Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Informations

Hollow Nanospheres of Loosely Packed Si/SiOx Nanoparticles Encapsulated in Carbon Shells with Enhanced Performance as Lithium Ion Battery Anodes

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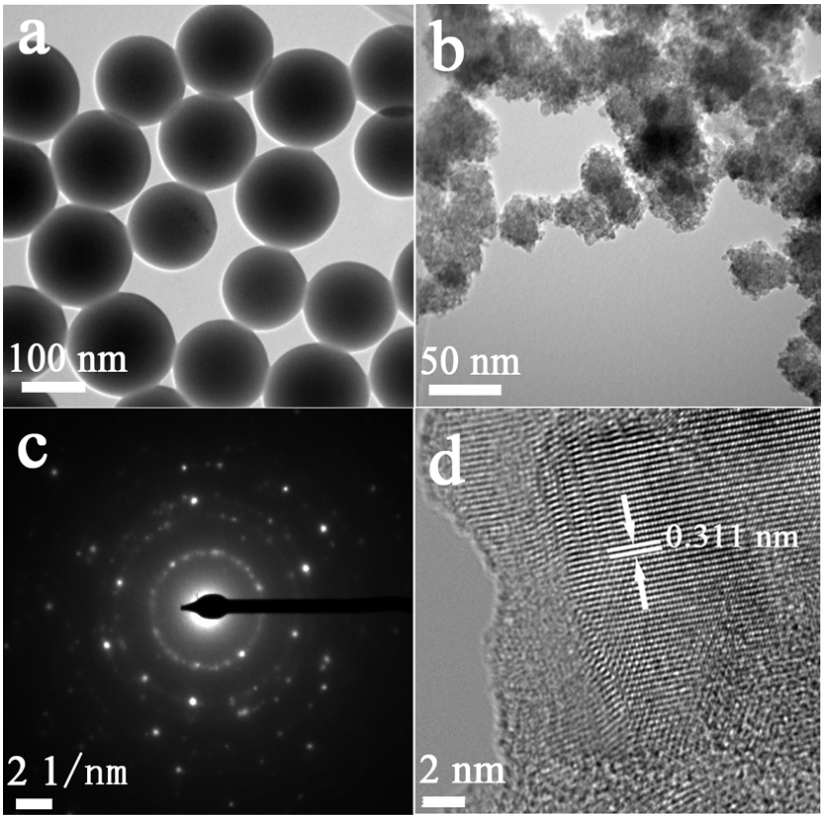


Figure S1 TEM image of as-prepared SiO_2 spheres (a), TEM (b), HRTEM (b) images and SAED pattern (c) of pure reduced silicon nanoparticles.

The TEM images of directly reduced Si are shown in Figure S1b, the SiO_2 nanospheres are completely pulverized because of the volume shrinkage during the reduction process. The lattice fringe orientations in the HRTEM (Figure S1b) demonstrate clear lattice fringes with d-spacing of 0.311 nm, which is in good agreement with that of the (111) planes of Si. The corresponding ring-like selected-

area electron diffraction (SAED) pattern, as shown in Figure S1c, indicates that these Si nanoparticles are polycrystalline.

