Supplementary Information

A fluoride ion-mediated continuous etching-redeposition strategy to Si nanocomposites with appropriate SiO₂ coating layers for Li-ion batteries

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Experimental Section

1. Synthesis of silicon nanocomposites $Si@SiO_2$

Commercial Si nanoparticles (100 mg) were first dispersed in a mixture solution of ethanol (5 mL) and DI water (95 mL) by ultrasonication for 30 min. Then, ammonium fluoride (30 mg, Sinopharm Chemical Reagent Corporation) was added into the dispersion and the mixture was heated at 60 °C under stirring for 30, 60 and 120 min. The powders were collected by centrifugation, and washed for five times using DI water. For a large-scale production, 15 g of Si nanoparticles were also used in a similar process with the addition of 0.9 g of ammonium fluoride.

Commercial Si nanoparticles (100 mg) were first dispersed in a mixture solution of ethanol (5 mL) and DI water (95 mL) by ultrasonication for 30 min. Then, ammonium hexafluorotitanate (60 mg, Aldrich) was added into the dispersion and the reaction was left at 80 °C under stirring for 60 min. The powders were collected by centrifugation, and washed for five times using DI water.

Commercial Si nanoparticles (100 mg) were first dispersed in a mixture solution of ethanol (5 mL) and DI water (95 mL) by ultrasonication for 30 min. Then, sodium fluoride (60 mg, Aldrich) was added into the dispersion and the reaction was left at 65 °C under stirring for 150 min. The powders were collected by centrifugation, and washed for five times using DI water.

2. Material characterization

The structure of as-prepared samples were characterized by powder X-ray diffraction (XRD) on a X'PERT PRO MPD X-ray diffractometer (PANalytical B.V., Holland) using a Cu K α radiation source ($\lambda = 1.54178$ Å) operated at 40 kV and 80 mA. The samples were scanned from $2\theta = 10$ to 80°. Morphology of the materials was observed by field-emission scanning electron microscope (FESEM) of SU8020 (Hitachi Limited Corporation, Japan) with an acceleration voltage of 5 kV. Transmission electron microscope (TEM) of JEOL-2010 (JEOL Limited Corporation, Japan) with an accelerating voltage of 200 kV and energy dispersive spectroscopy (EDS) were used for further analysis. Raman spectroscopy testing was carried out using a micro-Raman spectrometer of HR Evolution (HORIBA Jobin Yvon, France) equipped with a 532 nm laser. X-ray Photoelectron

Spectroscopy (XPS) (KRATOS AXIS ULTRA, using a monochromated Al Ka source) was carried out to investigate chemical changes on the surface. All the XPS spectra were calibrated using C 1s peaking at 284.6 eV representing C-C bonding. Specific surface area and pore volume were calculated according to the data recorded on Autosorb-IQ3 (Quantachrome, American).

3. Electrochemical measurement

To make the working electrode, an aqueous slurry method was used. Si nanocomposites or pristine Si powders, carbon black (Beijing Chemical Reagents Corporation, China), and sodium alginate binder (Sinopharm Chemical Reagent Corporation, China) with a ratio of 60:20:20 were added to water, and stirred for over 8 h to ensure thorough stirring. The electrode films were prepared by casting the slurry on copper foil using a doctor blade to a thickness of 50 μ m, which was followed by drying in a vacuum oven at 80 °C overnight. The resulting electrode film was then stamped into discs with diameters of 9 mm to serve as anode, where the loading mass was 0.5~1 mg cm⁻² for those tested electrodes, and smooth lithium foils were applied to counter electrodes. The electrode density was calculated to be 0.5~1 g cm⁻³ (the film thickness was ~10 μ m measured by SEM). The electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1:1 in volume ratio, and the volume of the electrolyte used for each cell is ~ 150 μ L. Celgard 2400 membrane was used as the separator. The gravimetric capacity (mA h g⁻¹) was calculated based on the mass of active material and the areal capacity of mA h cm⁻²) based on the geometry area of the electrode disc. The initial areal capacities of the Si@SiO₂-60 and the pristine Si are 0.78 and 0.68 mA h cm⁻².

Tap densities of Si nanocomposites (Si@SiO₂-60) and pristine Si powders are measured. The powders (*m*, g) were added into a graduated cylinder, which was shaken until the volume of the powders (*V*, mL) remained constant. The tap density (*D*, g cm⁻³) was calculated by the following equation D = m / V. The tap density of each sample was measured for three times and the average tap densities of the Si@SiO₂-60 and pristine Si are calculated to be 0.277 and 0.197 g cm⁻³, respectively.

