

Lithium Storage Improvement from Hierarchical Double-Shelled SnO₂ Hollow Spheres

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Experimental Section

Synthesis of CH-SnO₂: The chemicals used in this study were of analytic grade and used as received (Aldrich). The approach of mesoporous silica preparing, remodeling and nanochain-loading has been reported previously.¹⁻³ In a typical synthesis, 125 mg remodeled-MS (rMS) was first dispersed in 30 ml of ethanol/water mixture with 37.5 % ethanol (vol %). 0.90 g of urea and 0.10 g of potassium stannate trihydrate were added to the above mixture. Then, the turbid suspension was transferred into 50 ml Teflon-lined stainless-steel autoclave, which was then heated in an airflow electric oven at 170 °C for 24 h. After the autoclave cooled down naturally, the product was harvested by centrifugation and washed with deionized water and ethanol before drying at 80 °C overnight. Coating SnO₂ onto as-synthesis SnO₂ nanochains loaded rMS was simply obtained by repeating the above hydrothermal process for 36 h. The rMS templates were finally removed by HF (2 wt %) after calcined at 600 °C for 5 h in air.

The CH-SnO₂ (80 wt %), conducting additive (10 wt %, Super-P carbon black), and polyvinylidene fluoride (PVDF, 10 wt %) binder in N-methylpyrrolidone (NMP) were mixed into homogeneous slurry. The slurry was then applied to a copper disk current collector and dried in vacuum at 120 °C. Electrochemical test cells were assembled in an argon-filled glovebox using the coated copper disk as the working electrode, lithium metal foil as the counter/reference electrode, and 1 M solution of LiPF₆ in a 50:50 w/w mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. The cells were charged and discharged galvanostatically at the rates of 100 mA g⁻¹ in the fixed voltage window from 5 mV to 2 V on a Neware CT - 3008W battery tester at room temperature.

Capacity calculation of SnO₂ loose aggregates network:

Since the CH-SnO₂ structure was consisted of H-SnO₂ shell and SnO₂LAs network inside, the specific capacity of CH-SnO₂ could be expressed by the following equation:

$$C_{CH} = (C_{LA} * P_{LA}) + (C_H * P_H) \quad (1)$$

Where C_{CH}, C_{LA} and C_H are the specific capacity of CH-SnO₂, SnO₂ LAs network and H-SnO₂ (mAh g⁻¹) respectively, P_{LA} and P_H are the mass fraction (%) of SnO₂ LAs network and H-SnO₂. As the SnO₂-synthesis procedure of CH-SnO₂ could be divided into SnO₂ Las-synthesis (S_{LA}) and SnO₂ shell-synthesis (S_H), the mass-increase of S_{LA} and S_H have been measured and were almost the same, we define:

$$P_{LA} = P_H = 50\% \quad (2)$$

Since C_{CH} (1885 mAh g⁻¹) and C_H (1192 mAh g⁻¹) has been measured by galvanostatic measurement, the value of C_{LA} could be calculated using equation (1), namely 2578 mAh g⁻¹.

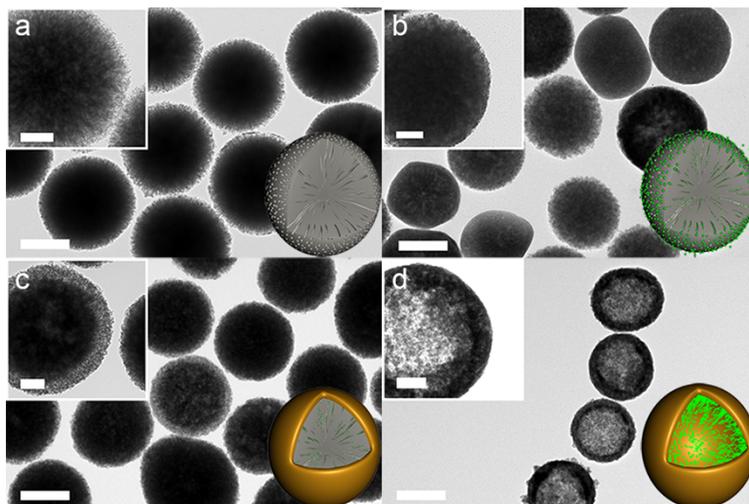


Figure S1. TEM images of rMSs (a), SnO₂ NCs loaded rMSs (b), CH-SnO₂ before (c) and after (d) removing rMSs. The insets of a-d are corresponding magnified TEM images and schematics respectively. The scale bars in a-d = 500 nm, in insets of a-d = 200 nm.

