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Title Lithiation/delithiation synthesis of few layer silicene nanosheets for rechargeable Li-O₂ batteries

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((Optional Dedication))

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Abstract: Silicene has recently received increasing interest due to its unique properties. However, the synthesis of silicene remains challenging, which limits its wide applications. In this work, a top-down lithiation and delithiation process is developed to prepare few layer silicene-like nanosheets from ball milled silicon nanopowders. It is found that delithiation solvent plays a critical role in the structure evolution of the final products. The use of isopropyl alcohol renders two dimensional (2D) silicene-like products with 30-100 nm in length and ~2.4 nm in thickness. The electrochemical characterization analysis suggests that the product shows high performance for rechargeable Li-O₂ batteries with 73% energy efficiency and high stability. The top-down synthesis strategy proposed in this work not only provides a new solution to the challenging preparation issue of few layer silicene but also demonstrate the feasibility of producing 2D materials from non-layered starting structures.

1. Introduction

Silicene is a monolayer of silicon atoms with buckling honeycomb structures similarly as graphene.^[1] The intrinsic carrier mobility of silicene is predicted to be only slightly lower than

graphene but in the same order of magnitude.^[2] Due to the strong dangling bonds on the surface and edges of sp^3 hybridized electronic structure, silicene has been expected to possess high affinity with water and high catalytic activity to water splitting and oxygen reduction reaction (ORR),^[3] although few experimental results have been reported to support these predictions. Moreover, the properties of silicene can be easily adjusted by alloying, doping, functionalizing and mechanically straining,^[4] which largely extends its applications. Last but not least, the abundance and low cost of silicon add up to the attractiveness of silicene-based materials for their practical applications.

However, the current synthesis approaches of silicene-based materials afford obvious disadvantages. For example, epitaxial growth^[5] depicts inefficient productivity and chemical exfoliation^[6] renders low yield based on starting materials. Thus it is a key challenge to develop a method with high productivity and high yield. Electrochemical lithiation and delithiation process (LDP) has been demonstrated for transition-metal dichalcogenides.^[7] In a typical LDP, layered electrode materials are inserted with lithium ions while the original layered structure keeps intact. These lithium ions are very active and can easily react with protic solvents, e.g. water and alcohols. The reaction will result in solvation of lithium ions and lead to expansion and exfoliation of the layered structures. However, no efforts have been attempted on the LDP of non-layered structures, like silicon. It is well known that Si as electrode materials shows enormous volume expansion when inserted with Li. How the subsequent delithiation will affect the final structure of the expanded Si has been unexplored and interesting. In this work, we demonstrate that it can lead to the formation of 2D silicene-like structures with proper choice of solvent to control the release rate of lithium ions.

Recently, fervid research effort has been put on Li-O₂ batteries (LOBs). Owing to their high theoretical specific capacity and energy, LOB is considered as one of the most promising candidates to substitute current energy storage/conversion systems, e.g. Lead-Acid batteries and Li-ion batteries.^[8] A typical LOB system involves ORR during discharging and oxygen

evolution reaction during charging on the cathode side. Due to the sluggish kinetics of oxygen reduction and evolution reactions, numerous catalysts have been explored and reported with high catalytic activities for LOB, e.g. noble metals, ^[9] perovskites, ^[10] graphene-based materials, ^[11] transition metal oxides, ^[12] metal organic frameworks ^[13] and other materials ^[14]. Although much improvement has been achieved with these catalysts, further enhancement is still needed for practical applications of LOB.

Here, we report few layer silicene nanosheets (SL) produced by a successive lithiation and delithiation process with selected protic solvents. Other products, e.g. silicon nanourchin (SU) and siliphite (SP), are also prepared with some modifications on the procedures. All products are studied to better understand the formation mechanism of various structures by LDP as well as their electrochemical properties. They are employed as catalysts for LOB cathodes. The analysis results show that SL depicts a highest energy efficiency of up to 73% with high stability for 20 cycles.

