Fabrication of a Nondegradable Si@SiOₓ/n-Carbon Crystallite Composite Anode for Lithium-Ion Batteries

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Supporting Information

ABSTRACT: A Si-based anode maintaining its high electrochemical performance with cycles was prepared for the nondegradable lithium-ion battery. Nanoscaled Si particles were mechanochemically coupled with approximately 3 nm thick oxide layer and n-carbon (nanoscaled carbon) crystallites to overcome silicon’s inherent problems of poor electronic conductivity and severe volume change during lithiation and delithiation cycling. The oxide layer of SiOₓ was chemically formed via a controlled oxygen environment during the process; meanwhile, the n-carbon crystallites were obtained by mechanical fragmentation from ~70 μm sized multilayered graphene powders with a low degree of agglomeration. The Si-based composite anode, processed by the above-mentioned mechanochemical coupling, maintained a superior discharge capacity of 1767 mA h/g through 100 cycles with a Coulombic efficiency exceeding 98% at a current density of 100 mA/g. According to our current study, the coupling of the Si particles with oxide layer and n-carbon crystallites was found to be a significantly efficient way to prevent the performance degradation of the Si-based anode.

INTRODUCTION

Modern electronic products require higher energy capacity and longer lifetime for power source, such as lithium-ion batteries (LIBs).1 Graphite, a popular anode material for LIBs, is known to possess a layered structure that could dampen any volume change arising from the intercalation and deintercalation of lithium ions, resulting in a longer lifetime of the anode electrode. Despite the excellent cyclic stability, graphite exhibits a serious drawback of relatively low theoretical capacity of 372 mA h/g.2,3

On the other hand, Si materials for the LIBs possess a high specific capacity of approximately 4200 mA h/g, but several critical issues, such as high capacity irreversibility and cyclic instability, need to be resolved.4–7 The high capacity irreversibility and cyclic instability are caused by the inherent low electronic conductivity and large volume change of silicon during lithium-ion insertion/extraction.8,9 Extensive approaches, such as the application of nanoscaled Si particles along with carbon coating, have been made to overcome their low electronic conductivity and large volume change in the anode Si-based electrode.10–17 However, the electrochemical performance through the approaches mentioned above showed a limited improvement; the discharge capacities measured decreased to less than 1500 mA h/g even before 50 cycles.