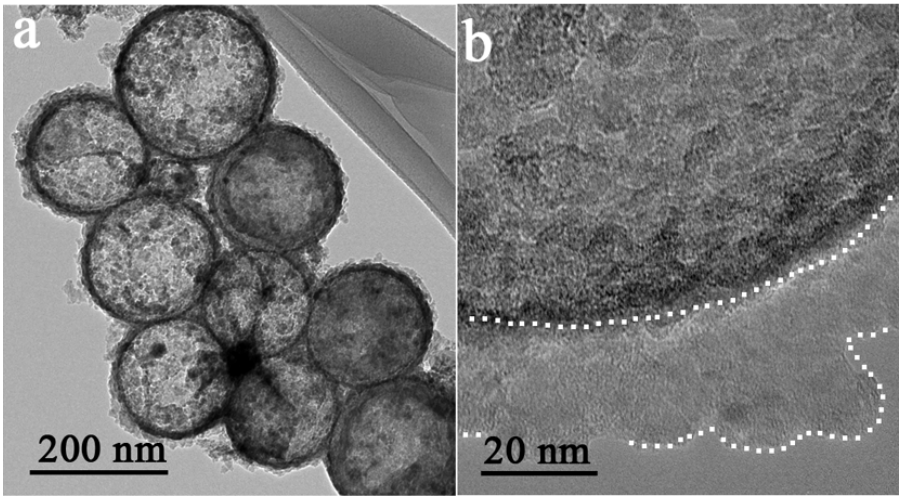
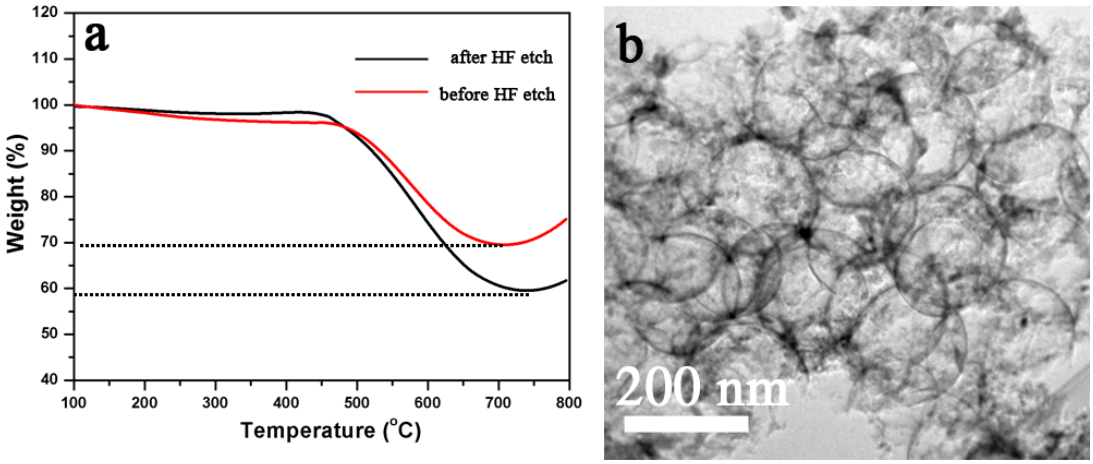


Figure S2 TEM images of hollow nanospheres (a) and carbon layer (b)

From the TEM images of hollow nanospheres, carbon layer can be easily observed and the main part of the nanospheres are consisted of many individual nanoparticles.



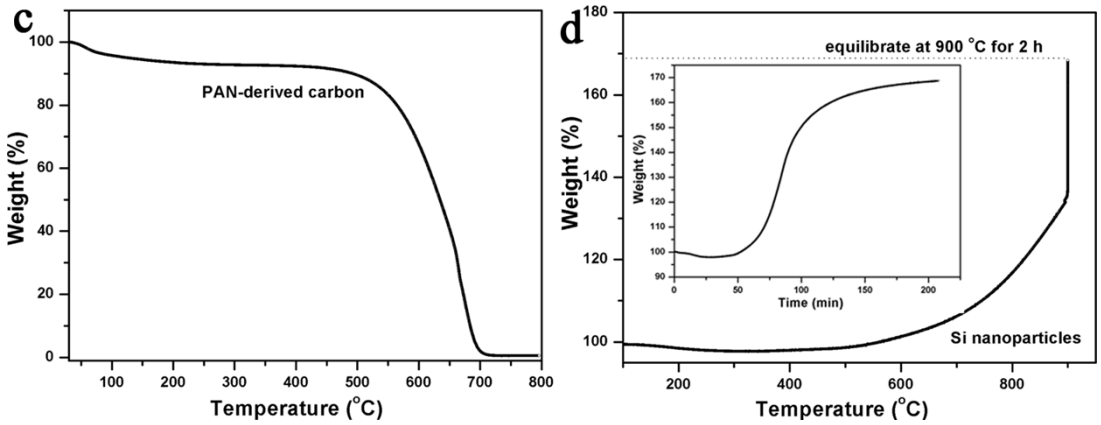


Figure S3 TGA curve of hollow nanospheres (a), TEM image of hollow nanospheres after HF etching (b), TGA curves of PAN-derived carbon (c) and directly reduced Si nanoparticles (d).

