Scalable Synthesis of 2D Si Nanosheets

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2D Si nanomaterials have attracted tremendous attention due to their novel properties and a wide range of potential applications from electronic devices to energy storage and conversion. However, high-quality and large-scale fabrication of 2D Si remains challenging. This study reports a room-temperature and one-step synthesis technique that leads to large-scale and low-cost production of Si nanosheets (SiNSs) with thickness ≈4 nm and lateral size of several micrometers, based on the intrinsic delithiation process of chemically leaching lithium from the Li13Si4 alloy. Together with experimental results, a combination of theoretical modeling and atomistic simulations indicates that the formation of single SiNS arises from spontaneous delamination of nanosheets from their substrate due to delithiation-induced mismatch. Subsequently, the synthesized Si nanosheets evolve from amorphous to nanocrystalline to crystalline structures during annealing at different temperatures. It is demonstrated that these SiNSs possess unique mechanical properties, in particular ultralow friction, in contrast to their bulk counterparts.

As a fundamental material for modern electronic/optoelectronic and photovoltaic industry, silicon has been extensively studied over many decades.[1–4] Compared with bulk Si, Si nanomaterials with nanoscale dimensions exhibit many interesting electrical, mechanical, optical, thermoelectric and electrochemical properties owning to their unique size effect and surface chemistry.[4–7] and therefore have been intensely studied for a wide range of practical applications including photovoltaic cells,[8,9] optoelectronic devices,[10,11] drug delivery systems,[12,13] sensors,[14] thermoelectrics,[15] and lithium ion batteries (LIBs).[15–17] During the past two decades, there has been great progress in the synthesis of low-dimensional Si nanostructures. In particular, multiple chemical and physical strategies including magnetron sputtering,[18,19] chemical vapor deposition (CVD).[20,21] ion implantation,[22] and chemical etching,[23,24] have been developed to fabricate Si materials in 0D Si (including Si nanoparticles and quantum dots),[22,23,26] 1D Si (including Si nanowires, nanotubes, and nanorods)[23,24,27] and 3D Si (including nanoporous Si).[28–30] However, synthesis of 2D Si materials with ultrathin thickness (lower than 5 nm) still remains a significant challenge. CVD is a well-established method for the growth of 2D materials and can be used for the fabrication of SiNSs with controllable thicknesses.[31] But such methods suffer from high costs due to their demanding fabrication conditions. Another well-studied method is treating CaSi2 with aqueous HCl at a low temperature (<273 K).[32] CaSi2 is a Zintl silicide with packed sheets of 2D Si within its structure, which can be used to synthesize ultrathin SiNSs, albeit via a complicated synthesis method that involves some intermediate reactions taking more than 5 d for a low yield of 1%. On the other hand, the 2D Si nanosheets have been predicted to have many interesting physical properties. Theoretical calculation demonstrates that SiNSs possess extraordinary electronic and optoelectronic properties[33] and exhibit thickness-dependent photoluminescence (PL) at room temperature.[33] Moreover, external strain or electric field can tune SiNSs into direct bandgap semiconductors, making them particularly attractive for applications in photovoltaics and photocatalysis.[34] Thus, SiNSs could play a substantial role in numerous applications in electronic devices (such as field-effect transistors) and photonic devices (such as light-emitting diode). Furthermore, inorganic 2D materials have been widely studied and applied in catalysis, energy conversion, sensors,
and bioapplications,[35–37] and it is anticipated that SiNSs may have the potentials to be used in such fields.

Recently, Yushin and co-workers demonstrated a direct transformation of bulk bimetallic alloy into oxide nanowires by chemical leaching.[38] Here, we synthesized SiNSs via one-step chemical leaching of Li$_{13}$Si$_4$ powders in ethyl alcohol (Figure 1a). The SiNSs, which have a thickness of \( \approx 4 \) nm and in-plane size of several micrometers, can be well dispersed in the solution by ultrasonic processing. The as-synthesized SiNSs had an amorphous structure. Subsequent thermal annealing at different temperatures led to nanocrystalline and crystalline SiNSs. The SiNSs exhibit high cycling stability as an anode material for LIBs, as well as ultralow surface friction compared to bulk Si. Furthermore, using a combination of theoretical modeling and atomistic simulations, it is revealed that the formation of SiNSs arises from spontaneous delamination of delithiated SiNSs from substrate during the delithiation process.

