Crumpled Graphene-Encapsulated Si Nanoparticles for Lithium Ion Battery Anodes

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ABSTRACT: Submicrometer-sized capsules made of Si nanoparticles wrapped by crumpled graphene shells were made by a rapid, one-step capillary-driven assembly route in aerosol droplets. Aqueous dispersion of micrometer-sized graphene oxide (GO) sheets and Si nanoparticles were nebulized to form aerosol droplets, which were passed through a preheated tube furnace. Evaporation-induced capillary force wrapped graphene (aka., reduced GO) sheets around the Si particles, and heavily crumpled the shell. The folds and wrinkles in the crumpled graphene coating can accommodate the volume expansion of Si upon lithiation without fracture, and thus help to protect Si nanoparticles from excessive deposition of the insulating solid electrolyte interphase. Compared to the native Si particles, the composite capsules have greatly improved performance as Li ion battery anodes in terms of capacity, cycling stability, and Coulombic efficiency.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

Silicon is a promising high-capacity anode material for Li ion batteries. However, the large volume fluctuation upon Li⁺ insertion/extraction can fracture the material, leading to fast capacity fading due to the loss of electrical continuity. Another problem is that cracking exposes the new surface of Si to the electrolyte solvents, which can decompose at low potential to deposit a solid electrolyte interphase (SEI) layer of lithiated compounds on the new Si surface. During charge/discharge cycling, the insulating SEI layer can grow thicker, which further degrades the capacity and cycling stability of the Si anode. In an operating battery cell, continuous growth of SEI layer will also gradually deplete the available Li⁺ and the amount of electrolytes, thus deteriorating the overall performance.

Theoretical and recent in situ transmission electron microscopy (TEM) studies have shown that the strain induced by the expansion/contraction can be accommodated in Si nanoparticles with diameters <150 nm. Indeed, it has been shown that various Si nanostructures including nanowires, nanotubes, hollow spheres, nanoparticles, and nanoporosity can withstand Li⁺ insertion/removal without significant cracking or fracture. However, the formation of SEI layers on these bare Si nanostructures limits their Coulombic efficiency to be <99%, even after reaching steady state, which can drain the cathode and electrolyte in only tens of cycles. In comparison, the Coulombic efficiency of graphite anodes can readily reach 99.9% after the first few cycles. One way to prevent the deposition of SEI on Si is to avoid its direct contact with the electrolyte solvent by applying a surface coating, which needs to be electrically conducting and permeable to Li⁺. Carbon-based materials have been attractive options. However, a conformal carbon coating on Si would rupture upon volume expansion, exposing Si to electrolytes for SEI deposition. A new form of carbon coating that can accommodate the large volume expansion/contraction of Si is needed. This can be achieved by introducing void space between Si and its carbon coating. For example, very recently Liu et al. reported a yolk-shell design of carbon-encapsulated Si with high Coulombic efficiency up to 99.84% from cycle 500 to 1000. Their approach was to first oxidize the Si nanoparticles to form a SiO₂ surface layer and then form a thin shell coating of polymer, which was later pyrolyzed to amorphous carbon. Upon HF etching to remove SiO₂, and reduce the size of the Si nanoparticles, void space was created inside the carbon hollow spheres that can accommodate volume expansion of Si during lithiation, thus preventing the rupture of the carbon shell and resulting in much improved cycling stability. Here we report another approach to encapsulate Si nanoparticles by using heavily crumpled graphene (aka reduced graphene oxide, r-GO) shells. This simple, one-step approach makes use of the folds and wrinkles of the crumpled graphene coating to allow Si nanoparticles to expand without fracturing the graphene shell, thus effectively protecting the Si particles.

