

Supporting Information for

**Multilayered Sturdy Shell Protects Silicon Nanoparticles
Si@void C@TiO₂ as Advanced Lithium Ion Battery Anode**

Li Hou, Ruiwen Cui, Shuangsheng Xiong, Xinyu Jiang, Dong Wang, Yang Jiang,
Shuolei Deng, Yuanyuan Guo and Faming Gao*

Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical
Engineering, 438 West Hebei Street, Yanshan University, Qinhuangdao 066004,
China

*Corresponding authors.

E-mail address: fmgao@ysu.edu.cn (F. Gao).

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Experimental section

Materials synthesis

Synthesis of core-shell Si@SiO₂ nanohybrids

Si nanoparticles (0.1 g, about 60 nm) were added to absolute ethanol (40 mL) and sonicated for 20 min. Then the solution was mixed with H₂O (9 mL), ammonia (3.3 mL) and stirred for a while, and the tetraethoxysilane (TEOS, 0.7 mL) was added which mixing with ethyl alcohol (30 mL), drop by drop slowly. Finally, the ethyl alcohol was added up to a total capacity of 100 mL, then stirred for 24 h. After centrifugation and desiccation, the Si@SiO₂ composite particles were obtained.

Synthesis of hollow Si@void@C nanohybrids

Si@SiO₂ composites (0.5 g) were distributed evenly on the quartz boat, then put in the middle part of the quartz tube furnace. The furnace temperature was heated to 800 °C at a heating rate of 5 °C min⁻¹ under an argon atmosphere. Then the ethyne gas was introduced in quartz tube and began to decompose at 800 °C. For 20 min deposition, there was a carbon layer formed on the surface of Si@SiO₂ nanoparticles. Stopped the acetylene gas and kept the argon gas flowing until the temperature dropped to room temperature. Then, 1 mol hydrofluoric acid aqueous solution was used to wash the product for 5 mins to remove SiO₂ shell, and ethanol and H₂O were used to washed for another three times to remove the hydrofluoric acid. Finally, the product was dried at 70 °C overnight and the hollow Si@void@C nanohybrids were collected.

Synthesis of Si@void C@TiO₂ nanohybrids

Configuring solution A containing ethyl alcohol (27 mL), acetic acid (6 mL), Butyl titanate (TBOT, 4 mL) and H₂O (0.1 mL) were stirred for 1 hour. Solution B was composed of 0.5g Si@void@C composites in ethyl alcohol (20 mL). The Solution B was put into solution A drop by drop slowly, then 0.2 mL H₂O was added 5 times per 30 mins, and the mixed solution was sealed in beaker stirred for 6 hours,

which was marked as sample Si@void C@TiO₂ a. Another comparative sample for 24 hours was marked as sample Si@void C@TiO₂ b.

The obtained two samples were washed and centrifuged with deionized water and ethanol, dried in a 70 °C drying box for 12 hours, and then calcined at 600 °C in a nitrogen atmosphere for 2 hours to obtain the final Si @ void C @ TiO₂ samples.

Materials characterization

The phase of samples was characterized with X-ray diffraction (XRD) analysis, which was carried out on a Philips diffractometer with Cu K α radiation. Field emission scanning electron microscopy (FE-SEM, S4800, Hitachi) and transmission electron microscopy (TEM, FEI Tecnai F30) were used to investigate the morphology of samples. High-resolution transmission electron microscopy (HR-TEM, FEI Tecnai F30) with a field emission gun operating at 200 kV to measure the structural details of samples. XPS results were obtained by using the ESCALAB 250Xi ThermoFischer and the reference carbon (C 1s = 284.6 eV) to calibrate all binding energies. Renishaw micro-Raman spectrometer ($\lambda=514$ nm) was used to study Raman scattering. In addition, nitrogen physisorption at 77 K on a Micromeritics V-Sorb 2800 P analyzer was carried out to obtain Nitrogen adsorption and desorption isotherms. Using BET method to calculate the surface area and the adsorption amount at a relative pressure (P/P₀) of 0.99 to confirm the total pore volume. Meanwhile, using the Barrette-Joynere-Halenda (BJH) method to obtain the pore size distribution (PSD) in a wide range to 200 nm.

Electrochemical measurement

2032coin type cells were used to investigate the electrochemical performance of samples. On the Cu foil, the sample, carbon black (Super-P) and polyvinylidene fluoride (PVDF) were mixed with a weight ratio 8:1:1, then the working electrode was obtained after drying in a vacuum environment for 12 h at the temperature of 70 °C. The electrodes were cut into Φ 12mm disks and pressed at 3 MPa with the electrode loading mass of about 0.7 mg cm⁻² on average. The ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) in the vol

ratio of 1:1:1 to constitute the electrolyte which was mixed with 1M LiPF₆. In an argon-filled glove box with less than 1 ppm environment of moisture and oxygen, we assembled the batteries. Using the Land-CT2001A instrument to test the electrochemical performance in the voltage range from 0.01-2.50 V at room temperature of 25°C. Through CHI 660E electrochemical workstation, the cyclic voltammetry (CV) tests were carried out in the potential window at range of 0.01-2.50 V (vs. Li/Li⁺) at a scan rate of 0.1 mV/s. And the electrochemical impedance spectra (EIS) were recorded at frequency ranges from 10⁻²-10⁵ Hz with voltage amplitude of 5 mV at room temperature.