2. Results and Discussion

In the 1st step, Si nanopowders are produced by dry ball milling for further processing. Lithiation is performed in Li-ion coin cells by inserting lithium ions into Si nanopowder electrodes during discharging. Subsequent delithiation is carried out by rinsing the electrodes with deionized water or isopropyl alcohol in ultrasonication bath. Deionized water and isopropyl alcohol are selected as the delithiation agents because of their different proton activities, which will significantly affect the delithiation processes and render different morphologies and phases of products.

Figure 1 shows the structural evolution of Si nanopowders upon lithiation and delithiation. The voltage curve in Figure S1 depicts a typical discharge plateau of Si electrode at 0.1-0.25 V versus lithium. Particularly, one electrode is discharged at 500 mAh g⁻¹ (denoted as Si500) and another two electrodes are fully discharged at 4200 mAh g⁻¹ (denoted as Si4200). Si500 affords a structure with a Si core and a lithiated Si outer layer. Afterwards,

Si500 is rinsed with isopropyl alcohol in ultrasound bath. And Si nanourchin (SU) is obtained eventually after centrifugation and drying.

Delithiation solvents play a critical role in the structure evolution of the final products. In a typical delithiation process, protons are reduced by lithiated Si and released in the form of hydrogen. Thus a high proton concentration results in fast delithiation. Particularly in this work, deionized water renders faster delithiation than isopropyl alcohol. After washing with deionized water, fully lithiated Si4200 nanopowders exhibits layered structure resembling graphite. Hence the products are denoted as ‘Siliphite’ (SP). The formation of SP can be explained with the fast delithiation by deionized water. In particular, as lithium is quickly removed from Si4200, Si nanosheets forms but restack together immediately. It is observed that the delithiation reaction with deionized water releases much heat and many gas bubbles promptly.

However, when rinsing with isopropyl alcohol, Si nanosheets with a few silicene layers (SL) are obtained. This is because isopropyl alcohol extracts lithium slowly from Si4200 which allows sufficient time for the newly formed surface to be functionalized. Therefore, these Si nanosheets can be stabilized and restacking of these nanosheets is successfully avoided. Meanwhile, it proves that the top-down LDP method is also applicable to non-layered starting materials.

In Figure S2a and b, the SEM and TEM images of the ball milled silicon nanopowders show that the particles sizes are 100-1000 nm and the crystal lattice distance of 0.313 nm corresponds well to the (111) crystal plane. Figure 2a and b show that SU depicts a sea urchin-like structure with a solid core and nanosheets outer layer covering on the surface of the core. Solid core clearly comes from Si which is not lithiated, while the nanosheets in the outer layer results from the delithiation of the lithiated Si. The sizes of SU nanostructures range from 300 to 400 nm. Figure 2c reveals that SP affords graphite-like hierarchical structures with sizes of 10-20 μm in length and a few hundred nm in thickness. As shown in

Figure 2d and e, SL exhibits graphene-like nanosheet morphologies with 30-100 nm in length. The wrinkles of SL can be clearly observed and the thickness of the wrinkles is estimated to be 2-3 nm. The thickness is further confirmed by AFM to be ~ 2.4 nm (Figure 2f).

The formation process of 2D materials prepared by LDP can be described in Figure S3. When layered starting materials are in contact with exfoliation agents (Figure S3a), lithium ions are extracted immediately and so 2D nanosheets are released.^[7] As for non-layered materials, e.g. lithium silicide in this work, lithium ions at the surface are removed and leave vacancies behind in the first step. Afterwards, neighboring lithium ions follow the vacancies and diffuse out of the bulk structure. Thus silicene nanosheets are formed with numerous buckling distortions at the atomic scale (Figure S3b).

The XRD patterns of the samples are shown in Figure 2g. The as-prepared Si nanopowders produced by dry ball milling and SU can be indexed to PDF#03-065-1060. Based on the (111) peak at $\sim 28.5^\circ$, the grain sizes of the ball milled powders and nanourchins are estimated using Scherrer equation to be ~ 32 nm and ~ 74 nm, respectively. For the fully lithiated samples, the crystal structure of Si changes from cubic to others after lithiation/delithiation process. The peaks of SP are indexed to the tetragonal phase (tetragonal-Si) of PDF#00-040-0932. The peaks of SL are consistent with the allo-Si metastable phase of PDF#00-041-1111, which is reported in a previous study.^[15] No other crystal phases can be detected.