Si contents in the hollow nanosphere was estimated to be 58 wt% after the SiO_x was removed by HF. But known from the structure changes of the sample after HF etching, there are some unreduced SiO_x in the prepared silicon@carbon nanospheres. And the SiOx weight ratio is about 10 wt%, these unreduced SiO_x can keep the unique sphere morphology of this sample. The TGA measurment for PAN-derived carbon and directly reduced Si nanoparticles were also conducted and the results are shown in Figure S3c and S3d, the PAN-derived carbon were totally burned up at the temperature of 700 ^oC in the air atmosphere. In order to make the directly reduced Si nanoparticles fully oxidized, the sample were maintained at 900 ^oC for 2 h. The weight increasement was about 170%, and this value will still increase with equilibrate time lasting, indicating the inner part of the Si nanopartilce is very difficult to be oxidized because of the oxygen diffusion rate.

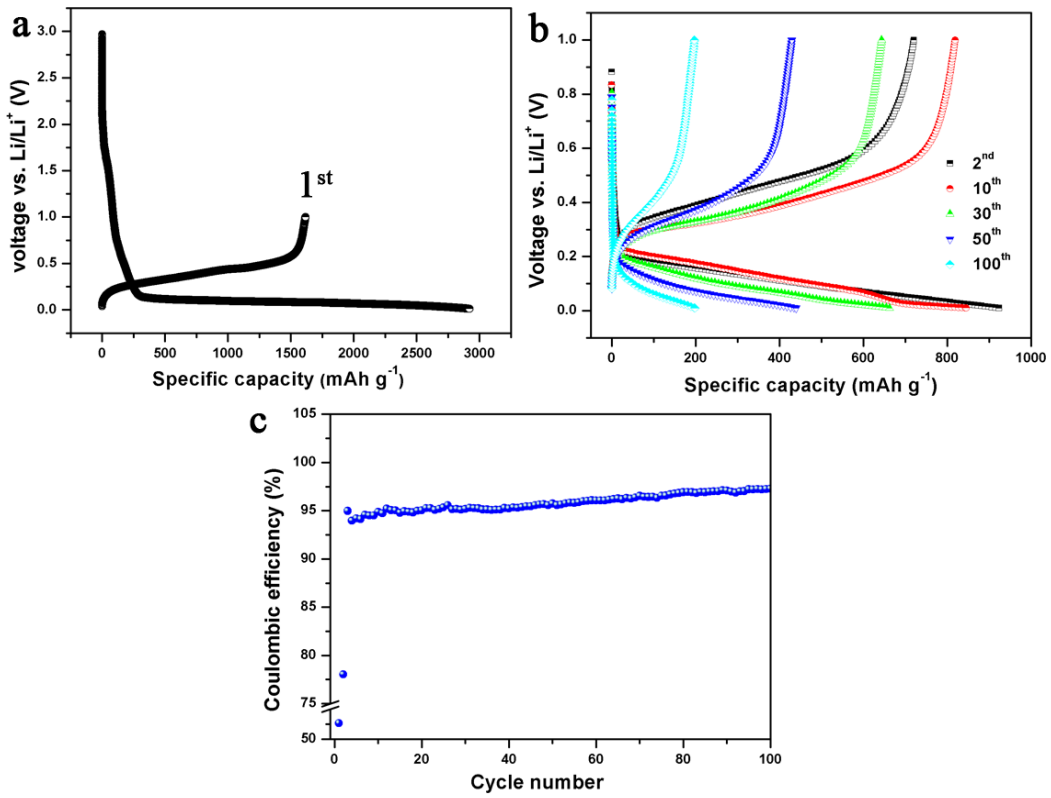


Figure S4 Voltage profiles plotted for the directly reduced silicon nanoparticles of the 1st cycle at the current density of 0.1 A g^{-1} (a), 2nd, 10th, 30th and 50th cycles at a current density of 1.0 A g^{-1} (b) and coulombic efficiency (c)

Figure S4 presents the first cycle process of the directly reduced Si nanoparticles. It can be seen that the sample delivers very high lithium storage capacity of 2932 mAh g^{-1} during the initial discharge process, but a very low reversible capacity of 1612 mAh g^{-1} is achieved, leading to an initial coulombic efficiency of around 55%. The discharge voltage plateau at about 0.1 V in the first cycle is quite different from those of other cycles, further indicating that irreversible reactions occurred in the first cycle.