Supplementary Figures

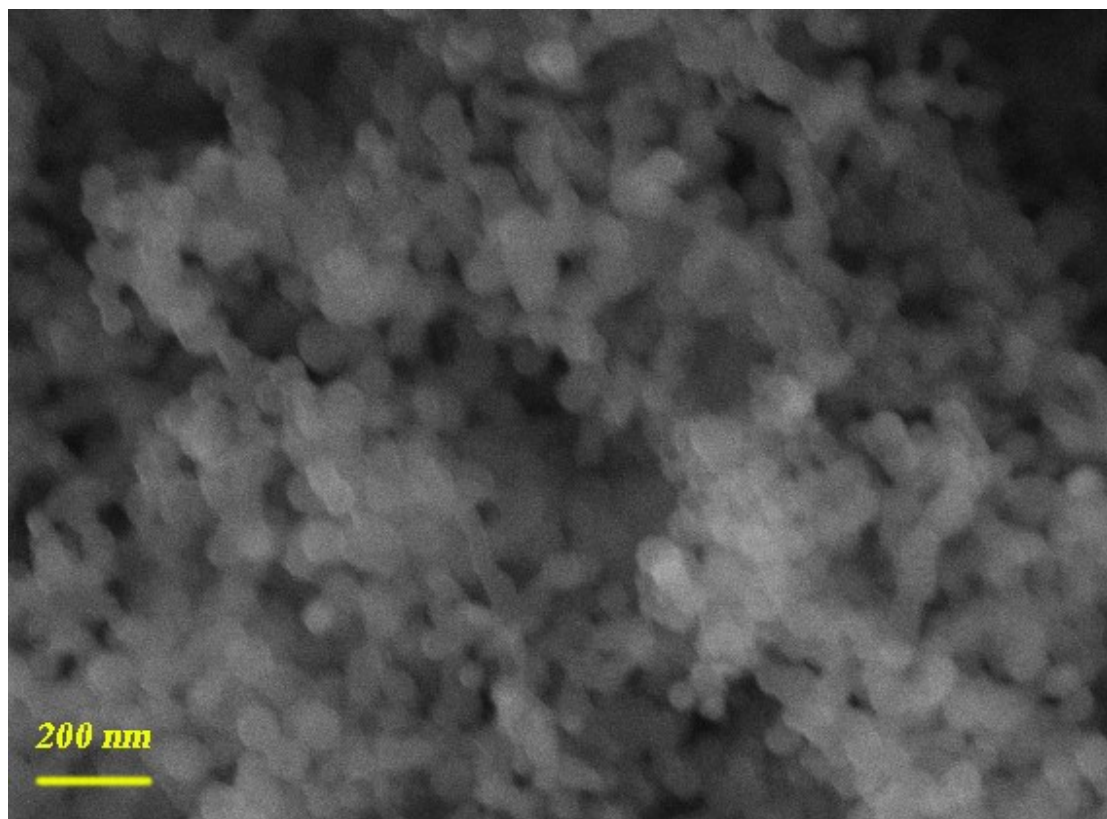


Fig. S1 SEM image of Si.

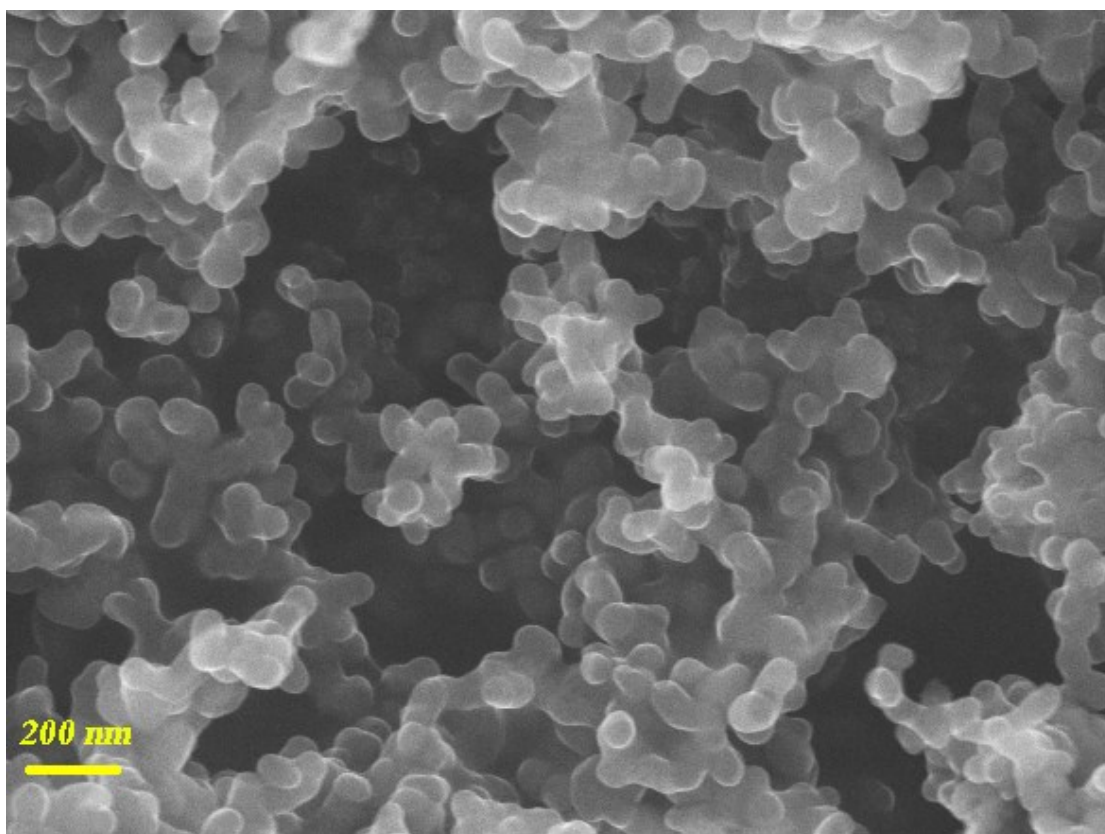


Fig. S2 SEM image of Si@Void C sample.

