Supporting Information

Fluorinated Organosilane Polycondensation Enables Robust Si Anode for Lithium Storage

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Experimental Section

Synthesis of Si@F-SiO$_x$/C composite

Commercial nano-Si powder (60-100 nm in size, 0.1 g) was uniformly dispersed in deionized water (DI water, 2 mL) under ultrasonic for 1 h. Another solution was prepared by adding vinyltri(2-methoxyethoxy)silane (VTES, 0.5 mL) dropwise into HCl solution (2 M, 10 mL), followed by the addition of trimethoxy(3,3,3-trifluoropropyl)silane (TFPS, 0.5 mL) under stirring. The two solutions were mixed and stirred for 5 min. The resulting mixture was aged at 45°C for 24 h. Afterward, the precipitates were collected and dried at 80°C for 12 h to yield the precursor (denoted as Si@POS). The final product, denoted as Si@F-SiO$_x$/C-1, was obtained by annealing the Si@POS at 800°C in N_2 flow for 4 h. For comparison, the Si@F-SiO$_x$/C-2 and Si@F-SiO$_x$/C-3 were prepared similarly, except for reducing the amount of VTES (0.1 mL) and TFPS (0.1 mL) or increasing the amount of VTES (2.5 mL) and TFPS (2.5 mL), respectively.

Synthesis of benchmark samples

For comparison, the Si@SiO$_x$/C was synthesized like the Si@F-SiO$_x$/C-1 production, except for increasing the VTES amount to 1 mL without TFPS. Similarly, the Si@F-SiO$_x$ was yielded by increasing the amount of TFPS to 1 mL while excluding VTES. All other conditions remained the same for the synthesis of Si@F-SiO$_x$/C-1.

Battery test

The battery tests were conducted using CR2016 coin cells with pure Li foil as the

counter and reference electrode. The working electrode consists of an active material, carbon black (Super P) and polyacrylic acid binder in a weight ratio of 6:2:2. The electrolyte used is 1.0 M $LiPF_6$ in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 10 wt.% fluoroethylene carbonate (FEC). The mass loading of the electrodes is around 1.0-1.5 mg cm^{-2}. Cell assembly was carried out in an Ar-filled glovebox with the concentration of moisture and oxygen below 1.0 ppm. The galvanostatic charge/discharge tests were performed using a LAND CT2001A battery tester at different current densities within a cut-off voltage window of 0.01-1.5 V (vs. Li/Li^+) at various current densities of 0.1-2.0 A g^{-1}. The specific capacities were calculated based on the total mass of the active materials. Cyclic voltammetry (CV) studies were conducted using an IVIUM Vertex.C. EIS electrochemical workstation between 0.01-1.5 V (vs. Li/Li^+) at different scan rates of 0.2-1.0 mV s^{-1}.

Material characterization

Scanning electron microscopy (SEM, JEOL JSM-7900F) with an energy dispersive spectrometer (EDS) and transmission electron microscope (TEM, Tecnai G2 F30 S-Twin) was employed to observe the morphology of the materials. X-ray diffraction (XRD, Bruker D8 Advance, Cu Kα), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250), Thermogravimetric analyzer (METTLER TOLEDO TGA/DSC3+) and Fourier transform infrared spectrometer (FTIR, NicoletIS50) were used to investigate the chemical composition of the samples. The F content was determined by using a fluoride ion meter (Leichi, PXSJ-270). The carbon content was determined by using a CS elemental analyzer (CS-3000G)

***In-situ* XRD tests**

In-situ XRD analysis were performed on half cells using Si anode as the working electrode and Li foil as the countered and reference electrode. The electrolyte is 1.0 M $LiPF_6$ in a 50:50 (w/w) mixture of EC and DEC with 10 wt.% FEC. *In-situ* XRD patterns were recorded using a X-ray diffractometer with a 2D detector (Bruker D8 DISCOVER) on a cell module with Be window. The XRD patterns were collected per 600 s in a 2θ range of 27 to 30°. Meanwhile, the discharge-charge tests of the half cells were conducted at a current density of 0.1 A g^{-1} between 0.01-1.5 V (*vs.* Li/Li^+).

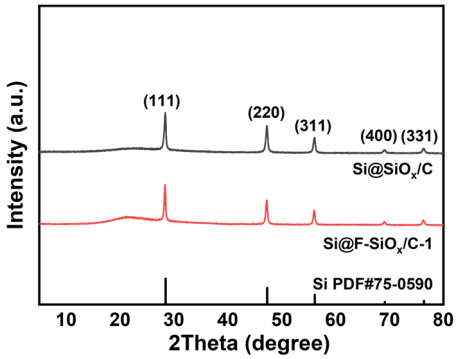

Fig. S1 XRD patterns of Si@F-SiO$_x$/C-1 and Si@SiO$_x$/C.