Recently, various graphene materials with a high conductivity, large surface area, and mechanical flexibility have been employed to improve the performance of Si-based anode materials.18–27 The performance and fabrication method of the Si/graphene composites are summarized in Table 1. The composites in the form of graphene sheets are prepared by various methods of hybridizing,18 wrapping,19 encapsulating,20,21 nanostructuring,22 and mixing23–27 of the Si particles with graphene (or reduced graphene oxide, rGO) materials. Liu et al. reported a reversible capacity of 1433 mA h/g after 100 cycles with a membrane-structured Si/rGO bilayer at 100 mA/g (capacity retention of about 78.9%).22 Chen et al. synthesized Si nanoparticles and ball-milled for 10 h with a sole purpose of mixing with graphene oxide, followed by a reduction process. The Si/graphene nanocomposite electrode with modified binders was fabricated. The prepared anode showed a considerably improved discharge capacity of 725 mA h/g.
| Title                                                                 | Journal                                      | Method                                                                 | Performance                                                                                                           | Property                                                                 | Refs |
|----------------------------------------------------------------------|----------------------------------------------|-----------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|------|
| Multilayered Si nanoparticle/reduced graphene oxide hybrid as a high-performance lithium-ion battery anode | Adv. Mater. (2014)                           | A multilayered Si/rGO nano-hybrid fabricated a dip-coating method using a porous Ni foam as a substrate | ~1500 mA h/g, 80% capacity retention (1–100 cycles) (0.01–2.0 V, 2.4 A/g)                                           | 1. using a porous Ni foam current collector; 2. high specific surface area and a short pathway for the Li ion; 3. multilayered structure offers ample space for the expansion of Si; 4. rGO layers provide a conductive network for the electronic transport | 18   |
| Silicon oxy-carbide glass–graphene composite paper electrode for long-cycle lithium-ion batteries | Nat. Commun. (2015)                          | A SiOC/graphene composite was prepared following a vacuum filtration technique | at 1st cycle, 702 mA h/g; at the 1020th cycle, 588 mA h/g (0.01–2.5 V, 0.1 A/g) | 1. the porous rGO matrix served as an effective current collector, while embedded amorphous SiOC particle-cycled Li ions with high efficiency; 2. elimination of inactive ingredients, such as metal current collector, nonconducting polymeric binder, and conducting agent to reduce the total electrode weight | 19   |
| Adaptable silicon/carbon nanocables sandwiched between reduced graphene oxide sheets as lithium-ion battery anodes | ACS Nano (2013)                              | A SiNW@G@rGO composite fabricated a kind of self-supporting binder-free Si-based anode via the encapsulation of SiNWs with dual adaptable apparels (overlapped graphene sheets and rGO overcoats) | ~1600 mA h/g, 80% capacity retention (1–100 cycles) (0.01–2.0 V, 2.1 A/g)                                           | in the architecture, the overlapped graphene sheets transform with the volume change in embedded Si, thus effectively preventing the direct exposure of encapsulated Si to the electrolyte during cycling | 20   |
| Precise perforation and scalable production of Si-particles from low-grade sources for high-performance lithium-ion battery anodes | Nano Lett. (2016)                            | Graphene was first ball-milled for 30 min at a speed of 800 rpm with 3 mm grinding balls. Then, porous silicon particles were added, followed by ball-milling for 2 h at a speed of 400 rpm to produce the Si/graphene composite | at 100th cycle, 1250 mA h/g, 65% capacity retention (1–1000 cycles) (0.01–1.0 V, 4.2 A/g) | this structure offers several advantages: highly porous silicon will have a much reduced volume change, whereas the graphene shell enhances the electrical conductivity and at the same time serves as a stable interface for stabilizing SEI formation | 21   |
| Sandwich nanoarchitecture of Si/reduced graphene oxide bilayer nanomembranes for Li-ion batteries with long cycle life | ACS Nano (2015)                              | The sandwich nanoarchitecture of rolled-up Si/rGO bilayer nanomembranes was designed via a strain-released strategy | at 100th cycle, 1433 mA h/g, 79% capacity retention (1–100 cycles) (0.01–1.5 V, 0.1 A/g) | 1. the inner void space and the mechanical feature of nanomembranes can help to buffer the strain during lithiation/delithiation; 2. rGO layers can facilitate electron transport, accommodate the volume change in the Si layer, and protect the nanomembranes from SEI formation | 22   |
| Graphene/carbon-coated Si nanoparticle hybrids as high-performance anode materials for Li-ion batteries | ACS Appl. Mater. Interfaces (2013)            | The G/Si composite was prepared through the hybrid electrostatic assembly. Then, G/Si/C hybrids are synthesized by coating a thin layer of amorphous carbon | at 100th cycle, 902 mA h/g, 68% capacity retention (1–100 cycles) (0.02–1.2 V, 0.3 A/g) | this method, which employs graphene as supporting sheets for the loading of active materials and carbon as covering layers, is demonstrated as an effective approach | 23   |
| title                                                                 | journal                  | method                                                                                                                                  | performance                                                                 | property                                                                 | refs |
|----------------------------------------------------------------------|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------|------|
| graphene/silicon nanocomposite anode with enhanced electrochemical   | *J. Power Sources* (2014)| Si/rGO composite started from GO low-molecular-weight PAA and Si. PAA is used to functionalize graphene oxide                          | at 100th cycle, 815 mA h/g, 78% capacity retention (1−100 cycles) (0.01−1 V, 0.5 A/g) | use of PAA-based polymers, both for GO functionalization and as an electrode binder, concur in stabilizing the electrode morphology and enhancing electrochemical performance | 24   |
| stability for lithium-ion battery applications                        |                          |                                                                                                                                       |                                                                           |                                                                           |      |
| facile synthesis of graphene/silicon nanocomposites with an advanced | *Solid State Ionics* (2014)| Si/G composite synthesized by using high-energy ball-milling followed by thermal treatment                                        | at 50th cycle, 725 mA h/g, 43% capacity retention (1−50 cycles) (0.01−1.5 V, 0.4 A/g) | xanthan gum is employed for the first time as an advanced binder. This binder could ensure excellent interfacial interaction between the polymer binder and the particles, with strong adhesion of the electrode layer to the Cu substrate | 25   |
| binder for high-performance lithium-ion battery anodes                |                          |                                                                                                                                       |                                                                           |                                                                           |      |
| facile synthesis of reduced graphene oxide/porous silicon composite   | *J. Power Sources* (2016)| the rGO/porous Si composite was prepared to combine a condensation reaction and subsequent thermal treatment                         | at 200th cycle, 830 mA h/g, (0.01−1 V, 1 A/g)                                                                                   |                                                                           | 26   |
| as a superior anode material for lithium-ion battery anodes           |                          |                                                                                                                                       |                                                                           |                                                                           |      |
| electrostatic self-assembly bmSi@rGO composite as an anode material  | *Electrochim. Acta* (2016)| bmSi@C/rGO composite was prepared through a two-step deposition process driven by electrostatic interactions                          | at 100th cycle, 935.77 mA h/g, 72% capacity retention (1−100 cycles) (0.02−1.5 V, 0.2 A/g) | chitosan is selected as a carbon source and bridge—charge to connect bmSi and GO. The carbon coating and the wrinkled graphene sheets formed a conductive matrix and a buffer zone | 27   |
| for lithium-ion batteries                                            |                          |                                                                                                                                       |                                                                           |                                                                           |      |
capacity retention of about 43.1%) after 50 cycles compared with 484 mA h/g (capacity retention of about 31.2%) with a conventional binder of carboxymethyl cellulose (CMC) at 400 mA/g. On the basis of the previous studies on the Si/graphene (or rGO) composite anodes in the form of graphene sheet, cyclic stability seems to be markedly improved by the employment of graphene materials rather than carbon coating, but the enhancement of capacity retention was still limited.