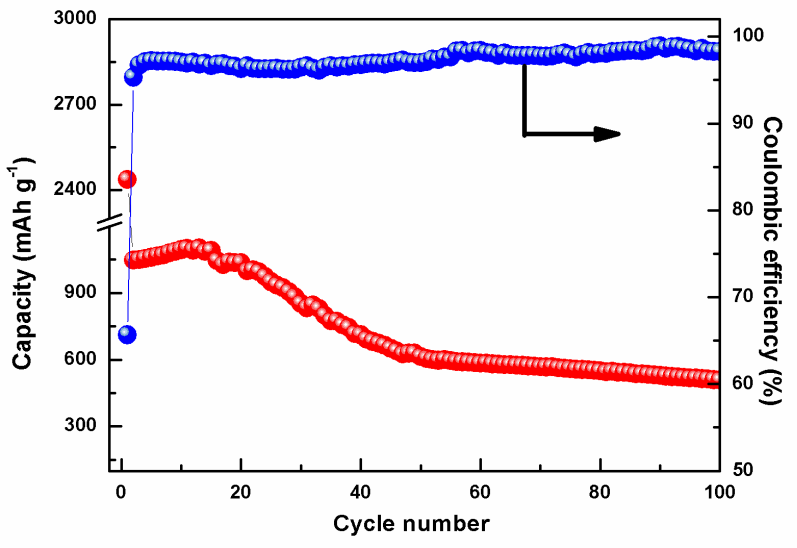


Figure S5 Cycle performance of hollow nanospheres after HF solution etching

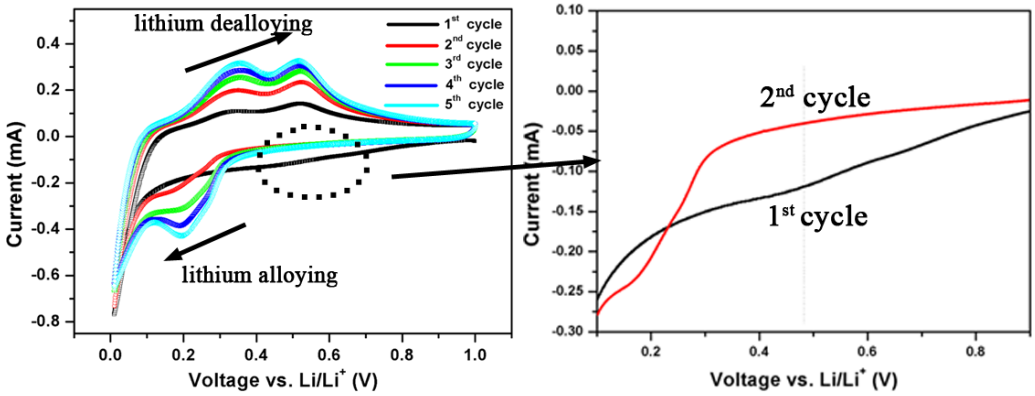


Figure S6 CV curves of the first five cycles of hollow nanospheres obtained at voltage range of 0.01 to 1.0 V at a scan rate of 0.1 mV s^{-1}.

Figure S6 shows the first five CV curves at room temperature between 0.01 and 1.0 V at a scan rate of 0.1 mV s^{-1}. It is clear that the CV curve of the first cycle is quite different from those of subsequent cycles, especially for the discharge branch. The first charge curve shows two oxidation peaks at 0.35 and 0.52 V, while in the following charge-discharge processes, two oxidation and reduction peaks can be

observed; the presence of these peaks indicates a conversion from crystal Si to amorphous Si during charge-discharge cycling.

