

Supporting Information

Interpenetrated Tunnel Route in Silicon/Carbon Hollow Sphere Anode to Boost Their Lithium Storage

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Experimental details

Material preparation

Synthesis of silica/resorcinol-formaldehyde composite hollow spheres (SiO₂/RF HSs). We obtained SiO₂/RF CSs by the microwave assisted method reported previously with minor modifications [1,2]. In a typical synthesis, 1 g resorcinol was dissolved in a mixed solution containing 40 mL ethanol and 100 mL water under magnetic stirring, and then 1 mL ammonia aqueous solution (NH₃·H₂O, 28 wt%) was added. After stirred for 20 min, 1 g cetyltrimethyl ammonium bromide (CTAB) was added in the above solution until completely dissolved. Then, a mixture solution containing 1.4 mL formaldehyde and 5 mL tetraethyl orthosilicate (TEOS) was added in solution mentioned above and continuously stirred for 24 h at room temperature. Subsequently, the obtained mixture was transferred into a round-bottom flask and heated at 100 °C for

30 min using a SINEO MAS-II microwave reactor under a setting mode with heating power of 700 W. Finally, the products both were obtained by centrifuging with water and ethanol, and dried overnight at 80 °C.

Synthesis of silica hollow spheres (SiO₂ HSs). SiO₂ HSs were obtained by calcining SiO₂/RF HSs synthesized by the above two methods at 650 °C for 5 h under air with a heating rate of 5 °C min⁻¹.

Synthesis of silicon hollow spheres (Si HSs). 0.4 g SiO₂ HSs synthesized by microwave assisted method were grounded with 0.4 g Mg powder, and then the mixture was annealed at 650 °C for 0.5 h under Ar/H₂ (7 vol%) atmosphere. The obtained powder was treated with diluted HCl and HF solution to remove MgO, unreacted Mg and SiO₂. Ultimately, Si HSs were obtained by being washed with water and ethanol, and then dried at 80 °C.

Synthesis of silicon/carbon hollow spheres (Si/C HSs). Firstly, SiO₂/C HSs were obtained by calcining SiO₂/RF CSs synthesized by microwave assisted method at 950 °C for 1 h under Ar with a heating rate of 3 °C min⁻¹. Subsequently, Si/C HSs were obtained according to the above synthesis method of Si HSs.

Material Characterization

XRD patterns of all samples were performed using X-pert diffractometer (PANalytical) with Cu K α radiation operated at 40 kV and 40 mA. The morphology and microstructure were studied using FE-SEM (Hitachi S-4800), TEM (JSM-2100F), and HRTEM (FEI Tecnai G²F20). Nitrogen adsorption-desorption isotherms were carried out on a COULTER SA 3100 apparatus at 77 K. Content measurements were performed

using thermogravimetric analysis (TGA, Q600SDT) in air.

Electrochemical measurements

To prepare working electrodes, active materials (Si/C composite and commercial lithium manganate (LMO)), acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 8: 1: 1 were mixed uniformly in 1-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry. The above Si/C composite and LMO slurries were coated onto Cu and Al foils respectively, and dried in a vacuum oven at 100 °C for 12 h. After compressed at 1.0×10^6 Pa for 30s, the Cu/Al foils were punched into 14 mm in diameter used as working electrode. The mass loading density of anode was 1.5 mg/cm^2 and the corresponding cathode was about 15 mg/cm^2 . In a typical assembly process of CR2025 type coin cells, lithium foil was used as the reference and counter electrodes, and Celgard 2400 membranes were used as separators. 1M LiPF_6 was dissolved into a mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1 v: v) as electrolyte. Galvanostatic charge/discharge tests were carried out on a LAND CT-2001A cell test system at different current densities in the voltage range of 0.01 to 3.0 V. Cyclic voltammetry (CV) was conducted using the electrochemical workstation (IM6e) between 0.01 and 3.0 V at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was performed using the same workstation from 100 kHz to 10 mHz.