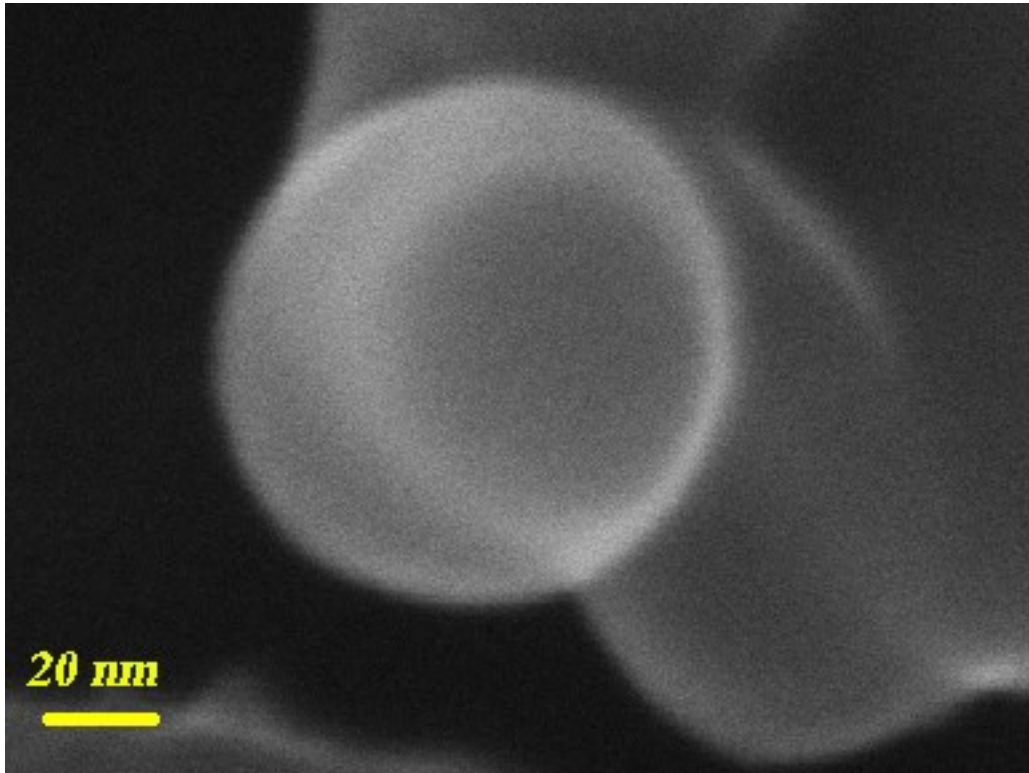


Fig. S3 SEM image of Si@Void C sample.