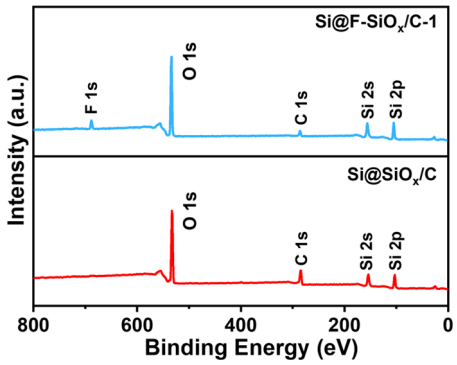

Fig. S2 XPS full-scan survey of Si@F-SiO$_x$/C-1 and Si@SiO$_x$/C.

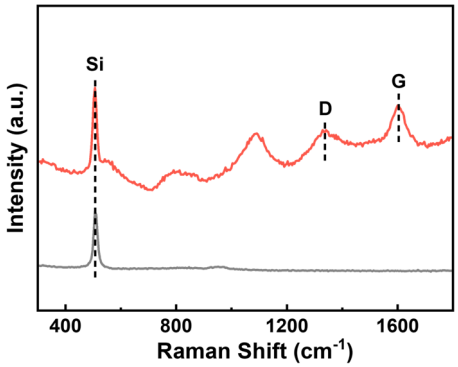

Fig. S3 Raman spectrum of Si@F-SiO$_x$/C-1 and Si nanoparticles.

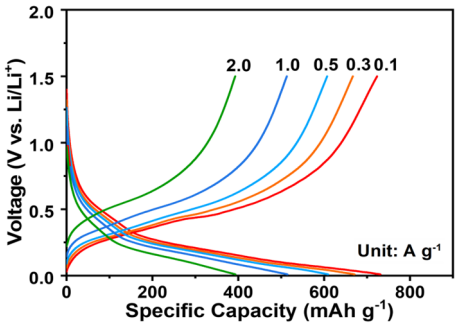

Fig. S4 Discharge-charge voltage profiles of Si@F-SiO$_x$/C-1 at different current densities between 0.01-1.5 V (vs. Li/Li$^+$).

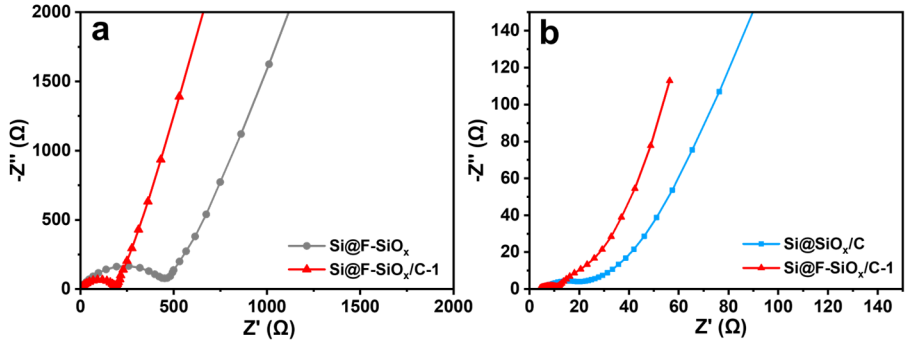

Fig. S5 EIS spectra of (a) Si@F-SiO$_x$/C-1 and Si@F-SiO$_x$ before and after cycling, and (b) Si@F-SiO$_x$/C-1 and Si@SiO$_x$/C (a) before and (b) after cycling.

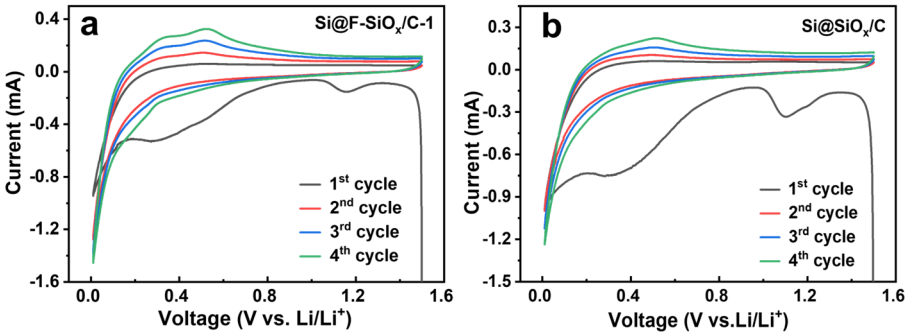

Fig. S6 CV curves of (a) Si@F-SiO$_x$/C-1 and (b) Si@SiO$_x$/C at a scan rate of 0.2 mV s^{-1}.

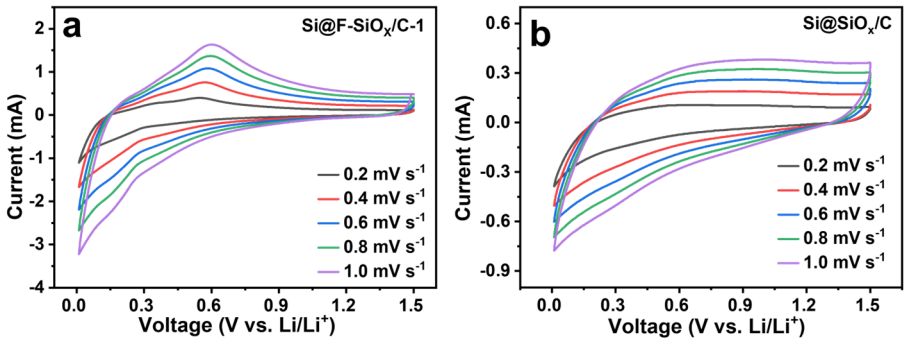

Fig. S7 CV curves of (a) Si@F-SiO$_x$/C-1 and (b) Si@SiO$_x$/C at various scan rates.