To examine the embedded components of the chemical elements in the products, XPS is performed on SU, SP and SL, respectively. Figure 3a-f show the deconvoluted O_{1s} and Si_{2p} spectra. Among all the samples, the peaks in the O_{1s} are composed of $Si(-O)_2$, $Si(-OH)_x$ and $Si(-O)_4$ at 531.9, 531.1 and 532.9 eV, respectively. No significant changes in the binding energy and FWHM are observed. Yet the percentage amounts of the components change obviously, which is mainly due to their different lithiation and delithiation procedures. Particularly, full lithiation leads to lower portion of $Si(-O)_2$ and higher portion of $Si(-O)_4$. And

delithiation with isopropyl alcohol results in suppressed $\text{Si}(-\text{O})_4$ and increased $\text{Si}(-\text{OH})_x$. The peaks in the Si_{2p} of SU are composed of $-\text{Si}$, $\text{Si}(-\text{OH})_x$ and $\text{Si}(-\text{O})_2$ at 99.0, 99.5 and 102.6 eV, respectively. However, the $\text{Si}(-\text{O})_2$ peak of SP shifts to 103.2 eV. And the $-\text{Si}$, $\text{Si}(-\text{OH})_x$ and $\text{Si}(-\text{O})_2$ peaks of SL shift to 98.3, 99.2 and 103.0 eV, respectively. The differences suggest that the extent of lithiation and the delithiation agents can affect the binding energies and the percentage amounts of those components. Specifically, full lithiation leads to higher binding energies of $\text{Si}(-\text{O})_2$ and lower portion of $-\text{Si}$. Moreover, delithiation with isopropyl alcohol elevates the portion of $-\text{Si}$ significantly in comparison to deionized H_2O , which is because the formation of silicene sheets increases.

Optical images of the aqueous dispersions of the samples are shown against time in Figure S4. Commercial natural graphite (NG) and mesocarbon microbeads (MCMB) are also introduced for comparison. NG and MCMB precipitate immediately once they are mixed with deionized water. Over a few hours, the as-prepared Si nanopowders dispersion shows obvious precipitation. Meanwhile, SU, SP and SL dispersions exhibit very slow settlement against time, which indicates their high stability in deionized water. This can be ascribed to the hydrophilic functionalities attached on the surfaces of SU, SP and SL nanostructures.

Delithiation is also performed with other solvents. The XRD patterns of delithiation products with various alcohols are shown in Figure S5. Delithiation with methanol and ethanol leads to formation of the tetragonal Si phase of PDF#00-040-0932, which is the same as deionized water. Delithiation with 1-butanol and 1-hexanol produces the allo-Si metastable phase of PDF#00-041-1111, which is the same as isopropyl alcohol.

As shown in the TEM images (Figure S6), delithiation with various alcohols renders silicene sheets with slightly different morphologies. Particularly, methanol produces interconnected nanosheets with 2-5 nm in thickness (Figure S6a). Thick nanosheets with ~10 nm thickness can be obtained by delithiation with ethanol (Figure S6b). Moreover, 1-butanol leads to formation of interconnected circular sheets (Figure S6c) and 1-hexanol produces

interconnected nanosheets with a thickness of ~ 5 nm (Figure S6d). Since the proton activities of these alcohols are all lower than deionized water, it suggests that these alcohols can provide the proper proton activity for silicene formation.

Electrochemical characterization of the products is carried out in LOB. SU, SP and SL are employed as the catalysts when preparing the electrodes with pure carbon. During discharging process in LOB, lithium peroxide will form and deposit on the electrodes, leading to the increase of internal electrical resistance of LOB. Thus discharge capacities are limited at 500 mAh g^{-1} in order to keep sufficient electrical conductivity and so to facilitate subsequent charging process. Therefore charging capacities are also confined at 500 mAh g^{-1} .

