Supporting Information

Step-by-step assembly preparation of core-shell Si-mesoporous TiO₂ composite nanospheres with enhanced lithium-storage properties

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Electronic Supplementary Information contains Experimental section and Figure S1-S10.

1. Experimental

1.1 Synthetic procedures

1.1.1 Preparation of polystyrene (PS) spheres

PS spheres with diameter of around 120 nm were prepared according to the literature.[1] In a typical synthesis, 8 g styrene monomers were added dropwise into 78 mL of deionized water containing 200 mg of [2-(acryloyloxy) ethyl] trimethylammonium chloride under magnetic stirring with N_2 protection. After stirred at 90℃ for 1 h, 0.2 g (0.22 mL) of 2,2'-azobis(2-methylpropionamidine) dihydrochloride was added into the solution. Then, monodisperse PS spheres (with concentration of 50 mg mL^{-1}) were obtained after the reaction proceeded at 90℃ for 10 h.

1.1.2 Preparation of PS@SiO₂ nanospheres

0.35 g of Cetyltrimethyl ammonium bromide (CTAB) were dissolved in 65 mL of water and 60 mL of ethanol. Next, 1.5 mL of ammonium hydroxide and 15 mL of above PS dispersion were added into the CTAB solution. After addition of 4 g of tetraethoxysilane (TEOS), the formed homogeneous solution was stirred at room temperature for 12 h. Thus, PS@SiO₂ core-shell nanocomposites were fabricated after

centrifugation and washing with ethanol for several times.

1.1.3 Synthesis of $HSiO_2$@$mTiO_2$ hollow spheres

The mesoporous TiO_2 shell was prepared according to the modified literature procedure.[2] At first, 0.5 g of PS@SiO_2 was added into 30 mL of ethanol containing 78.2 mg hexadecylamine and 109 μL of KCl (0.1 M) solution and sonicated for 20 min. Then, 0.4 mL of tetraisopropyl titanate (TBOT) was slowly added into the dispersion, and the formed emulsion was aged at room temperature overnight. Thus, an amorphous mesoporous TiO_2 layer was coated on the surface of PS@SiO_2. The produced solids were collected via centrifugation and washed with ethanol for several times. In order to remove the PS template and some organic surfactants, as well as to make the TiO_2 layer well crystallized, the obtained powders were calcinated at 600℃ in air for 10 h. Thus, the $HSiO_2$@$mTiO_2$ hollow spheres were produced.

1.1.4 Synthesis of core-shell Si@$mTiO_2$ composite nanospheres

A magnesiothermic reaction was employed to convert SiO_2 into Si NPs. Namely, 0.22 g Mg powders and 0.2 g $HSiO_2$@$mTiO_2$ hollow spheres were uniformly grinded, and the mixture were loaded in a tube furnace and heated at 650℃ for 5 h in Ar flow. After cooling to room temperature naturally, the obtained brownish black powder was washed with 1 M HCl solution and 0.5% HF solution, respectively. After washed with water and vacuum dried, the core-shell structured Si@$mTiO_2$ were obtained.

1.1.5 Preparation of Si NPs

For comparison, Si NPs were prepared according to the same approach without PS spheres and TiO_2.

1.2 Characterization

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance instrument using a Cu Kα radiation (λ = 1.54056 Å) at room temperature. Scanning Electron Microscope (SEM) images and Energy Dispersive Spectroscopy (EDS) were obtained on a Hitachi S-4800 field-emission scanning electron microscope at an

acceleration voltage of 5.0 kV and 20 kV, respectively. Transmission electron microscopy (TEM) characterization was carried out using a JEM-2100 (Japan). X-ray photoelectron spectroscopy (XPS) measurements were recorded with a PHI 5000 VersaProbe. Fourier-transformed infrared (FT-IR) spectra were measured on a FT-IR spectrometer (Vector22) with the KBr pellet method. Raman spectroscopy (LabRAM Aramis, Horiba) equipped with 632.8 nm laser was used to investigate the structure of silicon nanoparticles. Nitrogen sorption isotherms were collected at 77 K (Micrometrics ASAP 2020 analyzer) after vacuum degassing of the sample at 130 ℃ for 8 h.

