Supporting information

Porous Si@C Ball-in-Ball Hollow Spheres for Lithium-ion Capacitor with improved energy and power density

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Experimental

All Chemical reagents were purchased from Shanghai Chemical Co. Ltd., and they were directly used without further purification.

Materials Preparations

MHSiO₂: The preparation of MHSiO₂ was following a procedure reported in the literature. Typically, cetyltrimethylammonium bromide (CTAB, 0.3 g) was dissolved in ethanol aqueous solution (60 mL C₂H₅OH/100 mL H₂O) containing concentrated ammonia aqueous solution (2 mL, 25 wt%). Then, tetraethoxysilane (TEOS, 2 mL) was rapidly added to the mixture under vigorous stirring. After stirring at 35 °C for 24 h, the white precipitation was collected by centrifugation and washed with ethanol. Then, the product was dispersed in water and kept at 90 °C for 2 h. The product collected by centrifugation was dispersed into an ethanol solution (240 mL) containing concentrated HCl (480 μL, 37%) and stirred at 60 °C for 3 h, generating the template-free MHSiO₂.
MHSiO$_2$@Al$_2$O$_3$: MHSiO$_2$@Al$_2$O$_3$ nanospheres were prepared by a facile synthetic protocol in a buffer solution. In a typical synthesis, 0.63 g of ammonium formate was dispersed in 200 ml deionized water, and then formic acid was added till the pH value to 4.4. Then 0.1 g of MHSiO$_2$ and 0.3 g aluminum sulfate were added and dispersed by ultrasound treatment for 30 min. The solution was kept at 70 ºC for 2 h under vigorously stirring. The resulted core-shell NPs were collected by centrifugation, washed with water and ethanol, and dried at 80 ºC for 4 h.

MHSiO$_2$@Al$_2$O$_3$@C: Carbon coating of MHSiO$_2$@Al$_2$O$_3$ was carried out by thermal decomposition of acetylene gas at 800 ºC for 10min in a quartz furnace. The mixture of acetylene and high-purity argon (argon: acetylene = 9: 1 by volume) was introduced at a flow rate of 150 sccm.

SiO$_2$@C ball-in-ball hollow spheres: The obtained MHSiO$_2$@Al$_2$O$_3$@C was then immersed in a 1 M HCl solution for 6 h to remove Al$_2$O$_3$. Finally, the resulted powders were collected by filtration and washed with water for several times and vacuum-dried at 70 ºC for 6 h.

Porous Si@C ball-in-ball hollow spheres: Magnesium powder (0.3 g) was mixed with MHSiO$_2$@void@C (0.3 g) by grinding. The mixture was then heated in a tube furnace at 650 ºC for 5 h under an argon atmosphere containing 5 vol% H$_2$. The ramp rate was kept at 1 ºC min$^{-1}$. The obtained powder was then immersed in a 2 M HCl solution for 6 h to remove MgO and. Finally, the resulted powders were collected by filtration and washed with water for several times and vacuum-dried at 70 ºC for 4 h.
**MHSi@SiC@C**: The preparation process of Si@SiC@C is similar to the method of Si@void@C, except for the addition of void space between SiO$_2$ and carbon.

**RAC**: The RHs were firstly leached with a 10% HCl solution to remove the metal ions impurities. The leached RHs were heated to 700 °C, and then maintained at 700 °C for 2 h in a tube furnace under the protection of nitrogen to obtain carbonized RHs (CRHs). CRHs were mixed with KOH in a 1:5 mass ratio. The mixture was then transferred to ceramic boats and heated to 700 °C at a ramp rate of 2 °C min$^{-1}$, and then maintained at 700 °C for 1 h in a tube furnace under nitrogen. The resultant activation products were filtered and washed with water until the filtrate became neutral. Finally, the RACs were dried at 90 °C for 10h.

**Characterization**

X-ray diffraction (XRD) patterns were recorded on a D/max 2550VL/PC X-ray diffractometer (Rigaku, Japan) equipped with Cu Kα radiation ($\lambda = 1.5418$ Å, 40 kV, 30 mA). Raman spectra were acquired using an inVia-reflex micro-Raman spectrometer (Renishaw, UK) with a 532 nm wavelength incident laser. X-ray photoelectron spectroscopy (XPS) was performed on an AXIS Ultra DLD spectrometer (Kratos, Japan) with Al Kα radiation ($h\nu = 1486.6$ eV). Thermogravimetric analysis (TGA) was performed on an SDT Q600 thermoanalyzer (DSC-TGA, TA, USA) in air. The specific surface area and pore size distribution of materials were measured using a NOVA2200e analyzer (Quantachrome, USA). The morphology of samples was observed using a NOVA NanoSEM 230 field-emission scanning electron microscope.
(FESEM, FEI, USA). The microstructure of samples was characterized using a JEM-2100F transmission electron microscope (TEM, JEOL, Japan) operating at 200 kV.

