

Supplementary Information

Facile synthesis of hollow Cu₂Sb@C core-shell nanoparticles as a superior anode material for lithium ion batteries

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10 Experimental Sections

Preparation of hollow Cu₂Sb@C core-shell nanoparticles

All chemicals were used as received without further purification. Triethylene glycol (TEG, 99%, Alfa) was used as the solvent in all the experiment. Antimony chloride hydrate (SbCl₃ · 5H₂O, 98%), copper chloride hydrate (CuCl₂ · 2H₂O, 99%), and sodium borohydride (NaBH₄, 98%) were analytical reagents purchased from the Shanghai Chemical Company. Polyvinylpyrrolidone (PVP, MW = 360 000, Aldrich) and poly-(2-ethyl-2-oxazoline) (PEtOx, MW = 50 000, Alfa) as surface stabilizers, while sucrose (C₁₂H₂₂O₁₁, Shanghai) was used as carbon source.

In this study, we dissolved 2.0 g of PVP and PEtOx (0.45 g) in 100 mL of TEG. When the temperature reached 90°C, SbCl₃ (2.772 g in 84 mL of TEG) was added. Ten minutes later, NaBH₄ (2.772 g in 84 mL of TEG) was added into solution drop by drop. After the NaBH₄ solution was added, the black Sb colloids were observed immediately. Twice the amount of the NaBH₄ was used to ensure complete reduction of the metal ions. This mixed solution was stirred for 0.5 h under an Ar atmosphere and then heated to 170°C, at which CuCl₂ (2.772 g in 84 mL of TEG) was added dropwise. The temperature was kept constant for 1 h. After that, the solution was adjusted to 200°C and added sucrose (0.8g) into it. The solution was stirred vigorously for 2 h under an Ar atmosphere. The nanoscale carbon-coated Sb-Cu alloy nanoparticles were finally prepared, using sucrose as a carbon source.

Characterization of hollow Cu₂Sb@C core-shell nanoparticles

S-4800 SEM system was applied to observe the surface morphology of the nanocomposites. High resolution transmission electron microscope (HRTEM) images were obtained from a Tecnai F30 microscope. The phase structure of the as-prepared Cu₂Sb @C nanocomposites was determined by X-

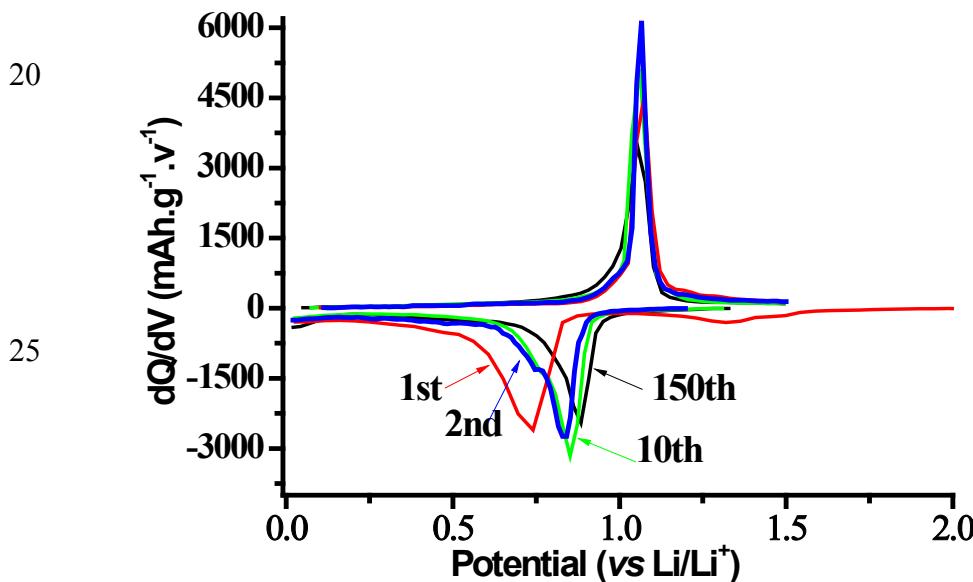
ray diffraction (XRD, Philips X' Pert Pro Super X-ray diffractometer Cu-K α radiation) at a scanning rate of 0.02°/s in 2θ range from 20° to 80°. Raman experiments were performed on LabRam I (Dilor, France) using 632.8 nm excitation line from a He–Ne laser with a laser power about 1.2 mW on the sample surface.