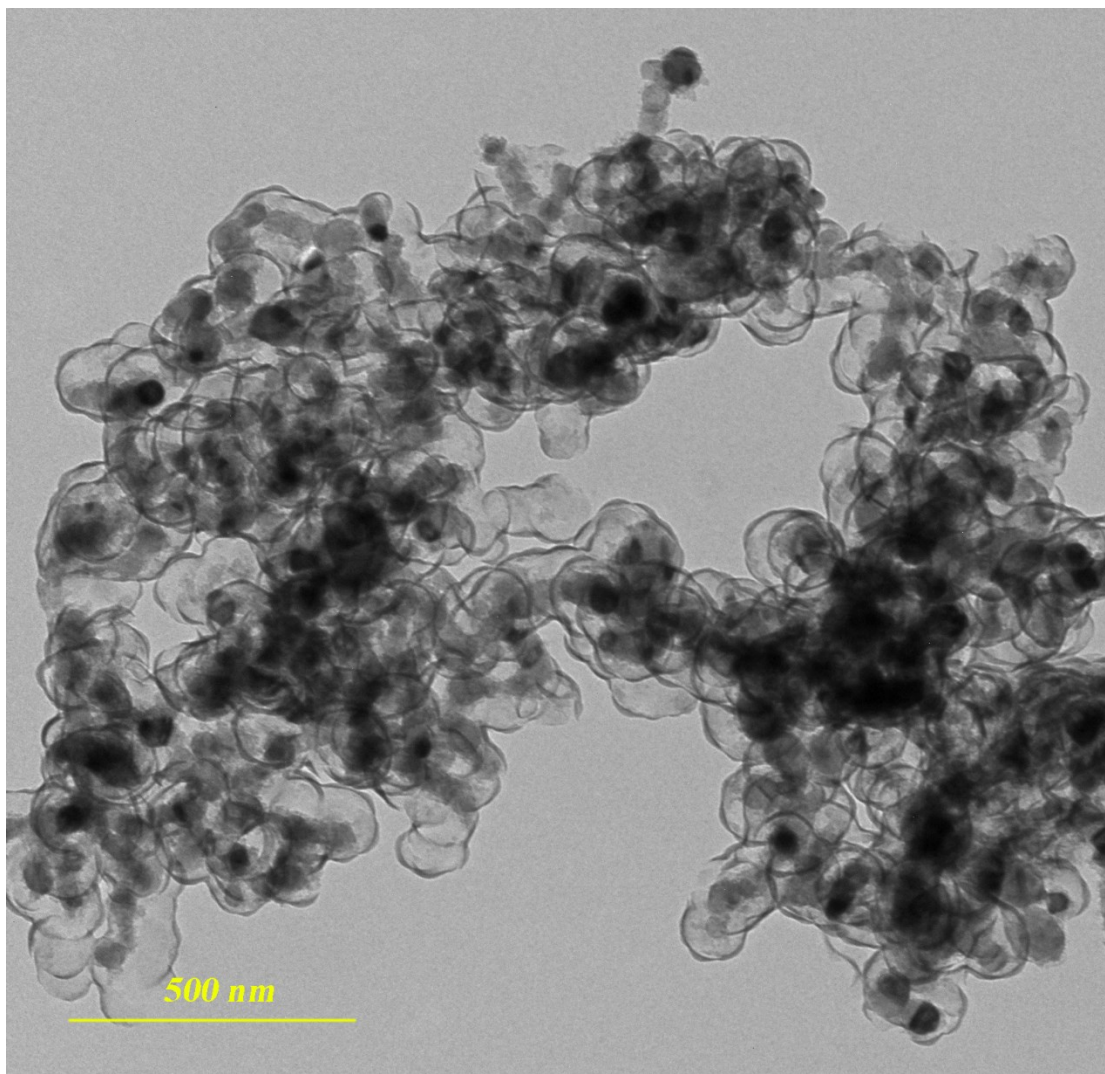


Fig. S4 TEM image of Si@Void C sample.

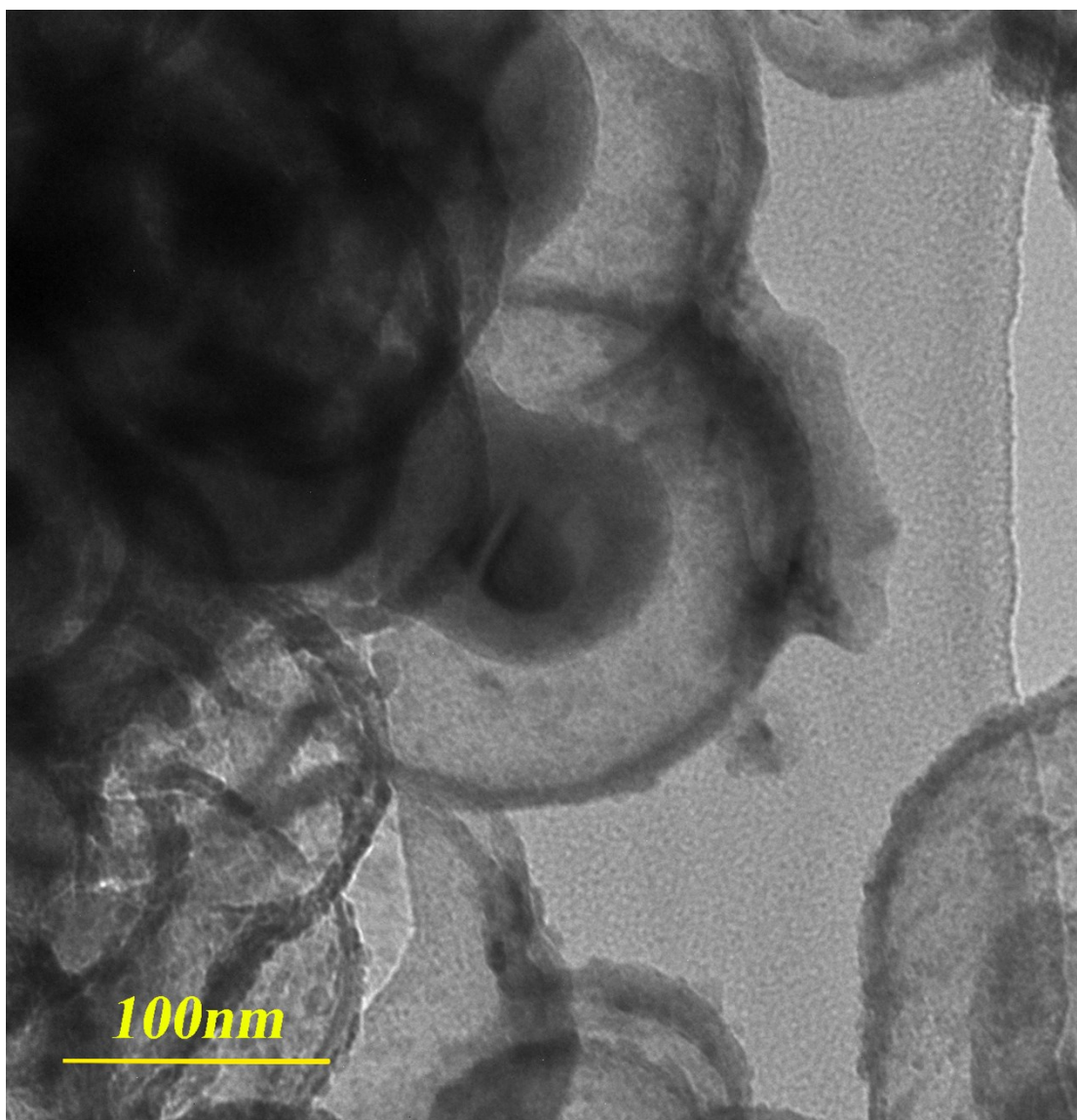


Fig. S5 TEM image of Si@Void C@TiO₂ b sample.