1.3 Electrochemical measurements

CR2025 cells were assembled in an argon-filled glove box to perform electrochemical experiments. The electrode was composed of 60 wt% of active material, 30 wt% of conductive graphite, and 10 wt% of sodium carboxymethyl cellulose as a binder. The mixture was stirred in water and blade-coated on a piece of Cu foil. After drying at 85°C in vacuum for 12 h, the foil was cut into disks of 12 mm in diameter. The electrolyte consisted of a solution of 1 M $LiPF_6$ in a mixture of 1:1 (vol/vol) ethylene carbonate / diethyl carbonate with 2 wt % vinylene carbonate added. Pure Li foils were served as counter electrodes. The discharge-charge measurements were performed on a Neware battery testing device (Shenzhen, China) at the constant current mode over the range of 0.01–2.5 V. The specific capacities were calculated based on total weight of active materials.

1.4 Calculation of theoretical capacity of Si@mTiO₂.

Suppose that SiO_2 were completely transferred into Si. From XPS and EDS spectra, the molar ratio of Si to Ti was estimated to be 5.3. Therefore, the theoretical capacity of Si@mTiO₂ anode was calculated based on the following formula:

$$C_{Si@mTiO_2} = \frac{5.3 * M_{Si}}{5.3 * M_{Si} + 1 * M_{TiO_2}} * C_{Si} + \frac{1 * M_{TiO_2}}{5.3 * M_{Si} + 1 * M_{TiO_2}} * C_{TiO_2}$$
$$= 2787.5 \ mA \ h^{-1}$$

where $C_{Si@mTiO_2}$ is the calculated theoretical capacity of Si@mTiO₂ anode, C_{Si} is the theoretical capacity of Si (4200 mA h g⁻¹), C_{TiO_2} is the theoretical capacity of TiO₂ (167.5 mA h g⁻¹), M_{Si} and M_{TiO_2} is molecular weight of silicon and TiO₂, respectively.
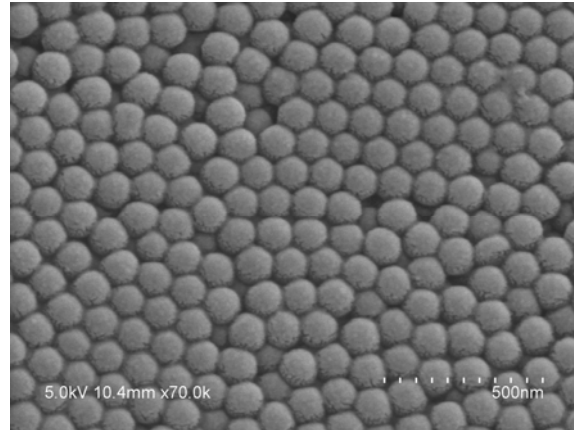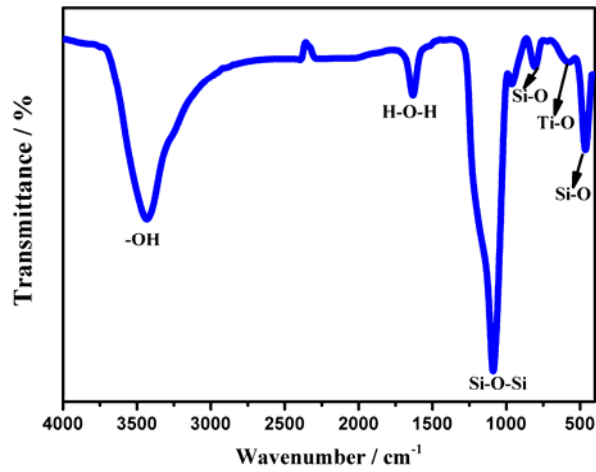

Figure S1 SEM image of PS nanospheres.

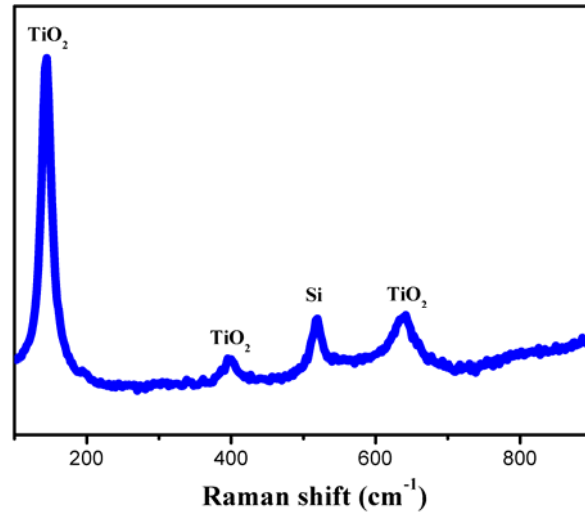**Figure S2** FT-IR spectra of HSiO₂@mTiO₂.