Electrochemical measurements

The electrochemical experiments were performed using CR2016 coin cells, which were assembled in a glove box filled with ultra-high purity argon. For half-cell testing, Si/C and RAC electrodes were used as working electrodes and Li metal as the reference electrode. The Si/C electrodes were prepared by casting a slurry consisting of 70 wt% of active material, 15 wt% poly(acrylic acid) (PAA) binder, and 15 wt% of Super-P carbon black on Cu foil. The RAC electrodes were prepared by mixing 80 wt% of active material, 10 wt% Cellulose Sodium (CMC) binder, and 10 wt% of Super-P carbon black on Al foil. The typical mass loading of the active materials in cathode and anode are 2 mg and 1 mg, respectively. 1 M LiPF$_6$ in a mixture of ethylene carbonate, dimethyl carbonate (EC/DEC, 1:1 by vol%) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte. The Si/C|RAC LICs were also assembly in coin cells with Si/C anode (pre-cycled for 3 cycles at 0.4 A g$^{-1}$) and RAC cathode in the same electrolyte, and the optimized mass ratio of anode and cathode was 1:7. The galvanostatic charge and discharge experiment were performed on a battery tester LAND-CT2001A at room temperature. The voltage range of Si/C electrode was 0.01-1.5 V, and the cell is conducted at a low current density of 0.4 A g$^{-1}$ in the first cycle to activate the anode materials. The RAC electrodes and the Si/C|RAC LICs were measured at the same voltage range of 2.0-4.0 V. Cyclicvoltammetry (CV) was conducted on an electrochemical workstation. Electrochemical impedance spectroscopy (EIS)
measurements were performed on a ZAHNER Zennium electrochemical workstation.

The energy density (E) and power density (P) were calculated from the galvanostatic charge/discharge curve by the equation

\[ E = \int_{t_2}^{t_1} I V \, dt \]

(I)

Where \( E \) (W h kg\(^{-1}\)) is energy density, \( I \) is the constant current density (A g\(^{-1}\)), \( V \) is the voltage, and \( t_i, t_2 \) is the start time and end time in the discharge process, respectively.

\[ P = \frac{E}{\Delta t} \]

(II)

Where \( P \) (W g\(^{-1}\)) is power density, \( \Delta t \) is discharge time (s). The mass includes both anode and cathode active materials.
Figure S1. SEM images of (a), (b) TEM images of (d), (e) and (f) SiO$_2$
Figure S2. SEM images of SiO$_2$@Al$_2$O$_3$@C (a) and (b). (c) SEM image of SiO$_2$@Al$_2$O$_3$@C and corresponding EDX elemental mapping images of Si (blue), Al (purple) and C (yellow). TEM images of SiO$_2$@Al$_2$O$_3$@C (d), (e) and (f) Magnified TEM images of SiO$_2$@Al$_2$O$_3$@C.
Figure S3. SEM images (a) and (b), and TEM images of (c) and (d) of SiO$_2$@C ball-in-ball hollow spheres.
Figure S4. TEM image of Si@SiC@C.
Figure S5. (a) Nitrogen adsorption/desorption isotherms obtained at 77 K and (b) pore size distribution of Si@C ball-in-ball hollow spheres.
**Figure S6.** CV curves of Si@C ball-in-ball hollow spheres.
Figure S7. Conductivity of Si@C ball-in-ball hollow spheres and Si@SiC hollow spheres.
Figure S8. (a) Nyquist plots of Si@C ball-in-ball hollow spheres and Si@SiC@C hollow spheres.
(b) TEM image of Si@C ball-in-ball hollow spheres after 1000 cycles.
Figure S9. Comparison of capacity at different rates for Si@void@C composite electrode with those of Si/C yolk-shell nanocomposite anodes reported.[1-5]
Figure S10. The energy and power density (based on the mass of RAC) of Li || RAC LIC.
Figure 11. Ragone plot of LICs using Si@C ball-in-ball hollow spheres as anode and RAC as cathode with various mass ratios.
References