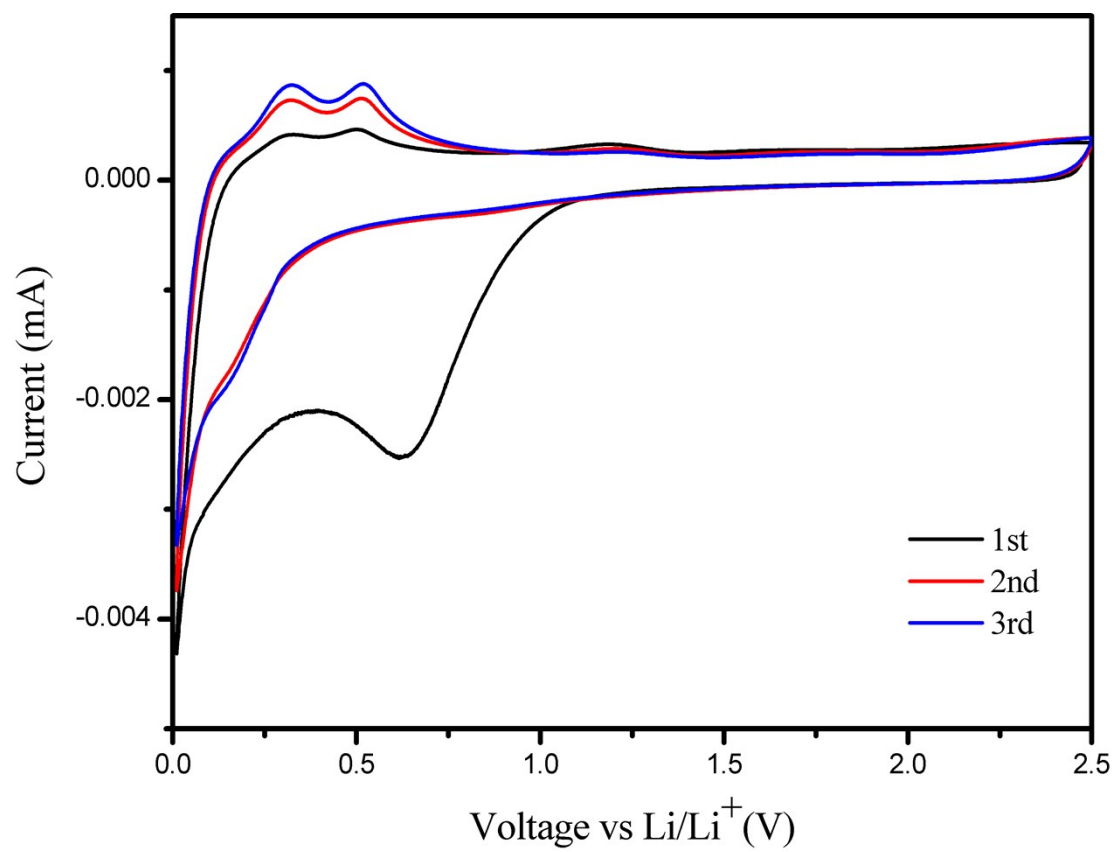


Fig. S6 Cyclic voltammety curves for the first three cycles of Si@Void

C

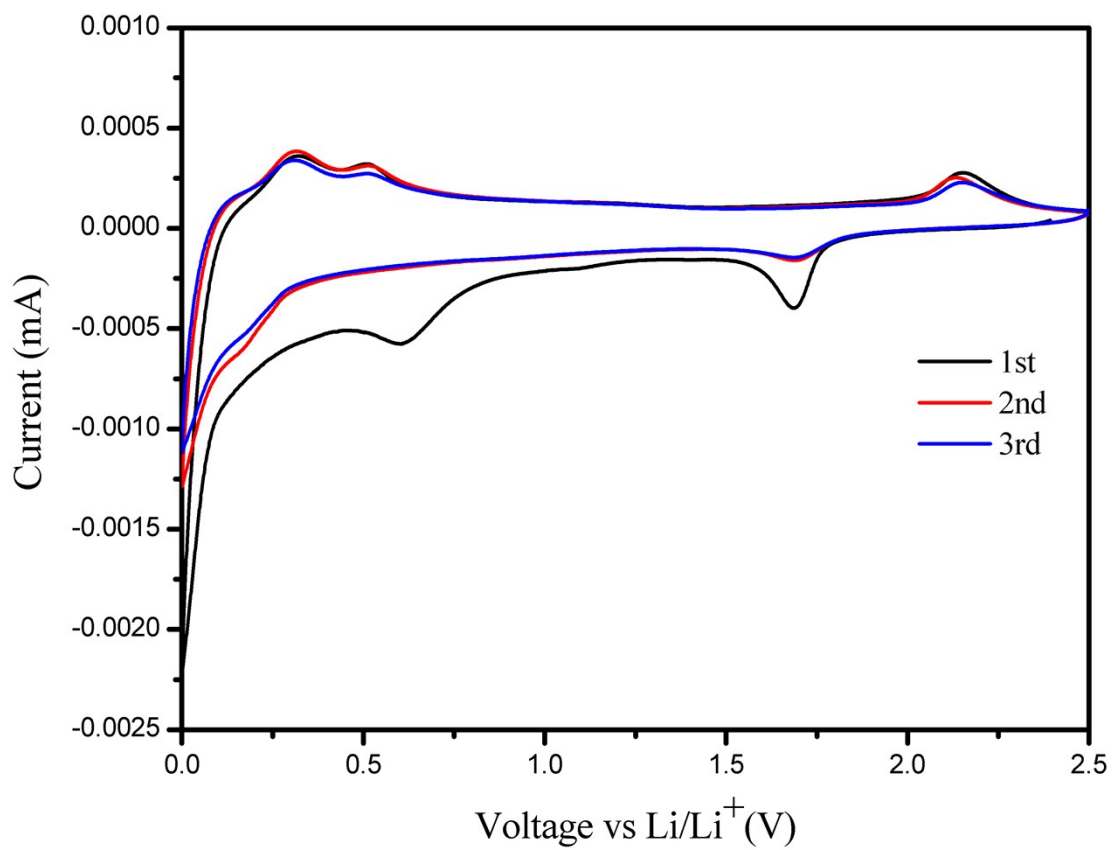