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The crumpled graphene-encapsulated Si particles were made by a facile, capillary-driven assembly route in aerosol droplets (Figure 2). We have shown previously that crumpled graphene oxide (GO) and graphene (i.e., r-GO) particles resembling crumpled paper balls can be made by capillary compression of the sheets in evaporating aerosol droplets.27 Scanning electron microscopy (SEM) images of the starting GO sheets and crumpled graphene balls are shown in Figure S1 (Supporting Information). The crumpled graphene particles are remarkably stable against unfolding or collapsing due to the large number of $\pi-\pi$ stacked folds. They are also aggregation resistant since the crumpled paper ball morphology prevents strong interparticle van der Waals attraction. By adding additional components in the starting dispersion, crumpled graphene wrapped particles28,29 can be obtained after the aerosol synthesis, which can also be converted to hollow graphene capsules29 after removing the particles. The aerosol synthesis route allows continuous mode of operation and is readily scalable. Here, we apply this technique to prepare crumpled-graphene-wrapped Si nanoparticles. In a typical experiment, commercially available Si nanoparticles (50–100 nm in diameter) in an aqueous suspension were directly added to a dispersion of micrometer-sized GO sheets. As shown in Figure 2, the colloidal mixture was then nebulized to form aerosol droplets, which were blown through a preheated tube furnace at 600 °C with a N$_2$ carrier gas. As water evaporates, the amphiphilic GO sheets migrate to the surface of the droplets to form a shell. Since the lateral dimension of the initial GO sheets is much larger than the Si nanoparticles, the graphene shell would be heavily crumpled due to capillary stress.
resulting in a raisin-like morphology that encapsulated the Si particles. The GO was partially reduced thermally before reaching the collector, and was further reduced after collection by annealing at 700 °C in Ar for 2 h.

Figure 3a,b are SEM images of the product, showing submicrometer-sized crumpled capsules. No unwrapped Si nanoparticles were observed. The graphene shells were highly crumpled. STEM images of a single capsule under (c) scanning mode and (d) Z-contrast transmission mode, clearly showing encapsulated Si nanoparticles. EELS elemental mapping for (e) carbon, and (f) EDX mapping of element Si of the same capsule further confirmed encapsulation of Si. (g) XRD pattern of the composite capsules showing the characteristic peaks of Si and a broad band centered around 25° of graphite (002) diffraction peak. The latter suggested turbostratic packing of the graphene (i.e., r-GO) sheets in the shell. Figure 3h shows the thermal gravimetric analysis (TGA) profile recorded during heating in air. A nearly 40% weight loss was recorded at 500 °C due to combustion of the graphene shells. The Si nanoparticles were stable against oxidation up to 700 °C due to a protective native oxide layer on their surface. Therefore, the mass fraction of Si in the final capsules was determined to be 60%.

The electrochemical performance of the composite capsules and native Si nanoparticles were evaluated using deep galvanostatic charge/discharge cycles between 2−0.02 V in a coin cell (CR2032) with lithium foil as the counter electrode and LiPF6 in EC/DMC as electrolyte. The storage capacities of the anodes made with the graphene-wrapped Si and with native Si were calculated based on the mass of the composite and the mass of bare Si nanoparticles, respectively. The first and second charge/discharge voltage profiles are shown in Figure S2. For the crumpled graphene-encapsulated Si nanoparticles, the Coulombic efficiency for the first cycle was 73% when tested at a constant current density of 1 A/g (Figure 4a). This was likely due to the irreversible lithium reaction with the residual functional groups in crumpled graphene and the initial SEI layer formation. However, for the unprotected Si, the first-cycle efficiency was only 37%. The nearly doubled Coulombic efficiency for the first cycle suggests the effective insulation of Si from the electrolyte solvents by the crumpled graphene shell. The Coulombic efficiency of the composite capsules increased quickly, reaching 99% after 5 cycles and 99.5% after 50 cycles, which is higher than that of Si nanoparticles−graphene paper composite (Figure S3), and among the best results for nanostructured Si anode to date. By contrast, bare Si particles exhibited only 90% Coulombic efficiency at the fifth cycle, and 95% at the 10th cycle. After the 20 cycles, the bare Si particles were severely deactivated, showing nearly 90% decrease in capacity (Figure 4b, green line). The low Coulombic efficiency and fast capacity fade of unprotected Si can be attributed to the loss of electrical connectivity due to the continuous growth of the SEI layer. Eventually, the growth of SEI layer would stop when the Si is completely covered, leading to gradually stabilized performance with improved Coulombic efficiency but very low capacity (Figure 4a, green lines). For the composite capsules, since the crumpled shell can expand without cracking, the Si nanoparticles were effectively protected while maintaining electrical contact, leading to much higher Coulombic efficiency throughout cycling. We postulate that even if there were some pinholes on the crumpled graphene shell, they would be plugged effectively by the SEI layer that is developed there to form a protective shell around clusters of Si particles. In this manner, the composite retains 83% of the charge capacity after 250 cycles. Half of the capacity loss occurred during the first 15 cycles, after which only about 0.05% of capacity loss was observed for each cycle, yielding a capacity about 940 mAh/g after 250 cycles. After cycling, the capsules were recovered from the cell and washed with acetonitrile and 1 M HCl to remove the SEI layer before SEM observation. Figure 4c shows that the expected crumpled capsule morphology is retained.

