Supplementary Information

A fluoride ion-mediated continuous etching-redeposition strategy to Si nanocomposites with appropriate SiO$_2$ 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 Kα radiation source ($\lambda = 1.54178$ Å) operated at 40 kV and 80 mA. The samples were scanned from 20 = 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 μm, 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 μm 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 μL. 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 (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 $D = \frac{m}{V}$. 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.
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@SiO$_2$-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 SiO$_2$ in the composites from 6 to 22 wt.%. 

Fig. S1 EDS mapping results of Si nanocomposites (etching reagent: NH$_4$F). (a) Si@SiO$_2$-30, (b) Si@SiO$_2$-60 and (c) Si@SiO$_2$-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\(_2\). These results confirm the formation of SiO\(_2\) in the nanocomposites, and the content of SiO\(_2\) increases with increasing the reaction time.
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 SiO$_2$ on the surface of Si nanocomposites.
The peaks with binding energy at about 99 eV and 104 eV can be assigned to Si$^0$ and Si$^{4+}$ (SiO$_2$), respectively. The peaks centered at about 103 eV and 99.5 eV are indicative of the presence of sub-oxidation states of silicon (SiO$_x$, 0 < x < 2). The intensities of signals assigned to Si$^0$ and SiO$_x$ decrease and the intensity of peak ascribed to Si$^{4+}$ increases when prolonging the reaction time. According to these results, we may conclude that the surface of as-received pristine Si is sub-oxidized and form SiO$_x$ coated on the pristine Si. Moreover, the SiO$_x$ layer will also be further oxidized to form SiO$_2$ layer at a certain temperature (60 °C, Fig. S8). The oxidized Si layer will be etched in the NH$_4$F solution to generate intermediates, which will be converted into SiO$_2$ 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: NH$_4$F).

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@SiO$_2$-30, Si@SiO$_2$-60, and Si@SiO$_2$-120 are 16.2, 20.4, 54.6 and 67.8 at.%, respectively. Consequently, the oxygen contents of SiO$_x$ (0 < x ≤ 2) can be calculated to be 8.4 (pristine Si), 10.4 (Si@SiO$_2$-30), 27.4 (Si@SiO$_2$-60) and 34.0 at.% (Si@SiO$_2$-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 N$_2$ adsorption/desorption isotherms of pristine Si and Si nanocomposites (etching reagent: NH$_4$F). (a) pristine Si, (b) Si@SiO$_2$-30, (c) Si@SiO$_2$-60 and (d) Si@SiO$_2$-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$_4$F) obtained at different reaction temperatures. (a-c) 25 °C, (d-f) 40 °C, (g-i) 60 °C and (j-l) 100 °C.
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 (Si$^{4+}$) can be detected, indicating that the surface of silicon nanospheres was oxidized to form SiO$_2$ 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 NH₄F solution. (a-b) 3 mM, (c-d) 5 mM, (e-f) 8 mM and (g-h) 12 mM.
In the initial reaction stage, pH values of the reaction system decrease sharply due to the hydrolysis reaction of NH$_4$F at 60 °C according to reaction equation 1. During this stage, Si nanospheres are also oxidized by dissolved oxygen or water$^5$ to form silicon dioxides on the surface (equation 2 or 3) and then SiO$_2$ 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 SiO$_2$ 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 (NH$_4$)$_2$TiF$_6$ 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.

\[
\begin{align*}
\text{NH}_4\text{F} + \text{H}_2\text{O} &= \text{NH}_3 \cdot \text{H}_2\text{O} + \text{HF} \\
\text{Si} + \text{O}_2 &= \text{SiO}_2 \\
\text{Si} + \text{H}_2\text{O} &= \text{SiO}_2 + \text{H}_2 \\
\text{F}^- + \text{H}_2\text{O} &= \text{HF} + \text{OH}^- 
\end{align*}
\]
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$_4$)$_2$TiF$_6$) 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 NH$_4$F 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 SiO$_2$ 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.
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@SiO$_2$-60 electrode when cycling at 2.1 A g$^{-1}$. 
Fig. S15 Electrochemical performances of Si nanocomposites (etching reagent: \((\text{NH}_4)_2\text{TiF}_6\)). (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 \((\text{Si@SiO}_2)\), which is similar to the results of the sample by using \(\text{NH}_4\text{F}\). \text{Si@SiO}_2 exhibit much reduced charge-transfer resistance during lithiation/delithiation in comparison with pristine Si. \text{Si@SiO}_2 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, \text{Si@SiO}_2 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: NH$_4$F).

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: NH₄F) at 2.1 A g⁻¹ for 300 cycles.

Too thick SiO₂ coating layer will diminish the reversible capacity and Coulombic efficiency. 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.
Table S1: Specific surface area and total pore volume of pristine Si and Si nanocomposites.

<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area / m² g⁻¹</th>
<th>total pore volume / cm³ g⁻¹</th>
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<tbody>
<tr>
<td>pristine Si</td>
<td>22.6</td>
<td>0.07</td>
</tr>
<tr>
<td>Si@SiO₂-30</td>
<td>33.2</td>
<td>0.16</td>
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<tr>
<td>Si@SiO₂-60</td>
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<td>0.22</td>
</tr>
<tr>
<td>Si@SiO₂-120</td>
<td>74.1</td>
<td>0.71</td>
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References