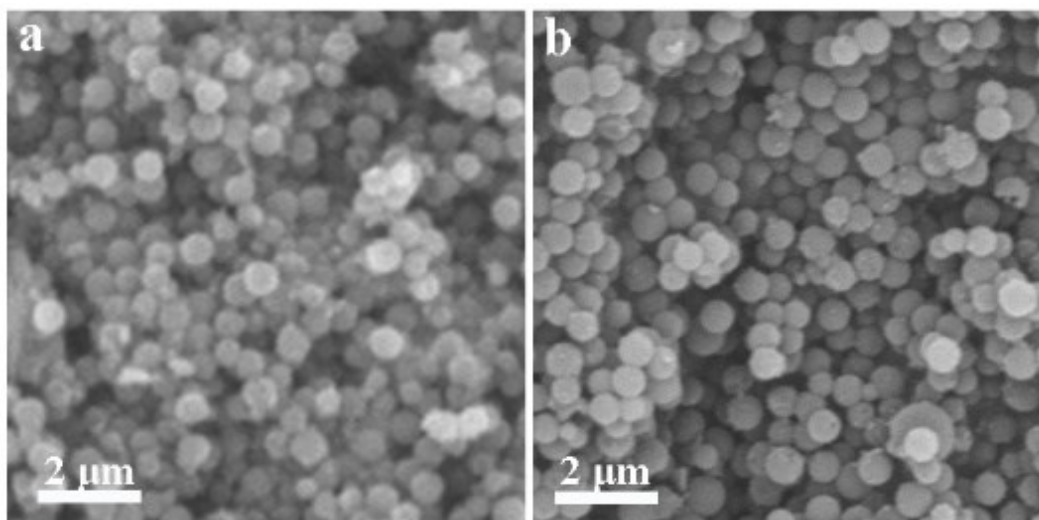


Figure S1. SEM images of (a) SiO₂/RF HSs and (b) SiO₂/C HSs.

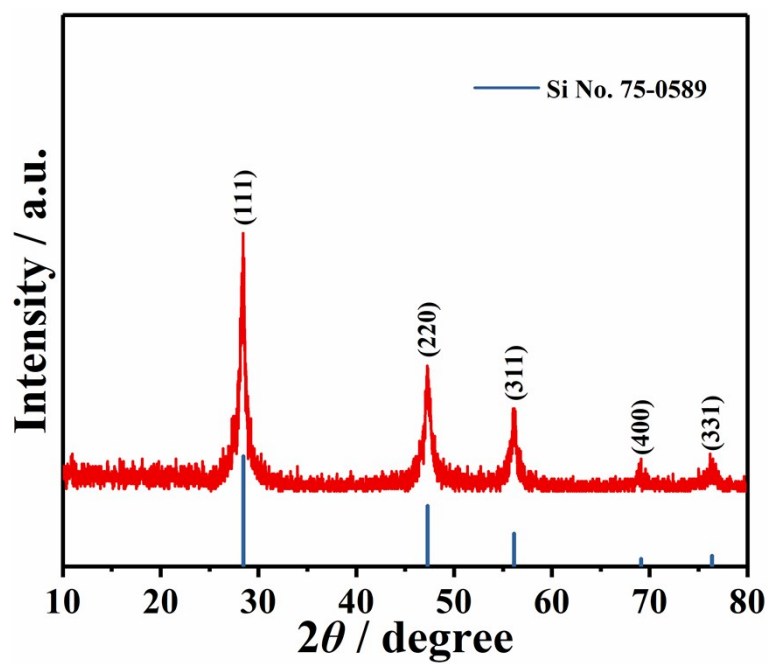


Figure S2. XRD patterns of Si/C HSs.

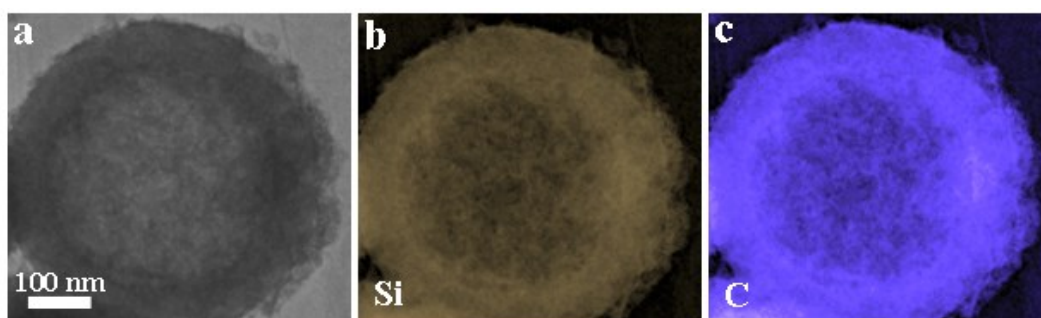


Figure S3. SEM-EDS element mappings of Si/C HSs.