In the current study, a Si-based composite anode of Si/SiOx/n-carbon crystallites was fabricated by a mechanochemical coupling process to take full advantage of the inherent characteristics of crystalline Si, oxide, and carbon crystallites, for the benefit of high capacity and cyclic stability of LIBs. The graphene of tens of microns was mechanically fragmented into n-carbon crystallites and simultaneously coupled with the Si particles in a uniform manner and without losing the crystallinity of the Si material. Meanwhile, the particles have gone through a chemical process through a controlled oxygen atmosphere to form a nanothick oxide layer onto the surface of the particles. The morphology and microstructural changes in the fabricated composite anode were investigated and discussed in connection with the electrochemical performance.

### RESULTS AND DISCUSSION

The mechanochemical coupling process adopted to fabricate the Si/SiOx/n-carbon crystallite composite is schematically shown in Figure 1a. For the process, spherical Si particles with the diameter of about 100 nm were mixed with rGO multilayered sheets in the size range of 70 μm in a chamber filled with 3-5 mm zirconia balls, which is connected with Ar and oxygen gas lines. Figure 1b shows X-ray diffraction (XRD) patterns for the composite samples that were processed for various times from 0 min to 24 h. Main diffraction patterns for cubic crystalline Si are observed for the processed samples up to 30 min at 28.4°, 47.3°, and 56.1°, which correspond to (111), (220), and (311) lattice planes, respectively. However, the sample processed for more than 1 h showed a peak of SiO2 and a considerably decreased principal Si peak at 28.4°, suggesting the development of crystalline SiO2 (stishovite phase) at the expense of Si. This result is consistent with
oxygen percentage analysis performed with the samples, as summarized in Table 2. This result was also confirmed by the

| element wt (%) | before mechanochemical coupling process | after mechanochemical coupling process for 30 min | after mechanochemical coupling process for 1 h |
|----------------|-----------------------------------------|-----------------------------------------------|-----------------------------------------------|
| O              | 15.75                                   | 21.10                                         | 29.66                                         |
| Si             | 84.25                                   | 78.90                                         | 70.34                                         |
| totals         | 100.00                                  | 100.00                                        | 100.00                                        |