Fig. S7 Cyclic voltammety curves for the first three cycles of Si@Void
C@TiO₂ b

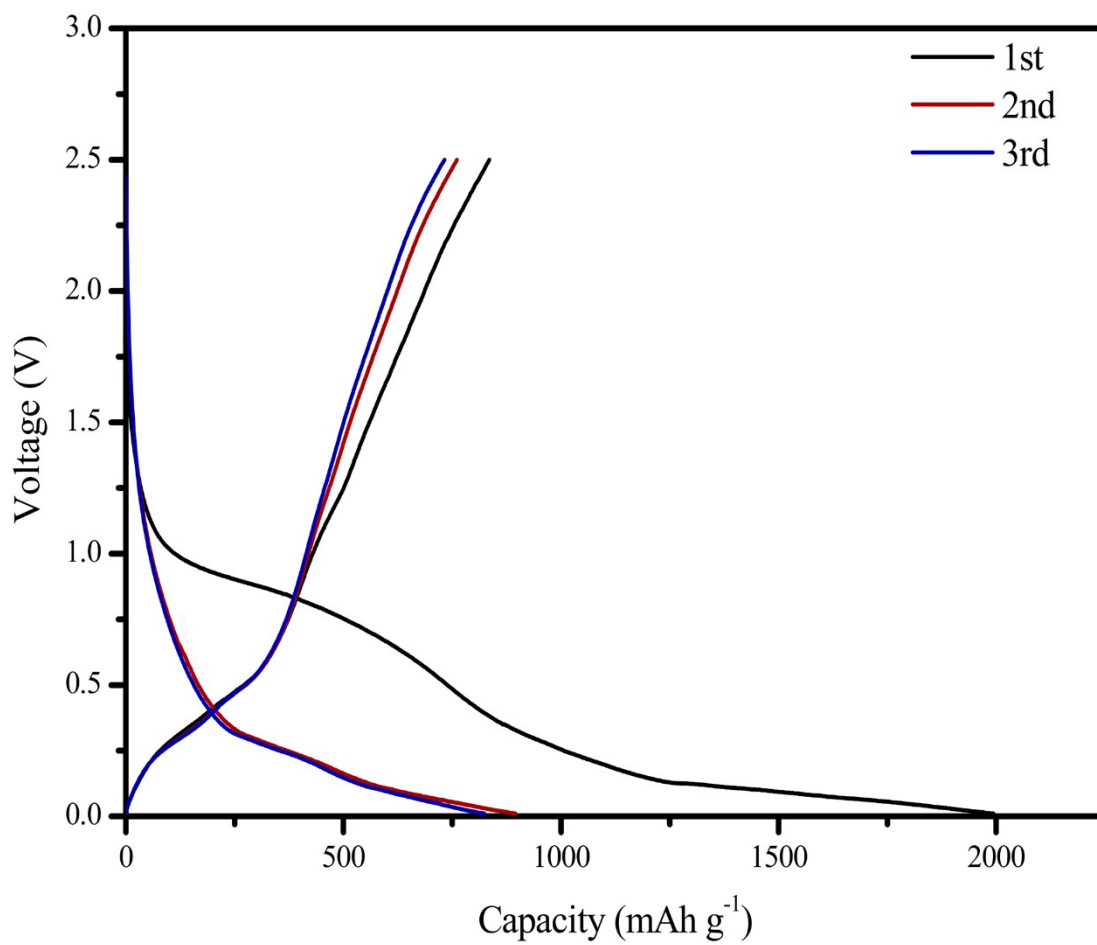


Fig. S8 Discharge/charge potential profiles of Si@Void C at a current rate of 100 mA /g