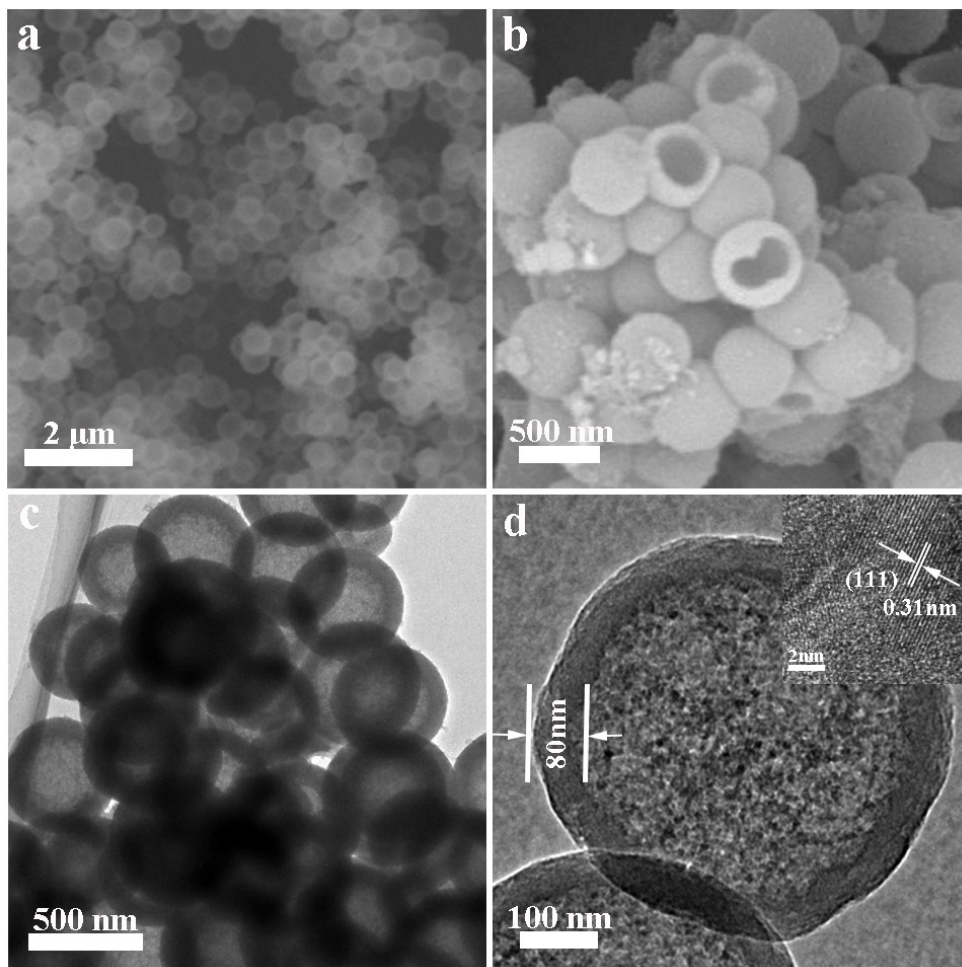


Figure S4. (a, b) SEM images, and (c, d) TEM images of Si HSs.