*Oxygen percent of the sample before the mechanochemical coupling process means the existence of native oxide layer on the Si particle.*

abrupt discharging capacity decrease with the sample processed for 1 h, as shown in Figure 4a. In addition, the appearance of broad patterns after 24 h processing indicates that the crystalline structure of SiO$_2$ (stishovite phase) turned into a disordered structure.

The Raman spectra obtained from the samples in Figure 1b show the characteristic peaks for carbonaceous materials, as shown in Figure 1c. Broad peaks at 1350 and 1590 cm$^{-1}$ represent the D and G disordered bands induced and graphitic features, respectively.28 The measured D/G peak intensity ratios of the samples increase from 0.74 to 0.99, indicating a microstructure with a higher fraction of disordered structure at up to 1 h and then cannot be measured at more than 1 h because of the final change in multilayered rGO particles into noncrystalline carbon particles. Notably, the intensity of a sharp peak at 519 cm$^{-1}$, an indication of the presence of Si, moved gradually to 512, 506, 505, 504, and 500 cm$^{-1}$ with the respective processing time of 10 min, 30 min, 1, 2, and 24 h, suggesting that Si particles are mechanically stressed and turn into an amorphous structure.

The change in the morphology and mapping of the principal elements of C and Si in the composite samples after a selected processing time for 0 min, 30 min, and 1 h is observed by scanning electron microscopy (SEM)/focused ion beam (FIB), as shown in Figure 2. Figure 2a–c shows the morphology change with processing time. Meanwhile, Figure 2d–f displays the elemental mapping in the samples, in which yellow and blue color refer to carbon and Si element, respectively. From Figure 2a, a multilayered graphene sheet is observed to be present separately with spherical Si particles before the mechanochemical coupling process. The corresponding elemental mapping is shown in Figure 2d, which is coincident with the layout of the graphene and Si elements. With the progress of the mechanochemical coupling process, the multilayer graphene was transformed into a particular shape and intermixed with the Si particles as observed in Figure 2b,c, where (b,c) refers to the morphology after 30 min and 1 h processing, respectively. The elemental mapping of the samples after 30 min (refers to Figure 2e) and 1 h (refers to Figure 2f) processing, however, showed a clear contrast among them. Mostly, carbon particles seemed to occupy the void formed among the Si particles that are loosely combined with 30 min processing, resulting in the apparent carbon dominant mapping, as shown in Figure 2e. It can be inferred from this observation that the multilayered graphene sheets have gone through brittle fracturing and transformed into smaller particular powders and filled the voids among the loosely combined Si particles. On the other hand, 1 h processing gave rise to cold welding of the slightly deformed Si particles, culminating in the agglomerated lump of Si. The fractured, relatively smaller carbon particles were distributed onto the Si lump, resulting in the larger Si dominant mapping as observed in Figure 2f. These results are well in accord with the XRD and Raman data exhibited in Figure 1b,c, where the 1 h processed sample showed the crystallinity loss of Si and increased disorder in the graphene structure.

To investigate the effect of the process on the oxidation of Si particles, we conducted energy-dispersive spectrometry (EDS) analysis with the selected samples obtained before and after 30 min and 1 h processing. As expected, Si particles were progressively oxidized with the processing time. The results are summarized in Table 2. The oxide layer observed in transmission electron microscopy (TEM) exhibited thicknesses of about 3–5 and 8–10 nm after 30 min and 1 h processing, respectively (Figure S1).