Figure S3 Raman spectra of Si@mTiO$_2$.
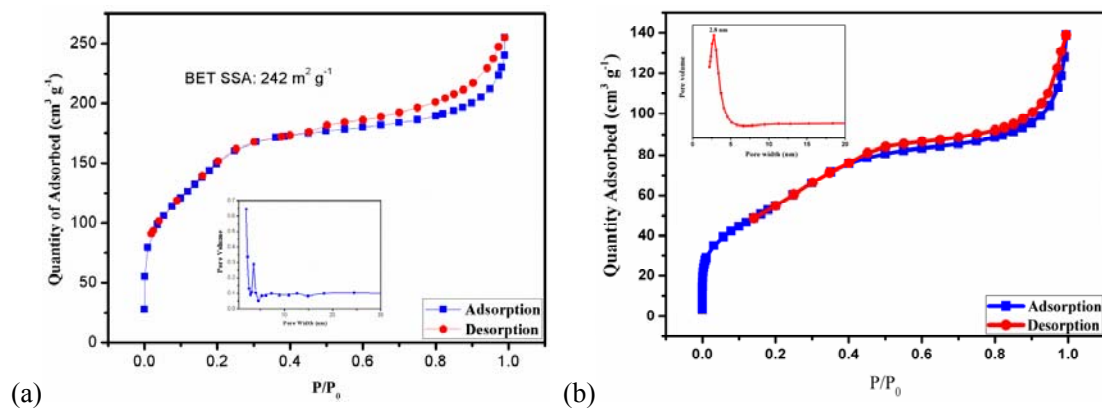
Figure S4. 77K N$_2$ adsorption-desorption isotherms of (a) HSiO$_2$@mTiO$_2$ and (b) Si@mTiO$_2$

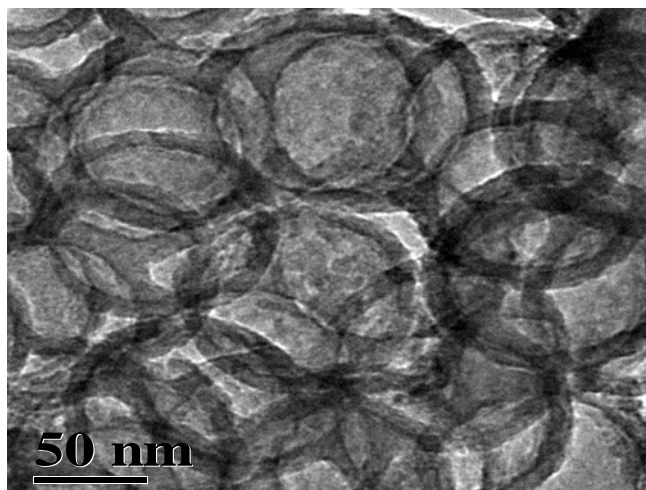(inserts show the pore distribution curves using BJH model).
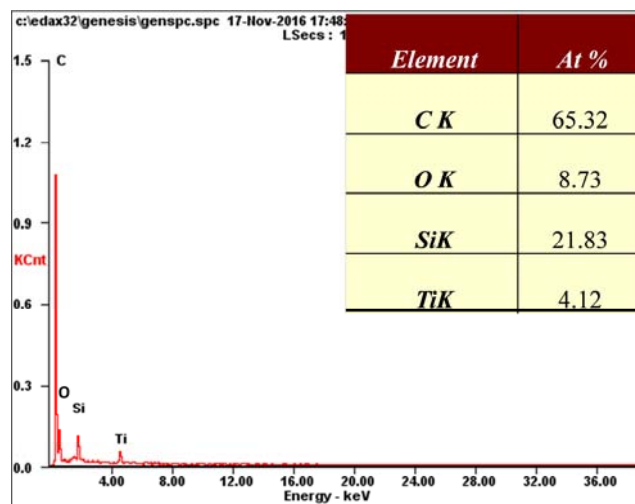
Figure S5. TEM image of Si@TiO$_2$.