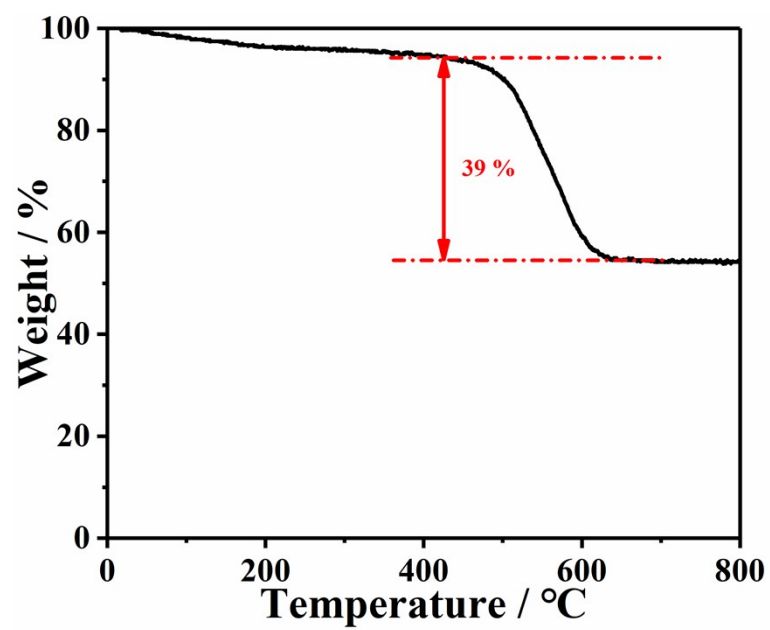


Figure S5. TGA curves of Si/C HSs.

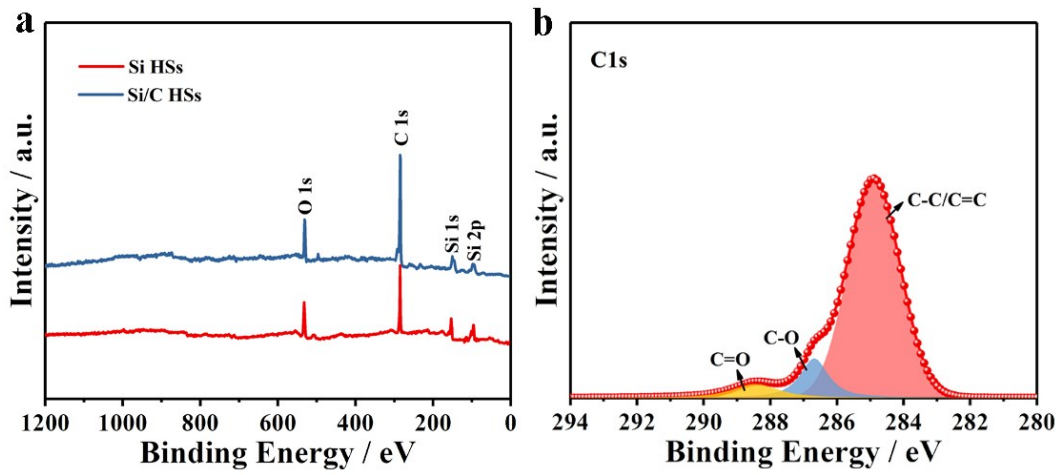


Figure S6. (a) XPS survey spectra of Si and Si/C HSs. (b) C1s spectra of Si/C HSs.

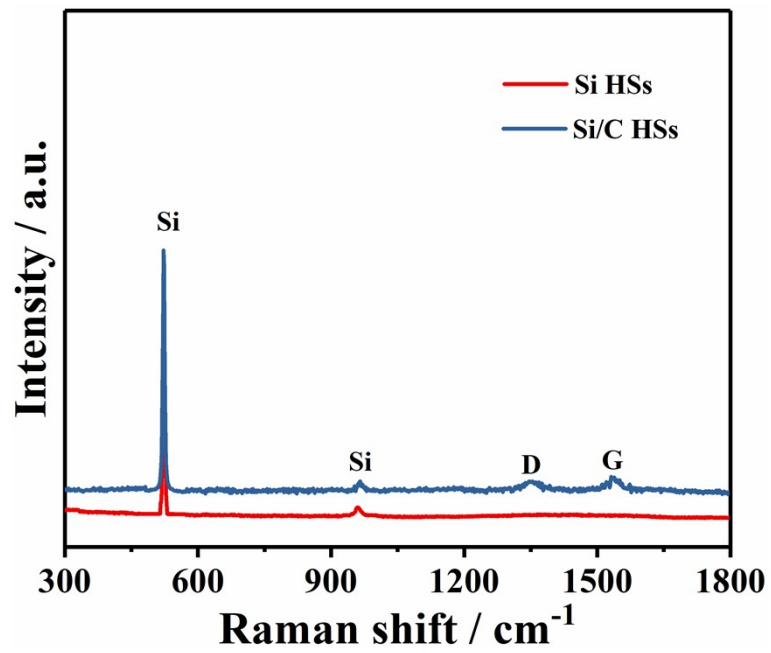


Figure S7. Raman spectra of Si and Si/C HSs.