The binary lithium silicide Li$_{13}$Si$_4$ possesses an orthorhombic structure. Different from CaSi$_2$, there are no packed layers of 2D Si in Li$_{13}$Si$_4$. This compound contains two types of Si atoms in different chemical states, i.e., isolated Si atoms and dimers.[39] We etched Li$_{13}$Si$_4$ (Figure S1, Supporting Information) with ethyl alcohol in ambient conditions to allow the lithium to react with ethyl alcohol and generate hydrogen. After the reaction, we filtered out the remaining Si particles and washed them with acetic acid to remove any lithium carbonate left in the system (Figure S2, Supporting Information). The synthesis process is schematically illustrated in Figure 1a. Figure 1b–f shows

![Figure 1. Synthesis and characterization of layered Si particles and a-SiNSs. a) Schematic illustration of the synthesis route of a-SiNSs. b) SEM images of the layered Si particles obtained by etching Li$_{13}$Si$_4$. Inset: a-SiNSs ethanol dispersion. C–f) SEM images of the layered Si particles obtained by etching Li$_{13}$Si$_4$. g) TEM image of the a-SiNSs. Inset: corresponding SAED pattern. h) AFM characterization of the a-SiNSs. Scale bar: b) 10 \( \mu \)m, c,e) 1 \( \mu \)m, d,f) 200 nm, and g) 100 nm.


scanning electron microscope (SEM) images of the Si particles, whose layered structures are shown in Figure 1c–f. We randomly selected more than 100 samples of the as-synthesized Si particles and found that more than 90% of the samples possessed obvious layered structure, indicating the synthesis is made in high yield. More SEM images of the as-synthesized Si particles were shown in Figure S3 (Supporting Information). Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) analysis (Figure S4a, Supporting Information) on the Si particles indicate that such layered Si particles remain air stable at 500 °C.

The layered Si particles can be broken by ultrasonic treatment into SiNSs dispersed uniformly in ethyl alcohol. The solution is not stable without ultrasonic treatment, and the SiNSs will settle down after letting the solution stand for more than 1 h. The morphology of the obtained SiNSs is clearly displayed in the transmission electron microscope (TEM) image (Figure 1g) and SEM image (Figure S5, Supporting Information). The selected area electron diffraction (SAED) result (Figure 1g) indicates that the as-synthesized SiNSs are amorphous. Energy-dispersive X-ray spectroscopy (EDS) patterns (Figure S6, Supporting Information) show that there is ≈10% (atomic percent) oxygen existing in the amorphous SiNSs (a-SiNSs). The atomic force microscope (AFM) image (Figure 1h) indicates that the thickness of a-SiNSs is ≈4.1 nm. We measured 10 samples and found that their thicknesses are nearly uniformly distributed between 3 and 5 nm. The a-SiNSs exhibit an unusual antioxidant property, which is quite different from other Si nano-materials, possibly due to their amorphous structure. As a result, the a-SiNSs can be exposed to air for a long time, which is important for many practical applications. Owing to the simple synthesis method, mass production of the a-SiNSs can be easily achieved (Figure 1b). Previous studies demonstrated that a-SiNSs exhibit lower volume changes compared with Si particles during lithiation and delithiation cycles,[40] and are desirable anode materials for LIBs. The a-SiNSs, when used as anode materials and tested in lithium ion batteries, were found to possess a much better cyclic performance compared with Si microparticles and exhibit an anode capacity of ≈1500 mAh g⁻¹ (Figure S7c, Supporting Information). The electrochemical performance of the a-SiNSs is further discussed in detail in Text 1 and Figure S7 (Supporting Information).