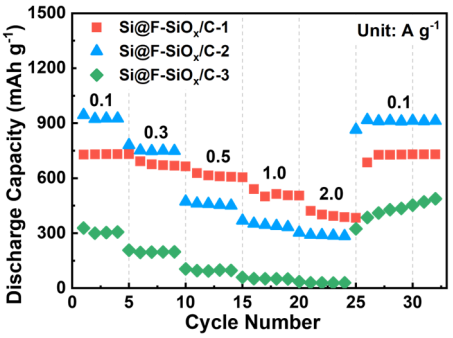

Fig. S8 Rate capability of Si@F-SiO$_x$/C-1, Si@F-SiO$_x$/C-2 and Si@F-SiO$_x$/C-3 at various current densities ranging from 0.1 to 2.0 A g^{-1}.

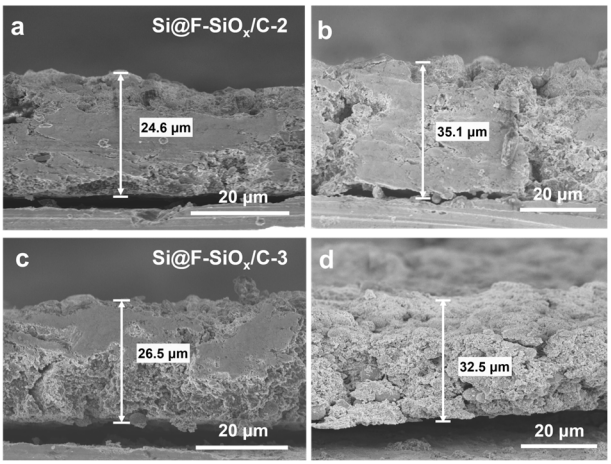

Fig. S9 Cross-section SEM view of (a, b) Si@F-SiO$_x$/C-2 and (c, d) Si@F-SiO$_x$/C-3 (a, c) before and (b, d) after cycling.

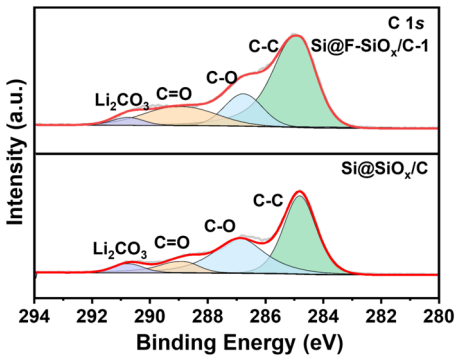

Fig. S10 High-resolution C1s XPS spectra of the SEI on Si@SiO$_x$/C and Si@F-SiO$_x$/C-1 after cycling.

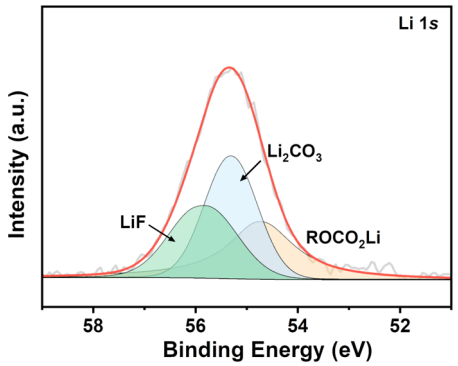

Fig. S11 High-resolution Li 1*s* XPS spectra of the SEI on Si@F-SiO$_x$/C-1 after cycling.

Table S1 A comparison of lithium storage performance between Si@F-SiO_x/C-1 and reported Si anodes

Anodes	Specific Capacities	Cycle life	Reference
Si@F-SiO_x/C-1	**570-670 mAh g^{-1}@ 0.1-0.3 A g^{-1}**	**500 cycles@1 A g^{-1}**	**This work**
Si/NC	563 mAh g^{-1}@ 0.5 A g^{-1}	300 cycles@0.5 A g^{-1}	Ref. S1
p-Si/SiO_x/C	740 mAh g^{-1}@ 0.1 A g^{-1}	50 cycles@0.1 A g^{-1}	Ref. S2
Si@NCC	630 mAh/g@ 0.1 A g^{-1}	100 cycles@0.1 A g^{-1}	Ref. S3
Si@SiO_x/HPCNFs	686 mAh/g @ 0.1 A g^{-1}	100 cycles@0.1 A g^{-1}	Ref. S4
Si@void@C/CNFs	627 mAh/g @ 0.1 A g^{-1}	100 cycles@0.1 A g^{-1}	Ref. S5
Si@SiO_x@C-800	460 mAh/g @ 1.0 A g^{-1}	100 cycles@1.0 A g^{-1}	Ref. S6

References

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