The galvanostatic charge-discharge tests of assembled cells were conducted in a range of 0.01-1.00 V (vs. Li/Li⁺) at room temperature (25 °C) using a battery testing system (BTS–5 V/10 mA and BTS–5 V/50 mA, Neware Technology Limited Corporation, China). Cyclic voltammetry tests were performed using on an CHI-660E electrochemical workstation from 0.01 to 2.5 V. Electrochemical impedance spectroscopic (EIS) measurements were measured on an electrochemical workstation (CHI-660E, Shanghai Chenhua Instrument Limited Corporation, China) within the frequency range from 100 kHz to 0.01 Hz and all the EIS spectra were tested on full charge state.



Fig. S1 EDS mapping results of Si nanocomposites (etching reagent: NH_4F). (a) Si@SiO₂-30, (b) Si@SiO₂-60 and (c) Si@SiO₂-120.

For all the Si nanocomposites, only silicon and oxygen elements can be detected. Especially, obvious yolk/shell structures can be observed in Fig. S1c for Si@SiO₂-120. The weak EDS signal of Si obtained near the edges (Fig. S1c) also suggests obvious typical yolk/shell structure. The content of oxygen element increases from 11 to 31 at.%, corresponding to the content of SiO₂ in the composites from 6 to 22 wt.%.



Fig. S2 Deconvoluted Raman spectra of Si nanocomposites (etching reagent: NH₄F). (a) Si@SiO₂-30, (b) Si@SiO₂-60 and (c) Si@SiO₂-120.

The broad peak around 500 cm⁻¹ for Si nanocomposites can be deconvoluted into three characteristic peaks at about 470, 488 and 508 cm⁻¹, as illustrated in Fig. S2a-c. The peak around 470 cm⁻¹ reveals the formation of several kinds of Si-O-Si bonds, and the peak around 488 cm⁻¹ is attributed to vibrations of planner threefold Si-O-Si rings for amorphous SiO_2 .¹ These results confirm the formation of SiO_2 in the nanocomposites, and the content of SiO_2 increases with increasing the reaction time.



Fig. S3 XPS survey spectra of pristine Si and Si nanocomposites (etching reagent: NH₄F).

We can find that only C, O and Si peaks exist in the XPS survey spectra of pristine Si and Si nanocomposites. The C1s peaks appear due to the absorbed carbon-containing compounds. So pristine Si and Si nanocomposites only contain Si and O element. The content of O element increases from 20.4 to 67.8 at.% while the content of Si element decreases from 74.2 to 31.5 at.%. These results indicate an increased content of SiO₂ on the surface of Si nanocomposites.



Fig. S4 Deconvoluted high-resolution Si 2p spectra of the pristine Si and Si nanocomposites (etching reagent: NH₄F).

The peaks with binding energy at about 99 eV and 104 eV can be assigned to Si⁰ and Si⁴⁺ (SiO₂), respectively.² The peaks centered at about 103 eV and 99.5 eV are indicative of the presence of suboxidation states of silicon (SiO_x, 0 < x < 2).³ The intensities of signals assigned to Si⁰ and SiO_x decrease and the intensity of peak ascribed to Si⁴⁺ increases when prolonging the reaction time. According to these results, we may conclude that the surface of as-received pristine Si is suboxidized and form SiO_x coated on the pristine Si. Moreover, the SiO_x layer will also be further oxidized to form SiO₂ layer at a certain temperature (60 °C, Fig. S8). The oxidized Si layer will be etched in the NH₄F solution to generate intermediates, which will be converted into SiO₂ to redeposit around the pristine Si core. These results further prove the etching-redeposition mechanism of Si nanocomposites in our work.



Fig. S5 Deconvoluted high-resolution O 1s spectra of the pristine Si and Si nanocomposites (etching reagent: NH₄F).