Figure 4a shows the representative voltage profiles of the electrodes at 100 mAh g^{-1} . The discharge voltage plateaus of all electrodes appear at $2.7 - 2.8 \text{ V}$. Although only slight differences can be identified on discharge curves, significant changes are observed during charging of the samples. The SL electrode shows the lower charging voltage at $\sim 3.6 \text{ V}$ while the others' are over 4 V . The resulting energy efficiencies, which are identical to the ratio between discharge energy and charge energy, of pure carbon, SU, SP and SL are estimated to be 60%, 63%, 61% and 73%, respectively. The SL electrode exhibits the highest energy efficiency. Besides, the full discharge voltage curve of SL electrode (Figure S7) reveals that the full specific capacity is $\sim 6930 \text{ mAh g}^{-1}$, which is higher than that of pure carbon electrode.

Rate responses of the SL electrode are tested at 100, 200, 300 and 500 mA g^{-1} afterwards (Figure 4b). The energy efficiencies are estimated to be 73%, 71%, 70% and 66%, respectively. The cyclability of the SL electrode is also examined at 100 and 200 mAh g^{-1} (Figure 4c and d). Over 20 cycles, its energy efficiencies slightly decrease only by 1% and no noticeable deterioration can be observed on discharge and charge voltages.

Cyclic voltammetry (CV) are also performed and shown in Figure S8. Based on the CV curves, the SL electrode shows reduction current onset point at $\sim 2.7 \text{ V}$, corresponding to the reduction of O_2 and the formation of Li_2O_2 on the electrodes. An oxidation shoulder

appears at ~ 3.3 V, corresponding to the oxidation of Li_2O_2 and release of O_2 . The CV curve of the silicene electrode is consistent with the discharge/charge voltage curves, where discharge and charge voltage plateaus are at ~ 2.7 V and ~ 3.5 V. In comparison, the siliphite, silicon nanourchin and pure carbon sample electrodes depict reduction current onset points at ~ 2.7 V and oxidation peaks at ~ 4.3 V. This indicates that oxidation process occurs at ~ 4.3 V, which is consistent with their discharge/charge voltage curves.

The electrodes are also characterized after electrochemical characterization. The SEM images show that discharge product deposits on the surface of both pure carbon and silicene electrodes (Figure S9). After charge, most discharge product disappears when residual can be observed on both electrodes. The XRD patterns (Figure S10) of the silicene electrode are collected after discharge and charge, respectively. The results reveal that hexagonal Li_2O_2 forms after discharge and disappears after charge. However, the peaks of carbon and silicene are not detected due to their small loadings on the electrodes. The FTIR spectrum of pure carbon and silicene electrode are shown in Figure S11. The peaks of Li_2CO_3 and Li_2O_2 are identified after discharge, which confirms the inevitable decomposition of electrolytes and reduction of oxygen during discharge. The peaks of Li_2O_2 are still present after charge. This is because Li_2O_2 on the electrodes is not fully oxidized during charge and the residual Li_2O_2 is detected by FTIR.

The photos of pristine and discharged SL electrodes are shown in Figure S12. SL electrodes are extracted from Li-O₂ batteries in a glove box filled with argon after full discharge and 20 cycles, respectively. The Li-O₂ batteries are heavily bent and opened using forceps. However, no crack or flaking is observed on the SL electrodes during extraction process, indicating good mechanical stability.

XPS is also carried out on SL electrodes. Figure S13 shows the deconvoluted Si_{2p} spectrum after 20 cycles. The peaks are composed of -Si, $\text{Si}(\text{-OH})_x$ and $\text{Si}(\text{-O})_2$ at 98.3, 98.8 and 102.5 eV, respectively. In comparison to pristine SL, $\text{Si}(\text{-OH})_x$ and $\text{Si}(\text{-O})_2$ peaks of SL

electrodes after 20 cycles shift to lower binding energies while the $-Si$ peak remains unchanged. However, the portion of $-Si$ peak reduces after 20 cycles, indicating that oxidation of silicene occurs during cycling.

