanol for further characterization.

*Synthesis of CoSnO*₃ *nanoboxes.* Certain amount of CoSn(OH)₆ nanoboxes was successively annealed in N₂ flow at 150 °C, 300 °C and 500 °C with a slow ramp rate of 1 °C min⁻¹. At each stage, the temperature was maintained for 2 h to make the CoSnO₃ powder.

Synthesis of crystalline Co-Sn-O nanoboxes. Crystalline Co-Sn-O (Co_2SnO_4/SnO_2) nanoboxes were synthesize by annealing certain amount of $CoSn(OH)_6$ nanoboxes in N₂ flow at 700 °C for 2 h with a ramp rate of 1 °C min⁻¹.

Synthesis of $CoSnO_3@C$ nanoboxes. 0.07 g of $CoSnO_3$ nanoboxes was dispersed into 30 mL of aqueous solution of glucose (0.05-0.1 M). After thorough mixing, the suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept in an oven at 180 °C for 7 h. The resulting product was harvested by centrifugation and washed thoroughly with ethanol and deionized water. After being fully dried at 60 °C, a certain amount of as-obtained powder was loaded into a tube furnace and annealed in N₂ flow at 500 °C for 4 h with a temperature ramp of 1 °C min⁻¹. *Materials characterization*. The samples were characterized by field-emission scanning electron micro-scope (FESEM, JEOL, JSM-6700F), transmission electron microscope (TEM, JEOL, JEM-2010 and JEM-2100F), powder X-ray diffraction (XRD, Bruker, D8-Advance X-ray Diffractometer, Cu Ka, $\lambda = 1.5406$ Å), N₂ adsorption/desorption (Quantachrome Instruments, Autosorb AS-6B) and thermogravimetric analysis (TGA, Shimadzu, DRG-60).

Electrochemical measurements. The electrochemical measurements were conducted using twoelectrode Swagelok cells with pure lithium foil as the counter and reference electrode at room temperature. The working electrode consists of $CoSnO_3$ nanoboxes with or without carbon coating, carbon black (Super-P-Li) and polyvinylidene difluoride (PVDF) in a weight ratio of 7:2:1. The electrolyte used is 1.0 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. The galvanostatic charge/discharge tests were performed using a Neware battery tester at different current densities within a cut-off voltage window of 0.01-1.5 V.



Figure S1. TEM images of CoSn(OH)₆ nanoboxes.



Figure S2. A typical HRTEM image of a CoSnO₃ nanobox.



Figure S3. XRD patterns of $CoSnO_3$ nanoboxes with or without carbon coating and crystalline Co-Sn-O nanoboxes obtained by annealing $CoSn(OH)_6$ nanoboxes at 700 °C. XRD analysis suggests that the crystalline Co-Sn-O is actually a mixture of Co_2SnO_4 and SnO_2 .



Figure S4. N₂ adsorption/desorption isotherms of (a) CoSnO₃@C and (b) CoSnO₃ nanoboxes.



Figure S5. TGA curve of CoSnO₃@C nanoboxes in air.



Figure S6. Cyclic voltammograms (CVs) of $CoSnO_3@C$ nanoboxes, which are obtained between 0.01 - 3.0 V at a scan rate of 0.2 mV s⁻¹.



Figure S7. Discharge/charge voltage profiles of $CoSnO_3$ @C nanoboxes after the pre-lithiation treatment for the first two cycles. The pre-lithiation is performed by placing the electrode in direct contact with a lithium foil wet by electrolyte solution for 1 h. After that, the open-circuit voltage of the battery is just above 0 V vs. Li⁺/Li.



Figure S8. (a, b) TEM and (c) FESEM images of CoSnO₃@C nanoboxes after cycling for 400 cycles. In the FESEM image, the nanoboxes are marked with white circle.



Figure S9. A typical TEM image of CoSnO₃ nanocubes.