The high-resolution O 1s peaks of all the Si nanocomposites can be assigned to oxygen in the Si-O environment at about 532 eV and adsorbed oxygen components at about 533 eV.^{3,4} The oxygen contents from XPS spectra of the pristine Si, Si@SiO₂-30, Si@SiO₂-60, and Si@SiO₂-120 are 16.2, 20.4, 54.6 and 67.8 at.%, respectively. Consequently, the oxygen contents of SiO_x ($0 < x \le 2$) can be calculated to be 8.4 (pristine Si), 10.4 (Si@SiO₂-30), 27.4 (Si@SiO₂-60) and 34.0 at.% (Si@SiO₂-120) according to the deconvoluted O 1s spectra in Fig. S5. Considering that the oxygen element only exists on the surface of the pristine Si and Si nanocomposites, we can find that the oxygen contents estimated by XPS spectra are consistent with the results detected by EDS technique.



Fig. S6 N₂ adsorption/desorption isotherms of pristine Si and Si nanocomposites (etching reagent: NH₄F). (a) pristine Si, (b) Si@SiO₂-30, (c) Si@SiO₂-60 and (d) Si@SiO₂-120.

For the pristine Si and all the Si nanocomposites, a significant hysteresis loop can be observed, confirming the presence of mesopores. Moreover, characteristic shapes in adsorption/desorption isotherms, where the relative pressure is close to 1.0, demonstrate the existence of macropores. The macropores and mesopores originate from the aggregated Si nanospheres and interconnected SiO_2 small nanoparticles on the surface of Si nanospheres.



Fig. S7 SEM and TEM images of Si nanocomposites (etching reagent: NH_4F) obtained at different reaction temperatures. (a-c) 25 °C, (d-f) 40 °C, (g-i) 60 °C and (j-l) 100 °C.



Fig. S8 The high-resolution Si 2p XPS spectrum of the sample which was obtained from pristine Si treated at 60 °C in DI water for 2 h.

In contrast with the Si 2p XPS spectrum of pristine Si, after treating silicon nanospheres at 60 °C in DI water for 2 h, an apparent peak at 103.9 eV corresponding to silicon dioxide (Si⁴⁺) can be detected, indicating that the surface of silicon nanospheres was oxidized to form SiO₂ obviously, which could be further etched by fluoride ions in the following reaction.



Fig. S9 SEM and TEM images of Si nanocomposites obtained at different concentrations of NH_4F solution. (a-b) 3mM, (c-d) 5 mM, (e-f) 8 mM and (g-h) 12 mM.



Fig. S10 Time dependent pH evolution of the reaction system with Si nanospheres dispersed in (a) NH_4F , (b) $(NH_4)_2TiF_6$, and (c) NaF solution.

In the initial reaction stage, pH values of the reaction system decrease sharply due to the hydrolysis reaction of NH₄F at 60 °C according to reaction equation 1. During this stage, Si nanospheres are also oxidized by dissolved oxygen or water⁵ to form silicon dioxides on the surface (equation 2 or 3) and then SiO₂ will be etched. This etching reaction will consume hydrogen ions, causing an increase of pH value. The concentration of as-generated etching product will increase around the area where the reaction takes place with reaction time increased. Then the etching product will be transformed into SiO₂ due to the redeposition reaction which generates hydrogen ions simultaneously. When this two reactions achieve balance, pH of this reaction system will maintain a stable value. When choosing (NH₄)₂TiF₆ as etching reagent, the pH values of the reaction system show the same trend. In the case of NaF solution, we can observe the differences in the initial reaction stage. Due to the hydrolysis reaction of fluoride ions in NaF solution (equation 4), the pH value increases sharply. Then hydrogen ions will be consumed due to the etching reaction, so the pH value drops down. When the redeposition reaction takes place, a reduced drop rate for pH value can be observed. Finally, a balance will be established as well and the pH value maintain a stable value again.

$$NH_{4}F + H_{2}O = NH_{3} \cdot H_{2}O + HF$$
(1)

$$Si + O_{2} = SiO_{2}$$
(2)

$$Si + H_{2}O = SiO_{2} + H_{2}$$
(3)

$$F^{-} + H_{2}O = HF + OH^{-}$$
(4)



Fig. S11 Characterization results of Si nanocomposites (etching reagent: (NH₄)₂TiF₆). (a) TEM image of pristine Si. (b) XRD patterns, (c) Si 2p XPS spectra of pristine Si and Si nanocomposites.
(d) SEM, (e) TEM, (f) HRTEM images and EDS mapping of Si nanocomposites.