After reacting with the ethyl alcohol, the crystalline Li₁₃Si₄ (c-Li₁₃Si₄) was transformed into the amorphous Si (a-Si), which can be regarded as a chemical delithiation process. In our experiments, the delithiation process shows an apparent anisotropy in the production of layered structures. Such anisotropy might be related to the crystallographic structure of Li₁₃Si₄ and the associated energy barriers for reaction and diffusion of Li ions (or lithium ionic mobility). As illustrated by Figure 2a, for a semi-infinite c-Li₁₃Si₄, its top surface first reacts with the ethyl alcohol. If delithiation in the y direction is presumed to be faster than in other directions, an a-Si film normal to the y direction is produced on the top surface of c-Li₁₃Si₄. The delithiated film attempts to undergo a large volume shrinkage, but is constrained in-plane by the unde lithiated Li₁₃Si₄ (Figure 2a). This results in an internal mismatch stress σ_m in the delithiated layer. The elastic strain energy stored in the layer provides

![Figure 2](image-url)
from MD based on a cohesive-zone-volume-element (CZVE) separation relationship (i.e., a constitutive law for the interface) of the simulated strip. Here we extracted the traction–separation curve. More details are supplied in Experimental section. Figure 2b shows 4899 MD data points and a smooth traction–separation curve by averaging each 100 points. The obtained traction–separation curve is reminiscent of previous results on grain boundary fracture in Al at a low temperature. The traction–separation curve by averaging each 100 points. The obtained traction–separation curve is reminiscent of previous results on grain boundary fracture in Al at a low temperature. The traction–separation curve by averaging each 100 points. The obtained traction–separation curve is reminiscent of previous results on grain boundary fracture in Al at a low temperature.

\[ h_{\text{cr}} = \frac{E_1 \Gamma}{(1 - \nu_1) \sigma_m^2} \]  

(1)

where \( \Gamma \) is the interfacial fracture energy of the film-substrate system, and \( E_1 \) and \( \nu_1 \) are the Young's modulus and Poisson's ratio of the film, respectively. A detailed derivation of Equation (1) is supplied in Text 2 (Supporting Information). During delithiation, once the thickness of the delithiated layer reaches \( h_{\text{cr}} \), delamination of the layer occurs spontaneously and the process repeats until the whole sample is completely delithiated, leading to a layered structure.

To estimate the critical thickness \( h_{\text{cr}} \), we extracted two crucial parameters \( \sigma_m \) and \( \Gamma \) in Equation (1) from atomistic simulations. We first performed molecular dynamics (MD) simulations to mimic the delithiation of c-Li\(_{13}\)Si\(_4\). The details of MD simulations are given in Experimental section. Figure 2b shows the initial atomic configuration of c-Li\(_{13}\)Si\(_4\). During the simulations, the upper half part in Figure 2b underwent delithiation, while the lower part serving as the substrate was fixed. Figure 2c shows an intermediate state with a product of a-Li\(_{1.63}\)Si after partial delithiation. Figure 2d shows the atomic configuration of the upper part after complete delithiation, the radial distribution function (RDF) in Figure 2e indicating that the delithiated structure is amorphous. Figure 2f shows the contour of biaxial atomic stress \((\sigma_{xx} + \sigma_{zz})/2\) in the a-Si film, corresponding to the mismatch stress between the lithiated film and unliethiated substrate. Averaging the biaxial stress over all atoms in the a-Si film results in a delithiation-induced mismatch stress of \( \sigma_m = 4.58 \) GPa. This value is comparable to experimental measurements and theoretical predictions. The Raman spectrum (Figure 3d) shows that samples heated at 650 °C exhibit a high crystallinity, while those heated at 550 °C show relatively poor crystallinity. The Raman spectrum (Figure 3d) also reveals that c-SiNSs possess a high crystallinity and a low degree of oxidation. The peak of c-SiNSs appears at lower Raman shift (≈510 cm\(^{-1}\)) than that of bulk Si (≈520 cm\(^{-1}\)) in Raman spectrum, but with much higher signal intensity than that of nc-SiNSs and a-SiNSs, suggesting good crystallinity. The peaks of nc-SiNSs and a-SiNSs appear at an even lower Raman shift of ≈500 cm\(^{-1}\) and the signal intensity of nc-SiNSs is slightly higher than that of a-SiNSs. The Raman spectra are fairly consistent with the XRD patterns. The peaks of all the SiNSs shift toward lower frequencies with broader full width at half maximum, which is caused by the confinement effects of nanostructures. The peak between 300 and 450 cm\(^{-1}\) in the Raman spectrum is considered to be attributed to amorphous SiO\(_x\) (0 < x < 2) and SiO\(_2\). The low signal intensity between 300 and 450 cm\(^{-1}\) of all the SiNSs suggests low oxide contents. The AFM images (Figure 3e,f) indicate that the thickness of nc-SiNSs and c-SiNSs is very uniform (≈4 nm), indicating that the thickness of SiNSs was not affected by the heating treatment. The SEM images indicate the single layer Si nanosheet is the main product (Figure 5i).