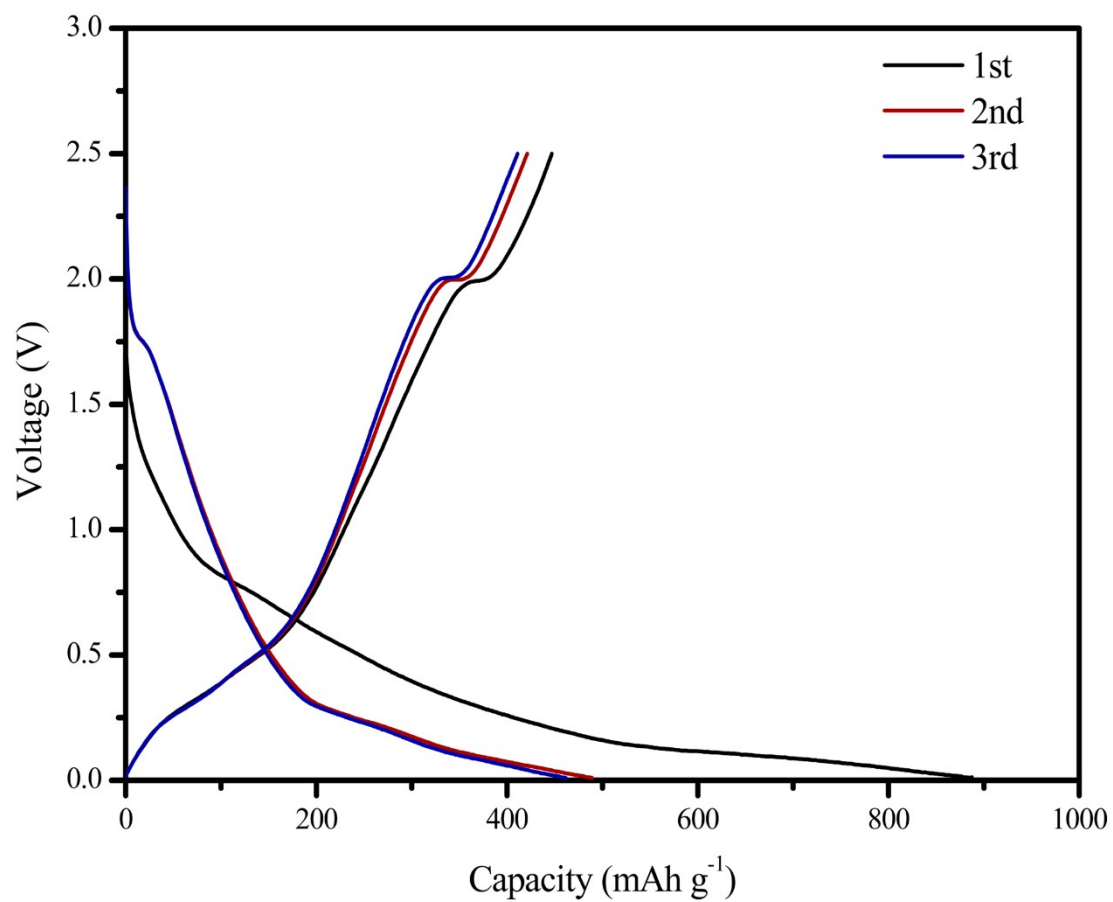


Fig. S9 Discharge/charge potential profiles of Si@Void C@TiO₂ b at a current rate of 100 mA /g