The excellent electrochemical properties of SL can be explained by the following reasons. First, SL can be easily attached with oxygen molecules as well as oxygen containing functionalities on its surface as supported by XPS results. This will facilitate the redox reactions in LOB, which involves reduction of oxygen molecules during discharge. Second, the two dimensional structure of SL affords large amounts of active sites, which can be exposed and readily attached/detached with oxygen molecules.

Based on this work, the LDP method provides a new solution for the synthesis of 2D silicene-like material. Although LDP is proved to be effective previously only for layered structures, e.g. transition-metal dichalcogenides,^[7] this work broadens LDP's capability to produce 2D materials from non-layered structures.

3. Conclusion

Silicene nanosheets with 30-100 nm in length and ~ 2.4 nm in thickness are prepared by the LDP method using fully lithiated Si nanopowders as the starting material and isopropyl alcohol as the delithiation agent. Based on the analysis of the materials characterization results, SL is detected to be in the $allo-Si$ phase and multiple functionalities are attached on its surface, e.g. $Si(-O)_2$, $Si(-OH)_x$ and $Si(-O)_4$. The SL electrode exhibits high energy efficiencies and high stability for LOB. The results proposed in this work might shed light on the future study of silicene-based materials. Moreover, the LDP method can be extended to produce 2D materials from non-layered structures.

4. Experimental Section

Lithiation of Si nanopowders: Si powders (crystalline, 99.5%) are ordered from Sigma Aldrich. The Si powders are transferred to milling jars and mixed with stainless steel balls

thoroughly in a glove box filled with argon. The weight ratio between Si powders and stainless steel balls is 1:20. A Fritsch planetary micro mill PULVERISETTE 7 premium is used for dry ball milling. 10 cycles of 15 min milling at 500 rpm and 15 min rest is applied under argon atmosphere. Si nanopowders are then collected after ball milling.

90 wt% of Si nanopowders obtained by the ball milling procedure and 10 wt% polyacrylic acid (PAA) are mixed in a mortar. The PAA works as a surface active dispersing agent and binder. Distilled water is added to prepare slurry, which then is coated on a piece of Cu foil using doctor blade. After drying at 50 °C in vacuum for overnight, the coated foil is ready for cell assembly. Li-ion coin cells are assembled in a glove box filled with argon gas with below 0.1 ppm in moisture and in oxygen content. Li foils are used as the counter and reference electrodes. 1 M LiPF₆ in ethylene carbonate (EC)/ Dimethyl carbonate (DMC) (1:1 by volume) is used as the electrolytes. Glass microfiber filter papers are employed as the separators. The cells are discharged on a NEWARE multi-channel battery test system at 20-50 mA g⁻¹.

Delithiation of lithiated Si: After lithiation of Si nanopowders, the lithiated electrodes are extracted from the coin cells and washed with DMC to remove residual electrolytes. Delithiation is carried out by washing the electrodes with deionized water or isopropyl alcohol. After ultrasonication, the products are rinsed with deionized water and centrifuged for few times, followed by drying in vacuum at 50 °C for overnight.

Material characterization: The sample morphology is examined using a field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The elemental compositions of the samples are determined with energy-dispersive X-ray spectroscopy (EDS) attached to the SEM instrument. Crystallographic data is collected using powder X-ray diffractometer (Bruker, Cu K α radiation with λ = 1.5406 Å). For transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) characterization, the powders are dispersed in ethanol and ultrasonicated for 10 minutes. The solution is then drop

cast onto carbon coated 200 mesh Cu grids. TEM/HRTEM study is conducted in a JEOL 2010 system operating at 200kV. X-ray photoelectron spectroscopy (XPS) is performed on a PHI-5400 equipment with Al Ka beam source (250 W) and position-sensitive detector (PSD). Fourier-transform infrared spectroscopy (FTIR) is carried out on Bruker TENSOR II FTIR Spectrometer.