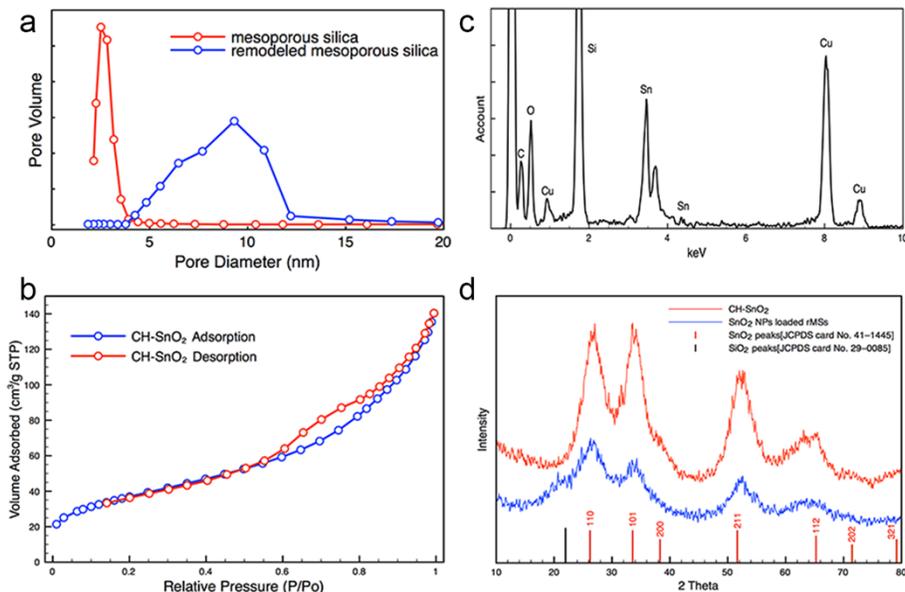


Figure S2. a) Pore diameter distribution of MS before and after remodeled; b) N₂ adsorption - desorption isotherm of CH-SnO₂; c) EDS patterns of SnO₂ nanochains loaded rMSs; d) XRD patterns of SnO₂ nanochains loaded rMSs (blue curve) and CH-SnO₂ (red curve); e, f) HRTEM image of SnO₂ nanochains loaded rMSs; g) HRTEM image of CH-SnO₂ shell; h) TEM image of CH-SnO₂; i) FESEM image of a broken H-SnO₂.