Previous literature reported experimental measurements of the Young's modulus and Poisson's ratio of a-Si to be 80.0 GPa and 0.22, respectively. By substituting these elastic constants (\( E_1 = 80.0 \) GPa, \( \nu_1 = 0.22 \)) and estimated parameters (\( \sigma_m = 4.58 \) GPa and \( \Gamma = 1.14 \) J m\(^{-2}\)) from MD simulations into Equation (1), we obtain a critical film thickness of \( h_{\text{cr}} = 5.57 \) nm, which is in agreement with the experimental result of 3–5 nm (Further for discussions see Text 2 in the Supporting Information). Together with experimental observations and characterizations on a-SiNSs, our theoretical modeling and atomistic simulations imply that the formation of layered a-Si structures originates from spontaneous delamination of a-Si film as a result of delithiation-induced mismatch stress.

To obtain crystalline SiNSs, the as-synthesized a-Si particles were heated in vacuum. The TG and DSC patterns (Figure 4b, Supporting Information) show that there is an exothermic peak between 500 and 600 °C, corresponding to the crystallization of a-Si. To investigate this, the samples were prepared by heating the precursor materials in an argon atmosphere under two sets of conditions: 550 °C for 30 min, and 650 °C for 60 min. The target temperatures were chosen to be 550 °C for partially crystalline layered Si particles and 650 °C for crystalline layered Si particles. Both temperatures are much lower than the melting point of Si (≈1400 °C), so the layered structure remained stable (Figure 3a,b, Figure S8, Supporting Information) and crystallization occurred within the layers. X-ray diffraction (XRD) patterns (Figure 3c) show that samples heated at 650 °C exhibit a high crystallinity, while those heated at 550 °C show relatively poor crystallinity. The Raman spectrum (Figure 3d) also reveals that c-SiNSs possess a high crystallinity and a low degree of oxidation. The peak of c-SiNSs appears at lower Raman shift (≈510 cm\(^{-1}\)) than that of bulk Si (≈520 cm\(^{-1}\)) in Raman spectrum, but with much higher signal intensity than that of nc-SiNSs and a-SiNSs, suggesting good crystallinity. The peaks of nc-SiNSs and a-SiNSs appear at an even lower Raman shift of ≈500 cm\(^{-1}\) and the signal intensity of nc-SiNSs is slightly higher than that of a-SiNSs. The Raman spectra are fairly consistent with the XRD patterns. The peaks of all the SiNSs shift toward lower frequencies with broader full width at half maximum, which is caused by the confinement effects of nanostructures. The peak between 300 and 450 cm\(^{-1}\) in the Raman spectrum is considered to be attributed to amorphous SiO\(_x\) (0 < x < 2) and SiO\(_2\). The low signal intensity between 300 and 450 cm\(^{-1}\) of all the SiNSs suggests low oxide contents. The AFM images (Figure 3e,f) indicate that the thickness of nc-SiNSs and c-SiNSs is very uniform (≈4 nm), indicating that the thickness of SiNSs was not affected by the heating treatment. The SEM images indicate the single layer Si nanosheet is the main product (Figure 5i).

Supporting Information). Together with experimental observations and characterizations on a-SiNSs, our theoretical modeling and atomistic simulations imply that the formation of layered a-Si structures originates from spontaneous delamination of a-Si film as a result of delithiation-induced mismatch stress.

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To further reveal the microstructures of the crystalline SiNSs, we conducted TEM images and scanning transmission electron microscope (STEM) analysis on these specimens, with corresponding images shown in Figure 4. The morphologies of the nc-SiNSs and c-SiNSs are shown in Figure 4a,c. The SAED pattern (Figure 4a) shows that there are many crystalline grains with different orientations in nc-SiNSs. The STEM images of nc-SiNSs show that a number of nanocrystalline grains with sizes ranging from 2 to 10 nm are embedded in an amorphous
matrix (Figure 4b). Typically, for the as-synthesized c-SiNSs, the SAED pattern is shown in Figure 4d. The STEM images present the perfect lattice structure of crystalline Si (Figure 4e), which is consistent with the (111) planes of Si (Figure 4f). As shown in Figure 4b, the lattice fringe of 0.31 nm labeled is consistent with the d-spacing value of the (111) planes of Si.