Element	At %
C K	65.32
O K	8.73
SiK	21.83
TiK	4.12

Figure S6. EDS spectra of Si@mTiO$_2$.
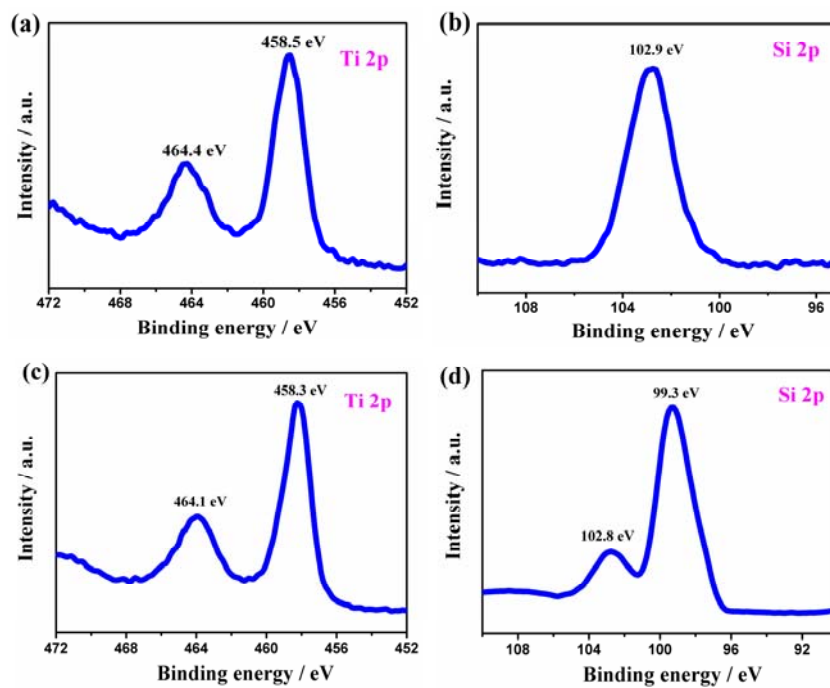
Figure S7. (a) Ti *2p* XPS spectra of HSiO$_2$@mTiO$_2$; (b) Si *2p* XPS spectra of HSiO$_2$@mTiO$_2$; (c) Ti *2p* XPS spectra of Si@mTiO$_2$ and (d) Si *2p* XPS spectra of Si@mTiO$_2$.
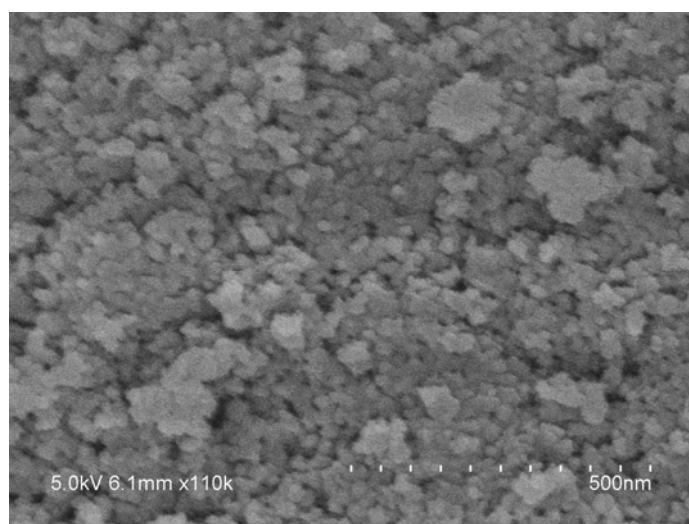

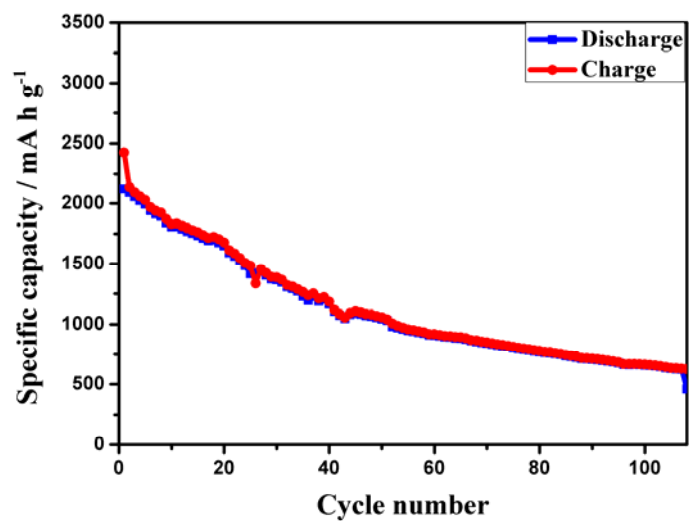**Figure S8**. SEM image of Si NPs.

Figure S9. Cycling performance of Si NPs anodes (current density: 0.5 A g^{-1}).

References

[1] D.Y. Chen, X. Mei, G. Ji, M.H. Lu, J.P. Xie, J.M. Lu and J.Y. Lee, *Angew. Chem. Int. Ed.* **2012**, *51*, 2409-2413.

[2] D. Chen, F. Huang, Y.-B. Cheng, and R. A. Caruso, *Adv. Mater*. **2009**, *21*, 2206–2210