Electrochemical impedance measurements (Figure S4) on coin-cell devices of bare Si nanoparticles and composite capsules were conducted to study the deposition of SEI layers on both types of electrodes. An arch in the impedance spectra corresponds to an electrochemical reaction, the diameter of
which can be interpreted as the resistance of charge transport. Since typically an SEI layer forms below cell voltage of 0.8 V, when the cell is biased at 2 V, the arches observed in the impedance spectra shown in Figure S4a,b correspond to charge transport during lithiation/delithiation of Si. Figure S4a shows the spectra of a bare Si nanoparticle electrode before and after cycling for 250 times. The arch becomes wider after cycling, suggesting that the SEI layer has grown thicker. For the graphene/Si capsule composite (Figure S4b), the arch also widens, but remains much smaller than those in Figure S4a. This suggests that SEI deposition in the capsule composite electrode has been greatly suppressed.

The typical galvanostatic charge/discharge profiles of the composite capsules at various current densities ranging from 0.2 to 4 A/g, corresponding to an area density of around 0.05 mA to 1 mA/cm², are shown in Figure 4d. The composite delivered about 1200 mAh/g at a low current density of 0.2 A/g. To extract the capacity contributed by Si, anodes made with crumpled graphene itself were tested (Figure S5). The capacity of graphene is calculated from the second cycle of charge curve to be 338 mAh/g at 0.2A/g (Figure S5a). Since graphene weighs 40% in the composite, considering it has reversible charge capacity, the contribution from Si particles would be around 1775 mA/g. This corresponds to a maximal lithiated state of Li1.85Si. It is possible that due to the crumpled morphology, some regions of the composite may have poor electrical contact with the rest of the composite, and Si particles in these regions are not utilized. Thus, the capacity of the composite capsules can be further improved if we can resolve this issue and utilize the Si nanoparticles more effectively. Nevertheless, an anode made of crumpled-graphene-wrapped Si particles has good rate capability: it lost less than half of its capacity when the current density was increased 20 times from 0.2 to 4 A/g (i.e., 20 min for a charge/discharge cycle, Figure 4d).

In conclusion, a rapid, high throughput, one-step aerosol-assisted capillary assembly technique has been developed to prepare crumpled capsules of graphene-wrapped Si nanoparticles. The highly crumpled graphene shell can accommodate the expansion/contraction of the encapsulated Si particles during charging/discharging without fracture, thus protecting the Si from SEI deposition. Encapsulation by crumpled graphene shells greatly improved the performance of the silicon as a Li ion battery anode including Coulombic efficiency, cycling stability, and rate capability. This concept of using crumpled graphene as smart wraps can be extended to envelop other expandable particles. Further engineering of the synthesis conditions to control the relative mass ratio of Si to graphene and the number of Si nanoparticles in each capsule could improve the battery performance further. The aerosol synthesis can be operated in a continuous mode at large scale and does not involve extensive engineering of Si nanoparticles, making it a promising technique to create bulk quantities of such high performance crumpled graphene/Si capsules.