A closer observation of the processed samples was carried out by high-resolution TEM (HR-TEM) images, with elemental mapping showing more detailed morphology changes with processing time. Figure 3a–c shows the detailed morphologies of the samples after 30 min, 1 h, and 2 h processing. The corresponding carbon mapping is shown in Figure 3d–f. A single, not agglomerated Si particle of about 100 nm is observed, as in Figure 3a. After 1 h processing, the Si particles were observed to be agglomerated, as explained in Figure 2. With 2 h processing, severely fractured and agglomerated Si particles were observed, as shown in Figure 3c. The carbon mappings showed the carbon particles distributed into voids among the Si particles (Figure 3d) and
The abrupt performance deterioration drastically decreased to 1038 and 520 mA h/g after 1 and 2 h, respectively. The discharge capacity was markedly increased to 2151 mA h/g after 30 min processing with a higher reversibility of 73.5%. This substantial improvement had been achieved due to the formation of a homogeneous agglomerate of Si particles and n-carbon crystallites, as well as the electronic conduction by n-carbon crystallites is due to severe agglomeration and fracturing of the particles, as observed in Figure 2c. On the basis of the comparison of the performance with the morphology and structure of the samples, the uniform distribution of the Si particles onto the n-carbon crystallite support material and the optimal physical coupling between materials seem to play a pivotal role in the improvement of the performance of the Si-based anode. The composite after 30 min processing exhibits a considerably higher tap density of ∼0.730 g/cm³ compared with nanosized Si (∼0.131 g/cm³).

The effect of the mechanochemical coupling on the performance was also investigated with a sample. The sample was prepared as follows: each rGO and Si particles were mechanochemical-coupling-processed for 30 min separately, and then they were simply mixed to fabricate an electrode by a mortar and pestle. The measured initial discharging capacity and reversibility of the sample showed a considerably lower initial discharging capacity of 1020 mA h/g and a reversibility of 40%, compared with 2151 mA h/g and 73.5%, respectively, of the sample processed for 30 min of mechanochemical coupling as suggested above, verifying the effectiveness of the process (Figure S2).

The cyclic stabilities of the samples were monitored with charge–discharge capacity variations for up to 100th cycle as measured in Figure 4b at 100 mA/g with cutoff potentials of 0.01 and 1.5 V versus Li/Li⁺. The discharge capacity, 1690 mA h/g, of the sample prior to the mechanochemical coupling remained relatively stable for up to around 30th cycle and subsequently decreased abruptly and continuously to less than 1000 mA h/g. The abrupt discharging capacity decrease was also observed in the previous reports. This result implies that the coupling between Si particles and rGO was not strong enough to overcome the accumulated strain caused by the repeated volume change in Si during charge–discharge cycles, resulting in the drastic discharging capacity decline after 30 cycles because of the disconnection of Si particles from the rGO electronic network. By contrast, samples that were processed for up to 30 min maintained a high discharging capacity (about 1661 mA h/g for 10 min and 1767 mA h/g for 30 min processed samples) during 100 cycles. These outstanding results seemed to originate from the formation of agglomerate of Si particles and n-carbon crystallites, as well as the oxide shell formed onto the Si particle. On the contrary, the samples processed for 1 h and longer showed a markedly lower discharging capacity with the cycle, less than 500 mA h/g after 10 cycles for a 1 h processed sample and less than 100 mA h/g after 10 cycles for a 2 h processed sample. These results are in good agreement with the XRD and morphology observation for the samples processed for 2 h and longer; the failure of steady electronic conduction by n-carbon crystallites is due to severe agglomeration and fracture of the composite (Figure 2e). We can infer from the results discussed above that the sturdy and stable bonding among the constituent elements of the composite anode (such as Si and n-carbon crystallites) is an important factor to maintain high discharging capacity and to improve the cyclic performance of the composite anode, which was achieved in our study by a mechanochemical coupling process for an optimized short period of 30 min.

To confirm the superiority of n-carbon crystallite material to support Si electrode by the mechanochemical coupling process, we prepared and tested a set of composite materials composed of Si/Super P (SP, TIMCAL, Super P Li, a conventional conducting carbon for electrodes); sample (C) was manually...
mixed using a mortar and pestle, and sample (D) was mechanochemical-coupling-processed for 30 min. Sample (C) abruptly decreased the discharge capacity with cycles because of severe volume change during lithiation (charge) and delithiation (discharge) cycling, and sample (B) showed a relatively high stability with cycles but markedly lower discharge capacities compared with the counterpart prepared with rGO instead of Super P, suggesting that rGO is an optimum supporting material for the Si electrode by mechanochemical coupling (Figure S3).