The fluoride ion-initiated etching-redeposition strategy can be also adopted to fabricate silicon nanocomposites by using other mild etching reagents which can release fluoride ions. As proof of concept, ammonium hexafluorotitanate ($(NH_4)_2TiF_6$) was chosen to react with Si nanospheres in an aqueous solution at 80 °C. We can observe that typical yolk/shell structured Si nanocomposites have been successfully synthesized as shown in Fig. S8, which is similar with the product by using NH₄F as the etching reagent (Fig. 2k). XRD pattern of the Si nanocomposites (Fig. S8b) reveals the existence of crystalline Si in comparison with the pristine Si, which is consistent with the HRTEM result showing lattice fringes corresponding to the (111) plane of crystalline Si (Fig. S8f). The outer layer is also proved to be amorphous as demonstrated in Fig. S8f, and XPS spectrum confirms that the outer layer in the yolk/shell structured Si nanocomposites is composed by small SiO₂ nanoparticles (Fig. S8c). Moreover, only silicon and oxygen elements can be detected by using EDS technique, and the atomic percentage of silicon and oxygen are 73 and 27 at.%, respectively.



Fig. S12 TEM images of Si nanocomposites obtained by using NaF as etching reagent.



Fig. S13 TEM images of the Si nanocomposites prepared in a large scale.

The amount of the pristine Si we used was scaled up from 0.1 g to 15 g for a large-scale production, that is, the amount of the pristine Si is increased by more than two orders of magnitude. Similar yolk/shell structures can be observed for the Si nanocomposites by using TEM technique (Fig. S13). This result indicates that our method is very easy and effective for scale-up experiment which is important for practical application.



Fig. S14 Coulombic efficiency of the Si@SiO₂-60 electrode when cycling at 2.1 A g^{-1} .



Fig. S15 Electrochemical performances of Si nanocomposites (etching reagent: $(NH_4)_2TiF_6$). (a) Cyclic voltammogram curves of Si nanocomposites at a scan rate of 0.1 mV s⁻¹. (b) EIS spectra of pristine Si and Si nanocomposites. (c) Rate performance at different current densities and (d) charge/discharge profiles of Si nanocomposites at different cycles at 0.84 A g⁻¹. (e) Cycling test of Si nanocomposites at 0.84 A g⁻¹.

Typical lithiation/delithiation peaks at potentials for the reaction of silicon and lithium can be observed for Si nanocomposites (Si@SiO₂), which is similar to the results of the sample by using NH₄F. Si@SiO₂ exhibit much reduced charge-transfer resistance during lithiation/delithiation in comparison with pristine Si. Si@SiO₂ also show good rate capacities, with a specific capacity of mA h g⁻¹ at 0.21 A g⁻¹ and 626 mA h g⁻¹ at 8.4 A g⁻¹. Moreover, Si@SiO₂ demonstrate good cycling performance as well, possessing 1327 mA h g⁻¹ for 200 cycles at 0.84 A g⁻¹.



Fig. S16 EIS spectra of pristine Si and Si nanocomposites (etching reagent: NH₄F).

The Si nanocomposites $Si@SiO_2-30$ and $Si@SiO_2-60$ exhibit smaller impedance semicircles than pristine Si, indicative of lower charge-transfer resistance during lithiation/delithiation. However, $Si@SiO_2-120$ show higher charge-transfer resistance than pristine Si. This may be due to the fact that $Si@SiO_2-120$ with much thicker outer shells will hinder the transport of Li ions instead. This result also confirms that too thick SiO_2 coating layer plays a negative role in the electrochemical performance of Si nanocomposites.



Fig. S17 Cycling performance of pristine Si and Si nanocomposites (etching reagent: NH_4F) at 2.1 A g⁻¹ for 300 cycles.

Too thick SiO_2 coating layer will diminish the reversible capacity and Coulombic efficiency ⁶. In the case of samples produced at different reaction time with NH₄F as etching reagent (Fig. 1), Si nanocomposites Si@SiO₂-60 with appropriate thickness of SiO₂ coating layer (about 5 nm) possess both high reversible capacity and capacity retention during cycling.

sample	BET surface area	total pore volume
	/ m ² g ⁻¹	/ cm ³ g ⁻¹
pristine Si	22.6	0.07
Si@SiO ₂ -30	33.2	0.16
Si@SiO ₂ -60	39.8	0.22
Si@SiO ₂ -120	74.1	0.71

Table S1 Specific surface area and total pore volume of pristine Si and Si nanocomposites.

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