**EXPERIMENTAL SECTION**

*Synthesis of crumpled capsules.* GO was prepared by a modified Hummers’ method and purified by a two-step washing procedure. Si nanoparticles (50–100 nm, Meliorum Nanotechnology) were used as received. GO (1 mg/mL) and Si (0.6 mg/mL) were mixed in water and nebulized by an ultrasonic atomizer (1.7 MHz, UN-511, Alfesa Pharm Co.). The aerosol droplets were carried by N₂ gas at 1 L/min to fly through a horizontal tube furnace (tube diameter = 1 in.) preheated to
Characterization. SEM images were collected on a FEI NOVA 600 SEM microscopes. STEM was conducted on a Hitachi HD-2300A FESTEM operated at 200 kV. The elemental mapping of C was carried out using its EELS spectra imaging function. Si mapping was done by EDX. The XRD pattern was collected by an INEL CPS120 powder diffractometer with Cu Kα radiation (λ=1.5418 Å) at 40 kV. TGA (Mettler Toledo, TGA/SDTA851) was performed at the rate of 10 °C/min in air.

Electrochemical Test. Charge/discharge tests were done using a CR2032-type coin cell. Metallic lithium was used as the counter electrode. The working electrode was fabricated by first pasting a mixture of the crumpled capsules or bare Si nanoparticles, carbon black and poly(acrylic acid) binder (Mw = 3,000,000, Aldrich) with a weight ratio of 70:15:15 onto a copper foil (12 mm diameter) and compressing at 10 MPa. The typical mass loading level was about 0.2 mg of graphene/Si capsules per cm² area of the electrode. The electrode was dried at 80 °C for 12 h under vacuum before being assembled into a coin cell in an Ar-filled glovebox. The electrolyte solution was 1 M LiPF6/ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume). A microporous glass-fiber membrane (Whatman) was used as the separator. Galvanostatic charge/discharge measurements were conducted with a MTI battery analyzer BST8-WA at various current densities between voltages of 0.02 and 2 V vs Li/Li+. Lithium insertion into the Si electrode was referred to as discharge, and extraction was referred to as charge. The capacity was determined based on the mass of the capsules or bare Si nanoparticles. The electrochemical impedance measurements were conducted on the coin cells using an Autolab electrochemical interface instrument (PGSTAT 302N) within frequency range of 10 kHz and 10 mHz.

ASSOCIATED CONTENT

Supporting Information
SEM images of flat GO sheets and crumpled graphene, charge/discharge voltage profiles of composite capsules, Coulombic efficiency of Si—graphene paper composite, and electrochemical impedance and lithium storage performance of crumpled graphene. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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Supporting information

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Figure S1. SEM images of (a) starting GO sheets, and (b) crumpled graphene balls prepared by aerosol assisted capillary compression at 600 °C.
**Figure S2.** The first and second charge/discharge voltage profile of anode made with crumpled graphene encapsulated Si nanoparticles.

**Figure S3.** Coulombic efficiencies of Si/graphene electrodes with capsule (open circle) and paper-like structures (open triangle), respectively. The current density is 1 A/g. The Si to graphene mass ratio (60:40) is the same for both electrode materials.
**Figure S4.** Electrochemical impedance spectra conducted on cion-cells made of bare Si nanoparticles and composite capsules at 2 V, respectively, before and after cycling for 250 times.

**Figure S5.** (a, b) The first and second charge/discharge voltage profile of crumpled graphene electrode at 0.2 and 1A/g. (c) Charge/discharge cycling test of the crumpled graphene at a constant current density of 1 A/g.