To demonstrate the unique mechanical properties of our synthesized SiNSs, we also performed nanoscale tribological experiments using AFM in ambient conditions (temperature ≈ 25 °C, RH ≈ 30%; see Experimental Section). As shown in Figure 5a–c, both a-SiNSs and c-SiNSs exhibit extraordinarily low surface friction, roughly 1–2 orders of magnitude lower than that of bulk Si depending on the normal load. The overall ultralow friction property of SiNSs is possibly attributed to its clean and low-oxygen content Si surface in contrast to the relatively rough bulk Si surface with a natural oxide layer. It is interesting to observe that friction on a-SiNSs was noticeably lower than that on c-SiNSs. This is contrary to the traditional trend where a disordered surface usually exhibits higher friction resulting in stronger energy dissipation.[47–50] We suspect that this unusual behavior can be attributed to the lubrication effect of the in-plane disordered wall[51] or from the high mobility of surface atoms in amorphous Si.[52] As Si is widely used in micro- and nanofabrication, the SiNSs may have a high potential to be naturally integrated into various devices and sensors as an atomically thin lubricant for friction and wear reduction. Further investigations in the unique properties of SiNSs are left to future work.

Figure 3. Characterization of layered Si particles and SiNSs. a) SEM image of partially crystalline layered Si particles. b) SEM image of crystalline layered Si particles. c) XRD patterns of the layered Si particles. The peaks of Si (JCPDS Card number 27-1402) are labeled. d) Raman spectra of a-SiNSs, nc-SiNSs, and c-SiNSs. e,f) AFM characterization of the nc-SiNSs and c-SiNSs. Scale bar: a) 1 µm, b) 2 µm.
In summary, we have developed a facile and low-cost method for large-scale synthesis of a-SiNSs, nc-SiNSs, and c-SiNSs. The synthesized a-SiNSs are found to exhibit unique properties, including unusual antioxidant stability when exposed to air and ultralow friction. Furthermore, we revealed the formation mechanism of the observed layered structures, which may guide us to extend such large-scale synthesis methods for 2D materials to metals or semimetal elements that can alloy with Li to form structures similar to that of Li$_{13}$Si$_4$. Such materials have great potential for applications in electronic, photonic, electromechanical devices, as well as LIBs.

**Experimental Section**

**Preparation of a-SiNSs, nc-SiNSs, and c-SiNSs:** All materials used were of high purity (>99%). The Li$_{13}$Si$_4$ particles (2 g, China Energy Lithium Co., Ltd.) (Figure S1, Supporting Information) were added to ethyl alcohol (500 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.) slowly in ambient conditions. (Caution: keep the reaction temperature lower than 40 °C.) The reaction mixture was stirred by magnetic stirring for 120 min. Filtered out the remained Si particles and added them to acetic acid (100 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 60 min. Filtered out the Si particles and dried them at 100 °C in vacuum for 120 min. The yield of Si particles was ~56.5%. The as-prepared Si particles (40 mg) were added to ethyl alcohol (500 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 120 min. Filtered out the remained Si particles and added them to acetic acid (100 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 60 min. Filtered out the Si particles and dried them at 100 °C in vacuum for 120 min. The yield of Si particles was ~56.5%. The as-prepared Si particles (40 mg) were added to ethyl alcohol (500 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 120 min. Filtered out the remained Si particles and added them to acetic acid (100 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 60 min. Filtered out the Si particles and dried them at 100 °C in vacuum for 120 min. The yield of Si particles was ~56.5%. The as-prepared Si particles (40 mg) were added to ethyl alcohol (500 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 120 min. Filtered out the remained Si particles and added them to acetic acid (100 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.). The reaction mixture was stirred by magnetic stirring for 60 min. Filtered out the Si particles and dried them at 100 °C in vacuum for 120 min. The yield of Si particles was ~56.5%.