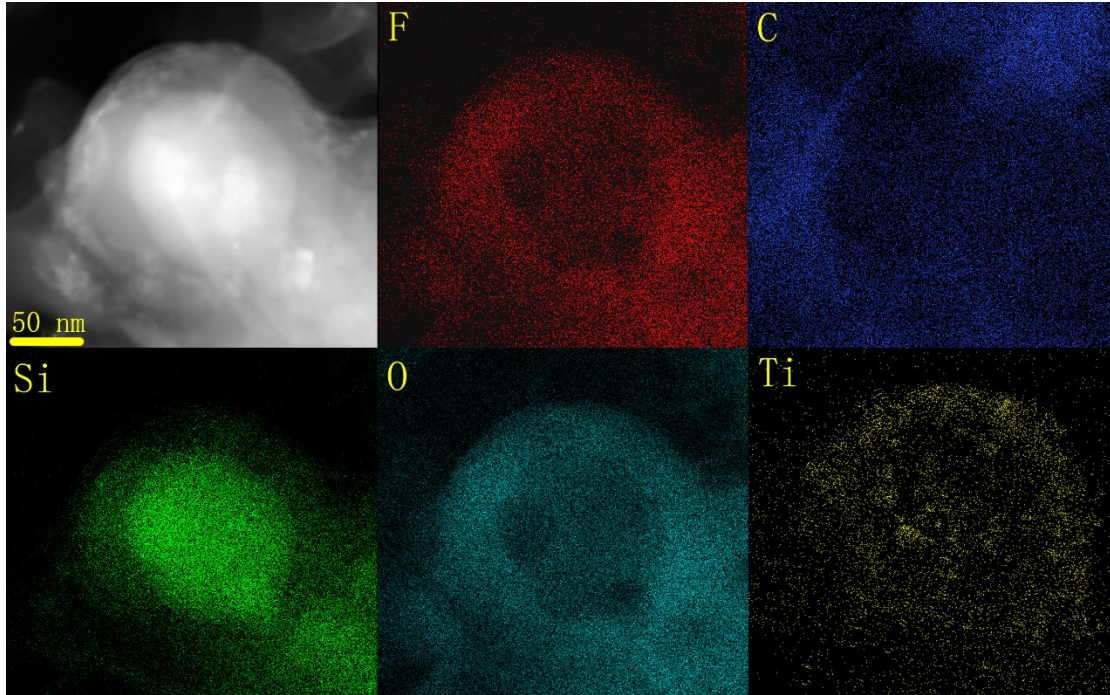


Fig. S10 STEM and EDS mapping images of Si@Void C@TiO₂ after 50 cycles

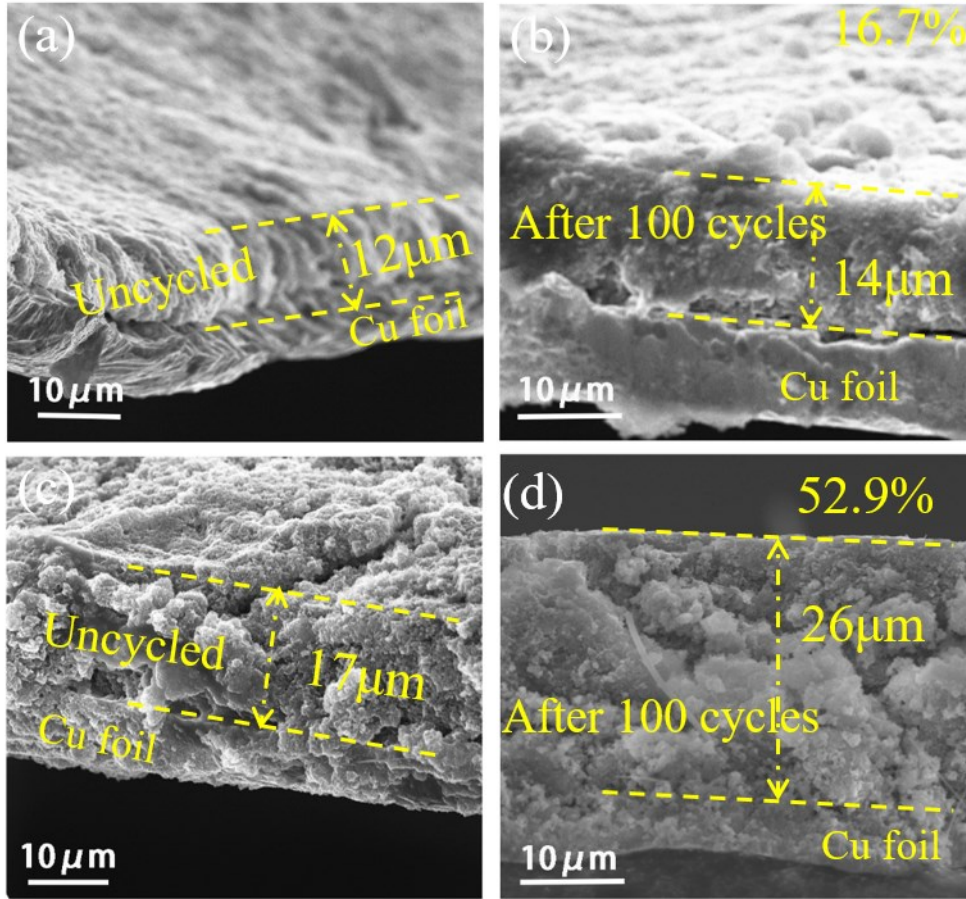


Fig. S11 Cross-section SEM images of different samples. (a) Si@void C@TiO₂ before cycling; (b) Si@void C@TiO₂ after 100 cycles; (c) Si@void C before cycling; (d) Si@void C after 100 cycles

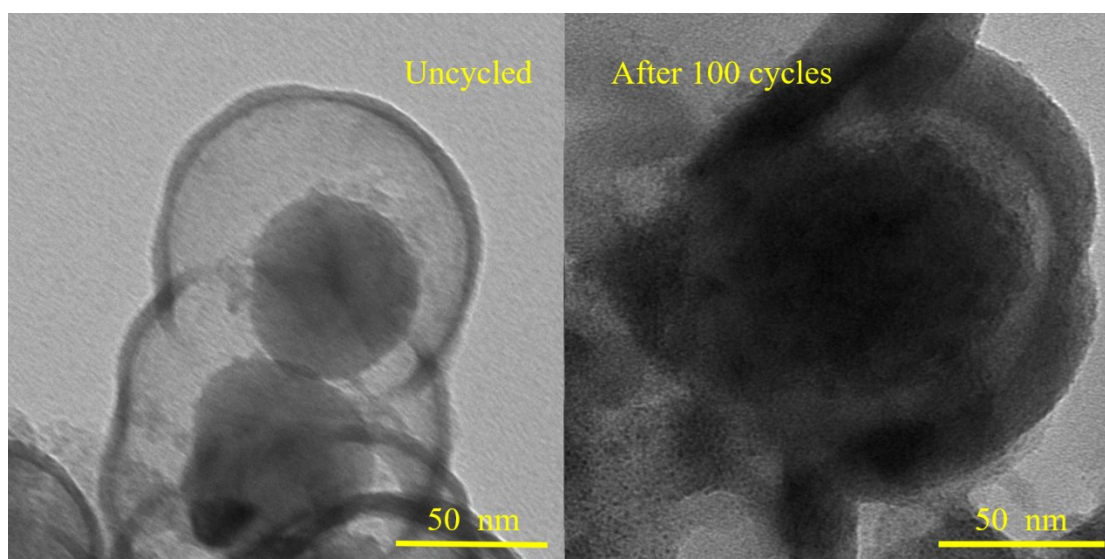


Fig. S12 TEM images of the Si@void C@TiO₂ electrode before and after 100 cycles