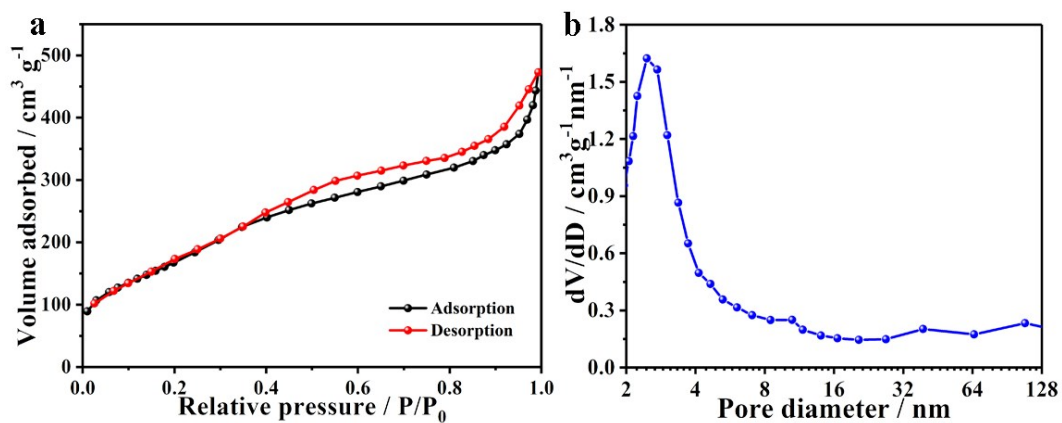


Figure S8. (a) N₂ adsorption/desorption isotherm curves and (b) the corresponding pore size distributions of Si/C HSs.

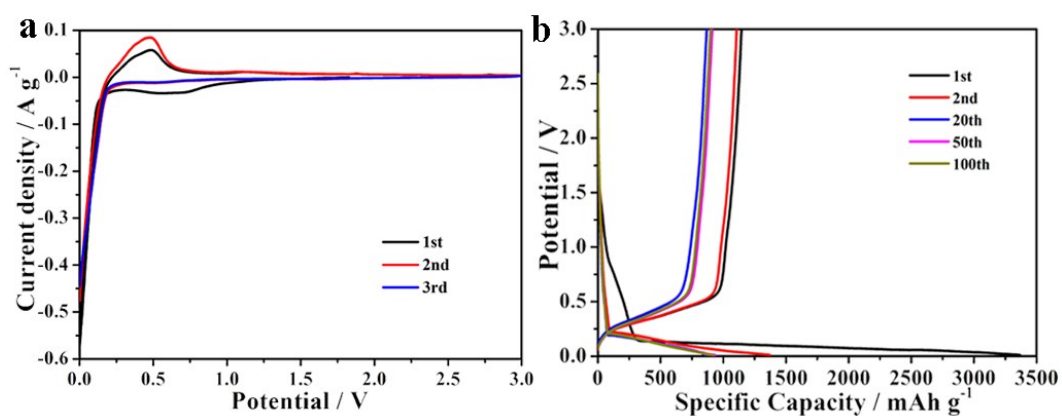


Figure S9. (a) CV curves of Si HSs for the first three cycles. (b) Galvanostatic charge-discharge profiles at 100 mA g⁻¹.