**Figure 4.** TEM images of nc-SiNSs and c-SiNSs. a) TEM image (inset: corresponding SAED pattern) and b) STEM image of the nc-SiNSs. c) STEM image, d) corresponding SAED patterns and e) STEM images of the c-SiNSs. f) Chemical structure diagram of crystalline Si. Scale bar: a) 100 nm, b) 2 nm, c) 200 nm, and e) 1 nm.
alcohol (100 mL, analytically pure, Sinopharm Chemical Reagent Co., Ltd.) and then the suspension was treated by ultrasonic dispersion (the power of ultrasonic treatment was 80 W) to obtain a-SiNSs. The as-prepared Si particles (1 g) were heated in a vacuum at 550 °C for 30 min and at 650 °C for 60 min (at 10 °C per minute elevated rate), respectively, and then cooled inside the furnace to room temperature. The heated Si particles (40 mg) were added to ethyl alcohol (100 mL) and then the suspension was treated by ultrasonic dispersion (the power of ultrasonic treatment was 80 W) to obtain nc-SiNSs and c-SiNSs for characterization.

Characterization: The XRD patterns of the rare materials and products were evaluated using a D/max-2500 diffractometer (Rigaku, Japan) equipped with a Cu Kα radiation source. The chemical states of the products were analyzed by XPS (Thermo Fisher ESCALAB 250Xi). The morphology of the samples was observed with a SEM (MERLIN VP Compact, ZEISS, Germany). The chemical composition of the samples was characterized using EDS (X-Max, Oxford Instruments). TEM, STEM, and HRTEM observations were conducted on JEOL-ARM-200F TEM operated at 200 kV. The thickness of the nanosheets was determined by AFM (MFP-3D, Asylum Research, Oxford Instruments).

Figure 5. Ultralow friction properties of a-SiNSs and c-SiNSs revealed by AFM. a) Topographic image (left panel) and lateral/friction force (right panel) of a-SiNSs. b) Topographic image (left panel) and lateral/friction force (right panel) of c-SiNSs. c) Comparison of friction versus normal load curves for a-SiNSs, c-SiNSs, and bulk Si.
The electrochemical performances of the batteries were measured by a BS-9300R/SV100mA MTI 8 channels battery analyzer and electrochemical analyzer (CHI800D, Shanghai Huachen Instruments). The TC/DSC curves were collected by a thermogravimetric analyzer (TGA, Q5000IR, TA Instruments). Raman patterns were observed by a spectrometer (Princeton sp-2500).

Atomic Simulations: To complement the experimental results of the formation of layered a-Si structures, we performed MD simulations for delithiation of c-Li13Si4 slabs via LAMMPS.[53] The initial sample has a size of 31.12 × 25.93 × 4.95 nm2 and contains ~239 360 atoms in total. The sample is oriented in [100], [010], and [001] along x, y, and z axes, respectively. Periodic boundary conditions are imposed in x and z directions. The interatomic interaction is described by a reactive force field, which is capable of accurately predicting mechanical properties and lithiation–delithiation behaviors of various Li4-xSi alloys.[54] Throughout simulations, the temperature was maintained at room temperature via a Nose–Hoover thermostat.[53] The time step was set to be 0.5 fs. After equilibration, the lower half part of sample is fixed, while the upper half part is free to implement the subsequent delithiation, as shown in Figure 2b. The delithiation is achieved by randomly removing 16 Li atoms, followed by a free relaxation for 50 fs. After delithiation, the c-Li13Si4 in the upper part was transformed into a-Si with a thickness of 3.85 nm, with a reduction of ~85.2% of initial thickness.