Meanwhile, electrical resistances of the samples before cyclic testing are shown in Figure 4c with the Nyquist plots measured by electrochemical impedance spectroscopy (EIS). The resistance of the samples is observed to gradually decrease with the process for up to 30 min and then markedly increased with 2 h processing. The resistance changes observed in EIS are consistent with the variation in initial discharging capacity and reversibility of the samples; the changes are reduced with the process time of up to 30 min and then abruptly increased after 1 h processing. These results support the effect of the sound coupling for the electronic network between Si particles and n-carbon crystallites.

The cyclic stability at various current rates was also examined with the sample, which had been processed for 30 min to see the high-speed charge and discharge performance. At different currents ranging from 100 to 5000 mA/g, the sample showed a stable performance (Figure 4d). Compared with the case of 100 mA/g in Figure 4b, the sample also showed high cyclic stability at a high loading current of 500 mA/g, as shown in Figure 4e, maintaining discharge capacity of approximately 1300 mA h/g through 300 cycles. In comparison, a mixture of Si/rGO particles prepared without the process showed severe
discharging capacity decay, validating the effectiveness of the mechanochemical coupling process.

**CONCLUSIONS**

In summary, for improving the electrochemical performance of the Si-based anode for the LiBs, a mechanochemical coupling process was pursued to provide an active Si material with the physical stability and electronic conductivity during charge-discharge cycles. The process was implemented by coupling nanosized Si particles to the excellent electronic network of n-carbon crystallites, with the simultaneous formation of SiOₓ layer onto the Si particles. Unlike the conventional way of utilizing the graphene in the form of sheets, the multilayered graphene sheet was, in our study, fragmented into particular type powders and made to direct contact with the individual, not agglomerated Si particles to maximize the effective contact surface among them. The mechanochemical coupling process was carried out by making use of a planetary ball mill under a controlled oxygen atmosphere. The Si@SiOₓ/n-carbon crystallite composite anode fabricated for the process for an optimized period of 30 min showed excellent performance; a high discharging capacity of 1767 mA h/g (corresponding to 1289 mA h/cm²) was maintained through 100 cycles with a Coulombic efficiency of more than 98% except for initial cycles at a current density of 100 mA/g. The excellent performance appears to be attributed to the mechanochemical coupling, a facile and economical method to fabricate a high-performance composite electrode, in which n-carbon crystallites have been utilized to physically and electronically support the Si@SiOₓ particles.

**EXPERIMENTAL SECTION**

**Material Preparation.** A set of homogeneous mixture was prepared with Si nanopowder (99%, APS ≈ 100 nm, Alfa Aesar Co.) and rGO powder (RGO-V30-100, STANDARD GRAPHENE Co.) in a weight ratio of 80:20 using a mortar and pestle for 10 min. Then, the prepared mixture was mechanochemical-coupling-processed under a controlled oxygen environment in a high-energy planetary mill loaded with 5 and 3 mm zirconia balls in a weight ratio of 2:1 at 300 rpm for 10 min to 24 h. The synthesized Si@SiOₓ/n-carbon crystallite composites were finally annealed at 900 °C for 3 h under an Ar + 4% H₂ atmosphere.

**Characterization.** To examine the morphology, crystallinity, and microstructure of the samples, SEM with FIB, XRD (Rigaku D/max 2500 diffractometer) using Cu Kα radiation, confocal Raman microscopy (FEX, Nost Co., Ltd) with 532 nm wavelength incident laser light, and TEM (HR-TEM, JEM-3010, JEOL Ltd) were utilized. Tap density of the samples was determined from the measurement of the weight of a given volume of the material under test. The density was also measured using a pycnometer.

**Supported Information.** The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00547.

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