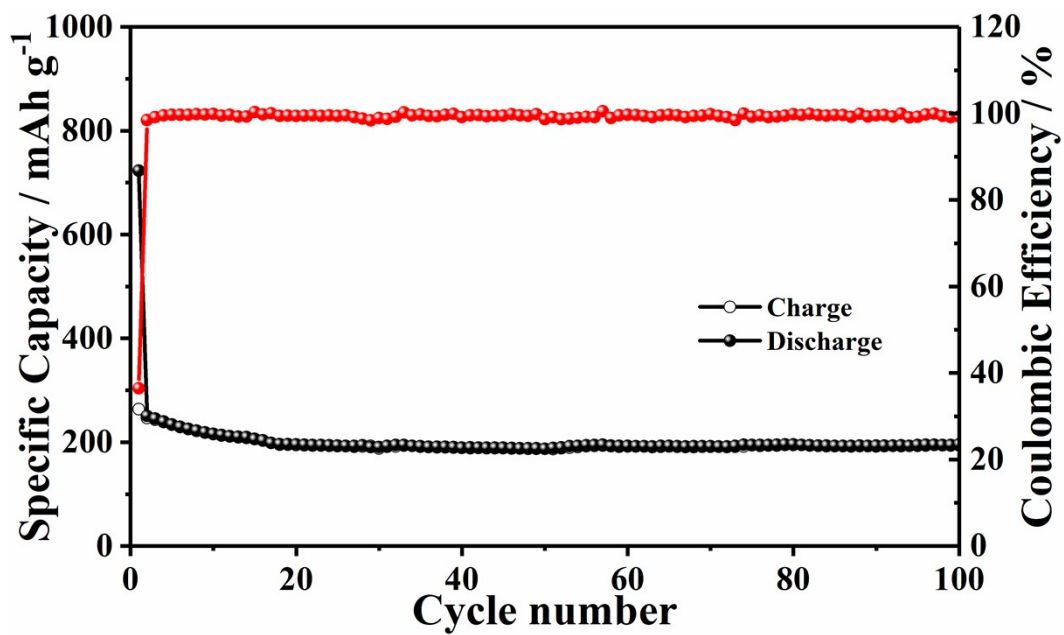


Figure S10. Cycling performance of pure carbon at 100 mA g⁻¹.

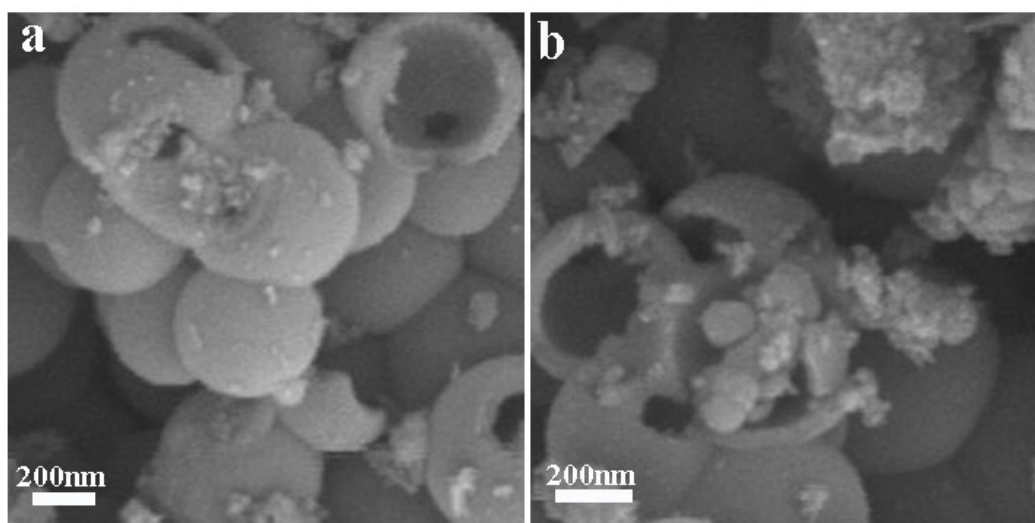


Figure S11. SEM images of (a) Si/C HSs and (b) Si HSs after cycling.

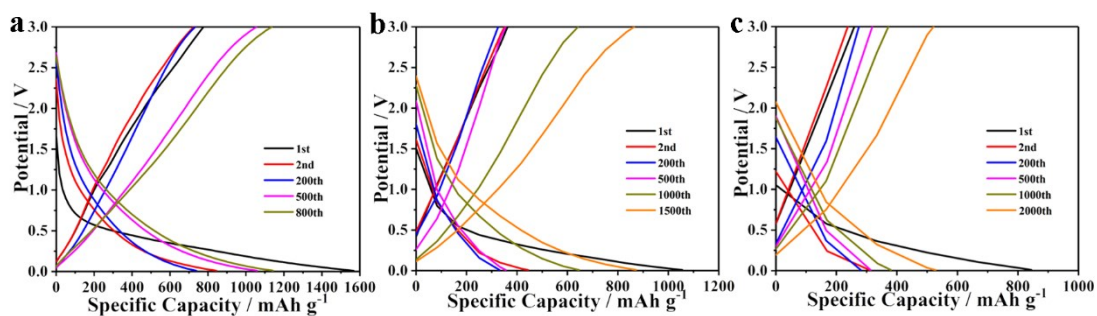


Figure S12. Galvanostatic charge/discharge profiles of Si/C anodes at (a) 1.0 A g^{-1} , (b) 5.0 A g^{-1} and (c) 10.0 A g^{-1} .