Furthermore, we used a strip sample with a central interfacial crack to estimate the interface fracture energy between a-Si and c-Li13Si4. As shown in Figure 2g, the strip sample consists of a-Si (upper half part) and c-Li13Si4 (lower half part) and contains ~193 550 atoms, with a size of 74.58 × 23.22 × 2.25 nm3. An elliptical sharp crack is introduced in the center of sample by deleting a few layers of atoms on the interface. Periodic boundary condition is only imposed in out-of-plane direction. The traction and separation of each CZVE (displacement of crack) is estimated by calculating the displacement of each mass point of the element. The traction and separation of each CZVE is averaged every 1 ps in a period of crack opening and propagation for 71 ps. Figure 2h presents 4899 MD data points, which provide adequate statistical average of atomic information (such as atomic stress, displacement) around the interface crack. This model has been used to capture the brittle and ductile fracture of interface crack along high-angle grain boundary in Al, showing excellent correlation with the continuum cohesive zone model.[54] As illustrated in Figure S10 (Supporting Information), the whole sample is divided into six regions. During simulations, the atoms in region VI are fully fixed in three directions, while the atoms in region I are imposed by a constant velocity of 10 nm ns−1 in y positive direction to apply a mode-I loading on the crack. The region III above the interface is used to slice CZVE. Each CZVE has a dimension 1.0 × 1.0 nm2 along x and y directions. Theoretical analyses showed that the delamination of thin film is not significantly dependent on the substrate. Thus, the atoms in region V are only fixed in y direction and still can be freely relaxed in other two directions. The region IV with a thickness of 0.25 nm acts as a transition region between regions III and V. The atoms in regions II, III, and IV can be freely relaxed in all three directions. In simulations, there are 75 CZVEs in total along the interface. To weaken the influence of free boundary in x direction, six CZVEs near both ends in x direction are not used for the subsequent statistics. The traction of each element is the average of atomic stress σ of all atoms in the element, while the separation (i.e., opening displacement of crack) is estimated by calculating the displacement of mass point of the element. The traction and separation of each CZVE is averaged every 1 ps in a period of crack opening and propagation for 71 ps. Figure 2h presents 4899 MD data points, which provide adequate statistics to extract a traction–separation curve by averaging every 100 points. The interface fracture energy was obtained by integrating over the traction–separation curve.

Friction Measurements: NT-MDT AFM was employed to perform friction and topography measurements in ambient conditions (20–25 °C, relative humidity 30%). During the AFM measurements, silicon probes (MikroMasch, CSC37/Al 85) were used with the normal and lateral force constants calibrated by Sader’s method[56] and a diamagnetic lateral force calibrator,[57] respectively. The mean friction was calculated by calculating the half difference of the trace and retrace lateral force signals, which were obtained on the region of 100 nm × 100 nm under the sliding velocity of 200 nm s−1.

Electrochemical Measurements: The a-SiNSs electrode was prepared by dropwise adding a-SiNSs dispersion solution onto a copper foil (United Copper Foils Co., Ltd) and then drying the electrodes in vacuum at 80 °C for 12 h. The dried electrodes were pressed using a rolling machine (~20 MPa). The mass loading of the electrodes was ~0.1 mg cm−2. Half-cells (2032 coin-type) were assembled with the a-SiNSs electrode and Li metal foil (MTI) as a counter electrode in an Ar-filled glove box. A 25 μm thick microporous polypropylene membrane (Celgard) was used as the separator and 50 μL of 1 M LiPF6 in ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (1:1:0.04 vol/vol/vol, Ferro Corporation) as the electrolyte. The micron-sized Si particle (Sinopharm, Chemical Reagent Co., Ltd) electrode was prepared by the similar method.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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J.L., B.D., and S.Z. contributed equally to this work. H.W. conceived the concept and experiments. X.L. and H.G. designed the modeling and simulations. J.L. and H.S. carried out the experiments, performed the materials characterizations and electrochemical measurements. B.D., X.L., and H.G. performed the theoretical modeling and atomistic simulations. S.Z. and Q.L. performed the tribological measurements. B.G. assisted the TEM characterization. J.L., B.D., S.Z., H.W., X.L., and H.G. co-wrote the paper. All authors discussed the results and commented on the manuscript. H.W. acknowledges the support from the National Basic Research of China (Grants 2015CB932500) and National Natural Science Foundations of China (Grants 51661135025 and 51522207). X.L. acknowledges the financial support from National Natural Science Foundation of China (Grant no. 11522218). The simulations were performed on the TianHe-1 supercomputer at the National Supercomputer Center in Tianjin. Q.L. gratefully acknowledges the support from National Natural Science Foundation of China (Grant no. 11422218 and 11432208) and the National Basic Research Program of China (Grant no. 2013CB93003 and 2015CB351903).

Conflict of Interest
The authors declare no conflict of interest.

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