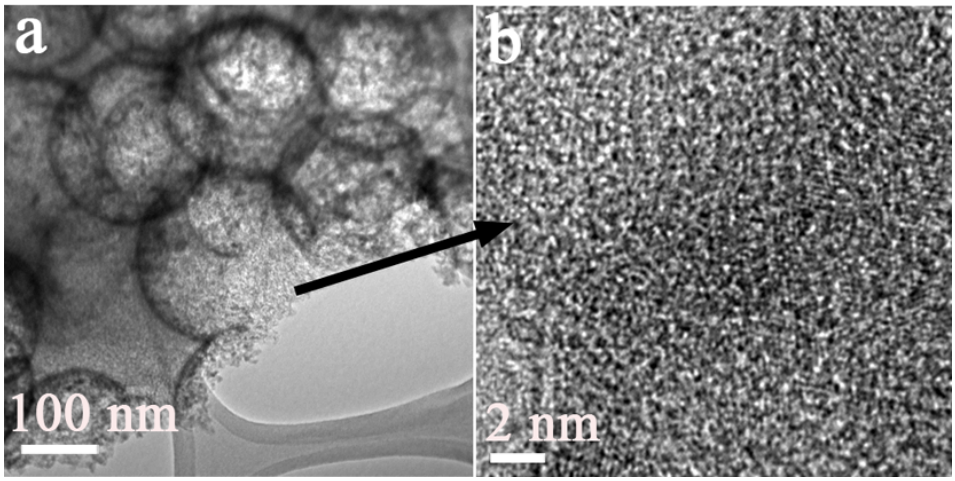


Figure S7 TEM (a) and HRTEM (b) images of hollow nanospheres after 50 cycles.

As shown in figure S6, although most of the nanospheres can keep the sphere morphology, a few of the hollow nanospheres still fracture after 50 cycles because of the huge volume change during charge-discharge process. The silicon crystal part has already transformed into amorphous crystal due to the lithium insertion/extraction process.

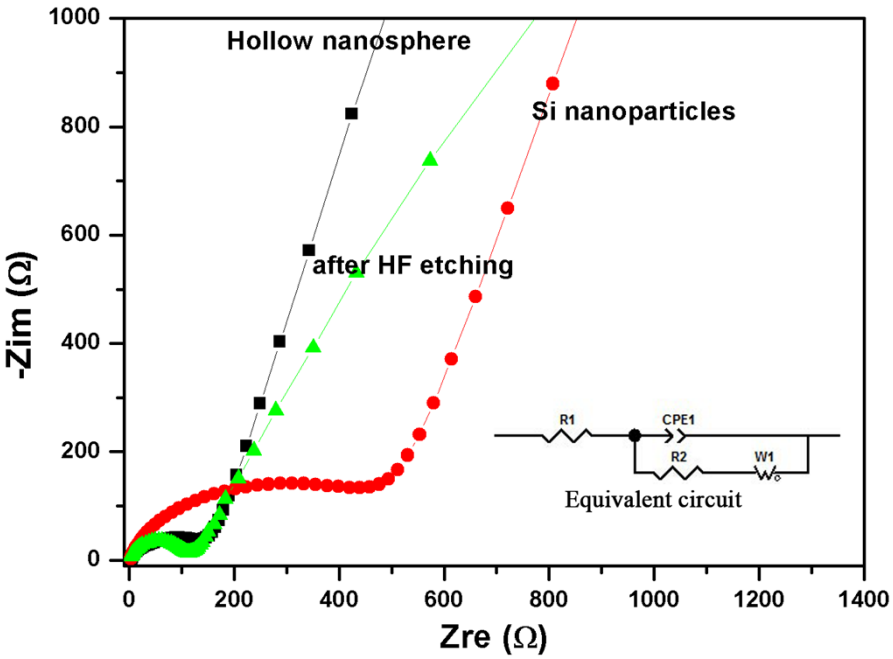


Figure S8 Nyquist plots of the silicon nanoparticles and hollow nanosphres at fresh cells over the frequency range from 100 kHz to 10 mHz.

The Nyquist plots were fitted by an appropriate electric equivalent circuit to obtain their kinetic parameters. Here R1 (Re) is the ohmic resistance of the electrolyte and cell components, R2 the charge-transfer resistance (Rct), CPE1 a constant phase element and Zw the Warburg impedance.

Table S1 LIB performance comparison of the Si/C nanocomposite using magnesium reduction method.

Reference	Si content	Current density	Capacity retention
1	100%	0.4 A g^{-1}	900 mAh g^{-1} after 90 cycles
2	56%	1 A g^{-1}	969 mA g^{-1} after 200cycles
3	Nearly 100% (Ag modified)	0.045 mA cm^{-2}	900 after 55 cycles
4	100%	1 A g^{-1}	923.5 mAh g^{-1}after 160 cycles
5	59.9%	1 A g^{-1}	905 mAh g^{-1} after 100 cycles
Our work	58%	1 A g^{-1}	940 mAh g^{-1} after 100 cycles

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