Electrochemical characterization: Super-P, delithiated products and polyvinylidene fluoride (PVDF) are mixed together at 8:1:1 weight ratio. The mixture is stirred magnetically for 24 hours and then coated on nickel foams. CR2032 coin cells with holes on cathode cases are used for testing Li-O₂ cells. The cells are assembled in a glove box filled with argon gas with below 0.1 ppm in moisture and in oxygen content. Li foils are used as the counter and reference electrodes. 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) is employed as the electrolyte. Glass microfiber filter papers are applied as the separators. Upon assembly and crimping, the coin cells are transferred to oxygen filled bottles and rested for 12 hours. Before being used, the oxygen filled bottles are purged with oxygen for a few minutes to remove residual gases. The cells are tested on a NEWARE multi-channel battery test system.

Supporting Information

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

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Figure 1. Scheme of lithiation and delithiation process of silicon in different scenarios.

Figure 2. (a, b) TEM images of silicon nanourchin. (c) SEM images of siliphite. (d) TEM, (e) HRTEM and (f) AFM images of few layer silicene. Inset of (f) showed the height profile across the black line. (g) XRD patterns of the products.

Figure 3. XPS of (a) O_{1s}, (b) Si_{2p} of silicon nanourchin, (c) O_{1s}, (d) Si_{2p} of siliphite and (e) O_{1s}, (f) Si_{2p} of few layer silicene.

Figure 4. (a) Representative voltage profiles of the electrodes in Li-O₂ batteries at 100 mA h g⁻¹. (b) Representative voltage profiles of the SL electrode at various current densities. (c, d) Selected voltage profiles of the SL electrode at 100 and 200 mA h g⁻¹.

Few layer silicene nanosheets are successfully prepared by a lithiation/delithiation approach with controlled lithiation extent and selected delithiation agent. These crystal nanosheets with 30-100 nm length and ~ 2.4 nm thickness are attached with oxygen molecules and oxygen-containing groups on their surfaces. They exhibit high catalytic performance for rechargeable Li-O₂ batteries.

Keyword lithiation/delithiation synthesis, silicene, rechargeable Li-O₂ batteries

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Title Lithiation/delithiation synthesis of few layer silicene nanosheets for rechargeable Li-O₂ batteries

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Supporting Information

Title Lithiation/delithiation synthesis of few layer silicene nanosheets for rechargeable Li-O₂ batteries

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Figure S1. Typical discharge curve for lithiation of Si nanopowder electrode. A current density of 20 mA g⁻¹ was applied for 36 hours, followed by 50 mA g⁻¹ applied for the rest discharging.

Figure S2. (a) SEM and (b) HRTEM images of silicon nanopowders produced by dry ball milling. Inset of (b) showed the selected area electron diffraction (SAED) pattern.

Figure S3. Formation of 2D materials from (a) layered structures and (b) non-layered structures. Green particles represent lithium ions.

Figure S4. Aqueous dispersions of the samples against time. Si: silicon nanopowders produced by dry ball milling. SU: silicon nanourchin. SP: siliphite. SL: few layer silicene. MCMB: mesocarbon microbeads.

Figure S5. XRD patterns of products delithiated with methanol, ethanol, 1-butanol and 1-hexanol, respectively.

Figure S6. TEM images of produced by delithiation with (a) methanol, (b) ethanol, (c) 1-butanol and (d) 1-hexanol.

Figure S7. (a) Full discharge voltage curve at 700 mA g⁻¹ of silicene electrode and pure carbon electrode.

Figure S8. Cyclic voltammetry curves of sample electrodes.

Figure S9. SEM images of (a) fresh, (b) discharged, (c) charged pure carbon electrode, (d) fresh, (e) discharged and (f) charged silicene electrode. Both electrodes are discharged to 500 mAh g⁻¹.

Figure S10. XRD patterns of silicene electrodes after discharge and charge.

Figure S11. FTIR spectrum of (a) pure carbon electrode and (b) silicene electrode before electrochemical measurement and after discharge/charge.

Figure S12. Photos of (a) pristine silicene electrode, (b) fully discharged silicene electrode and (c) silicene electrode after 20 cycles.

Figure S13. XPS of Si_{2p} of silicene electrode after 20 cycles.