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Electrochemical testing of hollow Cu₂Sb@C core-shell nanoparticles

The electrodes of hollow Cu₂Sb @C core-shell nanoparticles were prepared by dispersing 90% active material, and 10% polyacrylic latex binder (LA132) in water solvent to form a homogeneous slurry. The slurry was spread onto a copper foil. The electrodes were dried at 100 °C in a vacuum oven 10 for 12 h and then pressed to enhance the contact between the active materials and the current collector.

The coin-type cell (size 2025) was made from Cu₂Sb @C nanocomposites cathode and a lithium anode. The electrodes were separated by a separator material (Celgard 2400). The electrolyte reservoir was made from LiPF₆ (1M) in a mixture of ethylene carbonate (EC) / dimethyl carbonate (DMC) / diethyl carbonate (DEC) 1:1:1 (vol%, Provided by Guangzhou Tinci Materials Technology Co., Ltd, 15 Guangzhou, China). The cells were galvanostatically charged and discharged in a battery test system (NEWARE BTS-610, Neware Technology Co., Ltd., China) with a current density of 100 mA·g⁻¹ for a cut-off voltage of 0.02–1.5 V (*versus* Li⁺/Li) at room temperature.



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Figure S1 Differential charge-discharge capacity vs. voltage profiles of hollow Cu₂Sb@C nanoparticles electrode

Figure S1 shows the differential charge-discharge capacity vs. voltage profiles of hollow SbCu@C core-shell nanoparticle, in the first cycle, two cathodic peaks are observed at about 0.75 V and 1.5 V, respectively attributed to Li-insertion reaction of Cu₂Sb to Li₃Sb and SEI formation reaction. However, the first cycle profile only give one anode peak at 1.1 V, corresponding to the Li-extraction reaction of 5 Li₃Sb to Cu₂Sb. During the subsequent cycles, the peak at 0.75V shows a positive shifts, which is ascribed to polarization of the electrode materials in the first cycle. To be noticed, however, that, contrary to the two step deintercalation of lithium of Cu₂Sb nanoparticles, the hollow Cu₂Sb@C core-shell composite show only a step reaction, probably caused by inner low dimensional Cu₂Sb (few nms) and the high conductivity of carbon layer, which also can prevent the Cu₂Sb conglomerating to big size 10 particle.

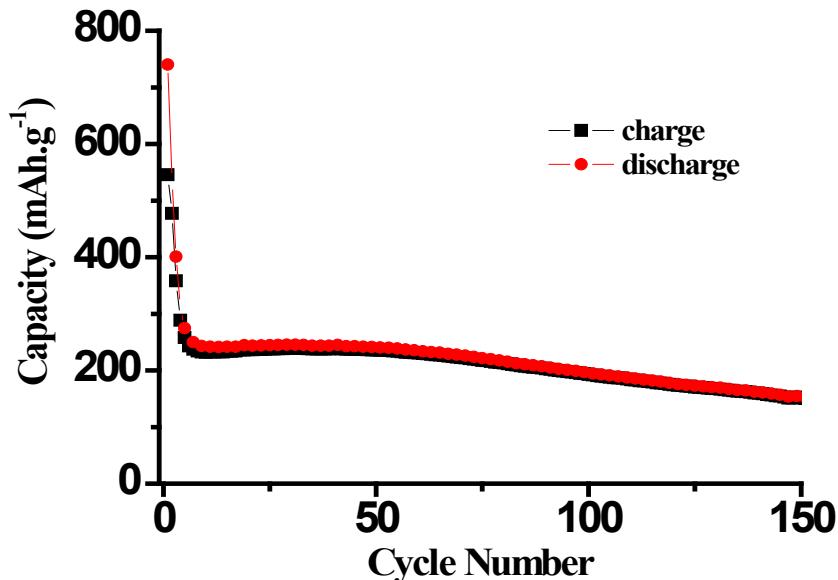


Figure S2 Electrochemical performance of Sb@C nanoparticles