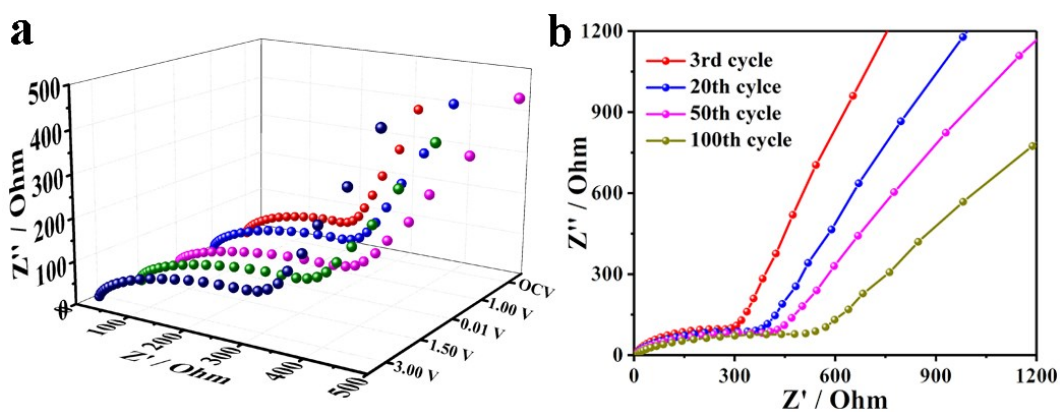


Figure S13. (a) *In situ* EIS spectra evolution of bare Si electrode at different charge/discharge potentials and (b) EIS spectra after different cycles.

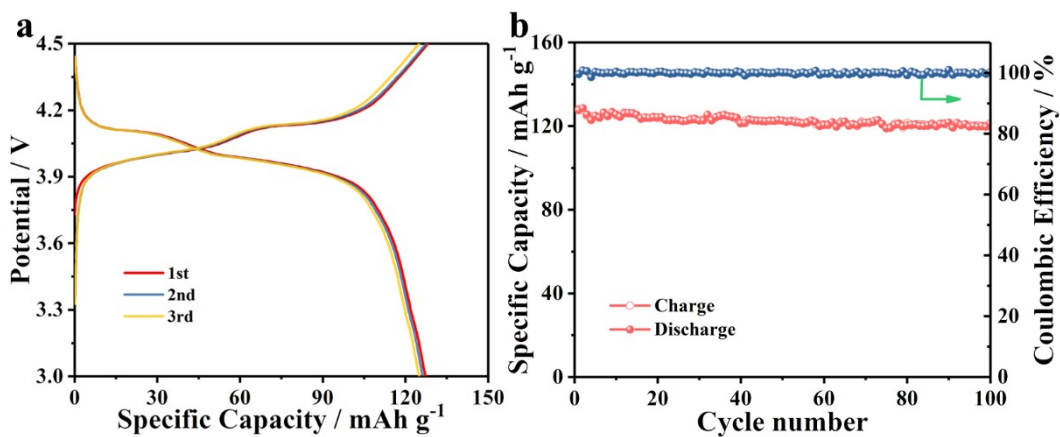


Figure S14. (a) Galvanostatic charge/discharge profiles and (b) cycling performance at 0.1 A g^{-1} of LMO.

Table S1. Comparison of electrochemical performance of Si-based anodes with long cycle life.

Samples	Current density (A g ⁻¹)	Cycle number	Capacity ^{a)} (mAh g ⁻¹)	References
Si nanoparticles	3	1000	870	12
Si/C composites	0.2	1000	634	49
Si/graphene	0.4	500	680	50
Hollow Si	2.4	500	960	51
	4.8	700	814	
Si/C composite	5	1550	930.7	This work
hollow spheres	10	2000	522.2	

^{a)} Residual capacity after cycling.

References

- [1] J. Hou, T. Cao, F. Idrees, C. Cao, A hydrothermal synthesis of tunable and uniform hollow carbon nanospheres with interconnected mesoporous shells, *Nanoscale* 8 (2016) 451-457.
- [2] X. Zhang, Y. Li, C. Cao, Facile one-pot synthesis of mesoporous hierarchically structured silica/carbon nanomaterials, *J. Mater. Chem.* 22 (2012) 13918-13921.