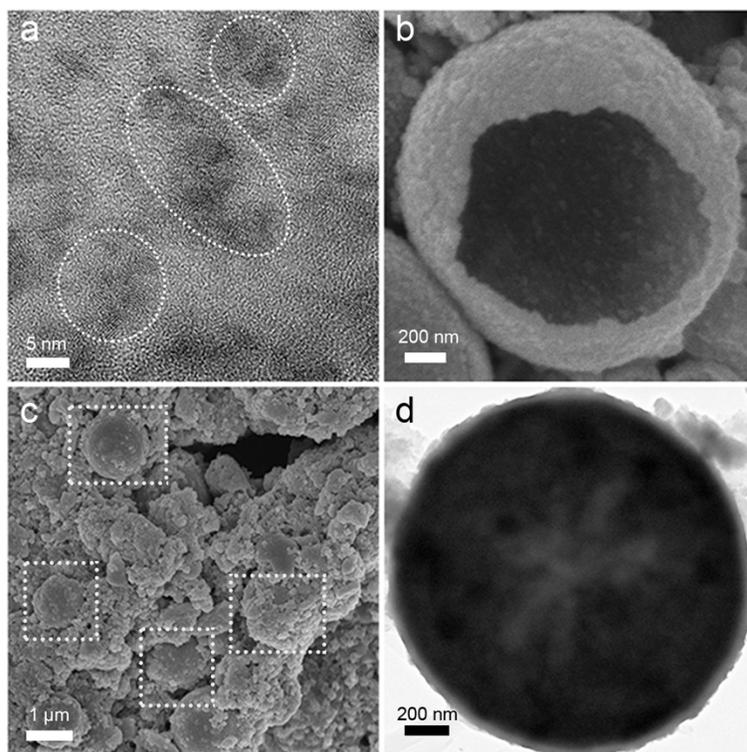


Figure S3. a) HRTEM image of SnO₂ nanochains loaded rMSs; b) FESEM image of a broken H-SnO₂; c,d) FESEM and TEM images of CH-SnO₂ after 50 cycles of charge and discharge.

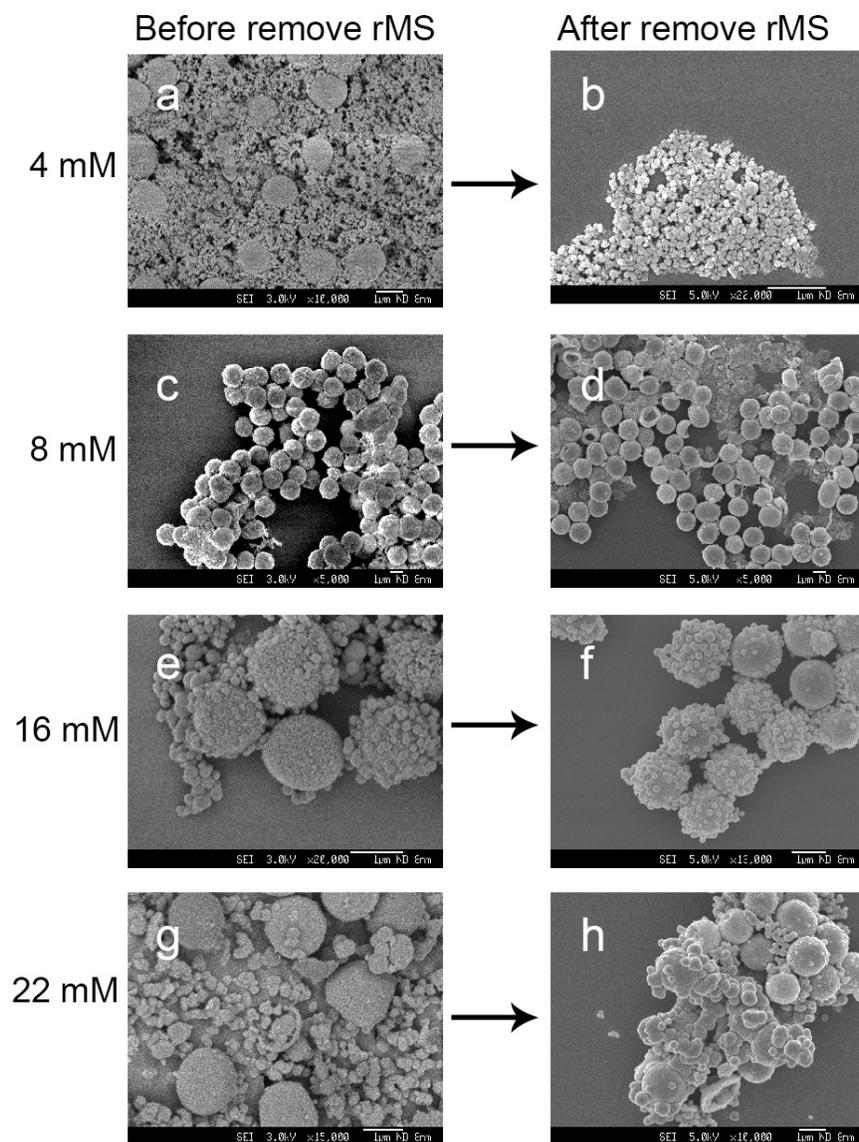


Figure S4. FESEM images of CH-SnO₂ before (left panel) and after (right panel) calcination and removal of rMSs. The concentration of stannate used in the synthesis as precursor of SnO₂ shells increased from A (4 mM) to H (22 mM).

REFERENCES

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