Electronic Supplementary Material (ESI) for Chemical Communications

Facile preparation of silicon hollow spheres and their use in electrochemical capacitive energy storage

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Synthesis of silica precursors: Silica sphere precursors were prepared according to the modified literature procedure:[23] The triethylamine (TEA, 50 mmol) was mixed with 15 mL of deionized water and 5 mL of ethanol, and stirred for 15 min at room temperature. The solution was then heated to 60°C, to which were added cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$, CTAB, 0.1 mmol), and followed by tetraethylorthosilicate (TEOS, 5 mmol). After 15 min of stirring, the solution was cooled to room temperature. The final molar ratios are TEOS/CTAB/TEA = 5/0.1/50. The precipitates were separated by filtration and washed with deionized water several times. The template CTAB was extracted by refluxing the as-synthesized samples in 15 mL of HCl in 120 mL of ethanol.

Preparation of silicon hollow spheres: The silica precursors were dispersed in ethanol by ultrasonic for 30 min and placed in a corundum crucible. The ethanol was then removed by heated at 140°C, and the magnesium powders were placed in the center of the vessel. The molar ratio of Mg : SiO_2 was 2:1. The crucible was put into a tube furnace and the temperature was ramped to 680°C in one hour and maintained for 4 h under a flowing Ar (≥99.999%). The products were treated with 2 M HCl to remove MgO, and then immersed in 5% HF for 24 h to remove unreacted silica.

Characterizations: The scanning electron microscope (SEM) images were obtained on a Hitachi S-4800 field-emission scanning electron microscope at an acceleration voltage of 5.0 kV. Energy dispersive X-ray spectroscopy (EDX) was performed by S-4800 II with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained by JEM-200CX transmission electron microscope. The samples were characterized by powder X-ray diffraction on a Bruker D8 Advance instrument with a Cu Kα radiation (λ = 1.5418 Å). A Micromeritics ASAP 2020 surface area porosimetry system was used to measure gas adsorption. Before the measurements, the samples were activated at 250°C for 5 h under dynamic vacuum.

Electrochemical Tests: The electrodes of silicon hollow spheres were fabricated by following steps: Silicon hollow spheres (50 wt%) and acetylene blacks (50 wt%) were well mixed and ground in an agate mortar, and then pressed onto a foamed nickel grid (1.0×10^7 Pa) that was served as a current collector. The effective mass of the electrode material was about 7 mg. An aqueous solution of 0.5 M Na_2SO_4 was used as electrolyte. The cyclic voltammetry and charge-discharge tests were performed on a CHI-660D electrochemical station at room temperature. Platinum wire and Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively.

The capacitances C (F g^{-1}) based on the CVs were calculated by

$$C = (\int IdV)/(vmV),$$

where *I is* the current density (A), *V is* the potential (V), $\int IdV$ is the area of the CV loop, *v* is the potential scan rate (V s^{-1}), and *m* is the effective mass of the active electrode materials (g).

The capacitances C (F g^{-1}) based on the discharge curves were calculated by

$$C = I\Delta t/(m\Delta V),$$

where *I* is the discharge current (A), Δt are the discharge time (s), ΔV is the voltage change (V) in the discharge process, and *m* is the mass of the active electrode materials (g).

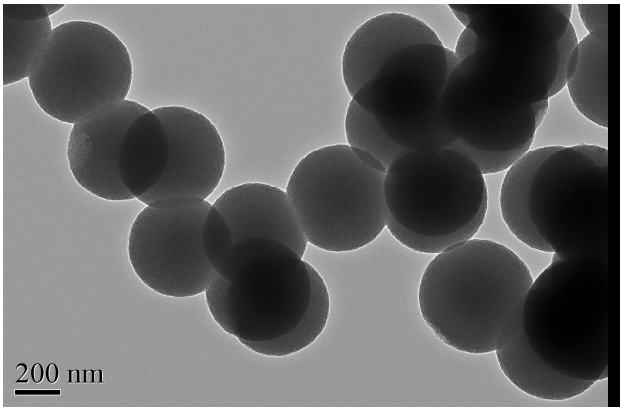

Fig. S1. TEM images of precursor silica spheres.

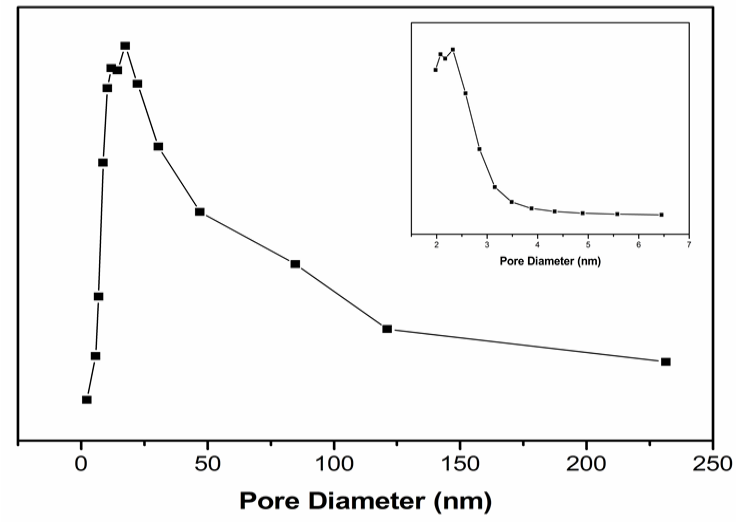

Fig. S2. BJH pore size distribution curves for silicon hollow nanospheres and precursor silica spheres (insert).

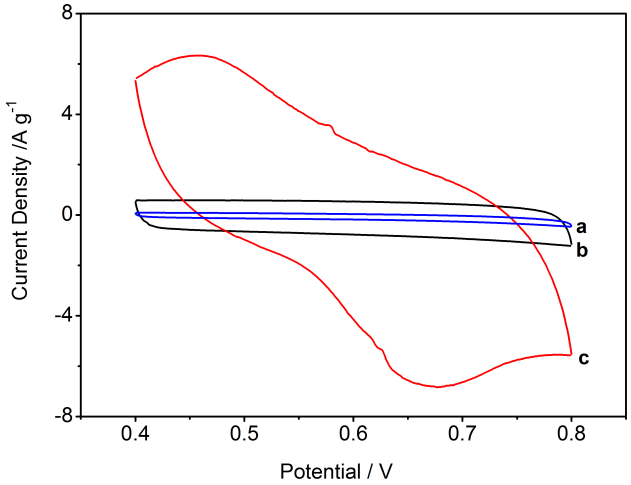

Fig. S3 CV curves of (a) commercial silicon powder, (b) acetylene black, and (c) silicon hollow spheres at a scanning rate of 100 mV/s.