Graphene-Bonded and -Encapsulated Si Nanoparticles for Lithium Ion Battery Anodes

Yang Wen, Yujie Zhu, Alex Langrock, Ayyakkannu Manivannan, Sheryl H. Ehrman, and Chunsheng Wang*

As electric vehicles and portable electronic device technology develop, the demand for lithium ion batteries with high energy density and long cycle life has increased rapidly in recent years. Silicon (Si) has been considered a very promising anode material due to its high theoretical capacity. However, high-capacity Si nanoparticles usually suffer from low electronic conductivity, large volume change, and severe aggregation problems during lithiation and delithiation. In this paper, a unique nanostructured anode with Si nanoparticles bonded and wrapped by graphene is synthesized by a one-step aerosol spraying of surface-modified Si nanoparticles and graphene oxide suspension. The functional groups on the surface of Si nanoparticles (50–100 nm) not only react with graphene oxide and bind Si nanoparticles to the graphene oxide shell, but also prevent Si nanoparticles from aggregation, thus contributing to a uniform Si suspension. A homogeneous graphene-encapsulated Si nanoparticle morphology forms during the aerosol spraying process. The open-ended graphene shell with defects allows fast electrochemical lithiation/delithiation, and the void space inside the graphene shell accompanied by its strong mechanical strength can effectively accommodate the volume expansion of Si upon lithiation. The graphene shell provides good electronic conductivity for Si nanoparticles and prevents them from aggregating during charge/discharge cycles. The functionalized Si encapsulated by graphene sample exhibits a capacity of 2250 mAh g\(^{-1}\) (based on the total mass of graphene and Si) at 0.1C and 1000 mAh g\(^{-1}\) at 10C, and retains 85% of its initial capacity even after 120 charge/discharge cycles. The exceptional performance of graphene-encapsulated Si anodes combined with the scalable and one-step aerosol synthesis technique makes this material very promising for lithium ion batteries.

1. Introduction

As electric vehicles and portable electronic device technology develop, the demand for lithium ion batteries with high energy density and long cycle life has increased rapidly in recent years. Silicon (Si) is a promising anode material due to its high theoretical storage capacity of 3589 mAh g\(^{-1}\) which is an order of magnitude beyond graphite anodes in current commercial cells. Besides, it features a low discharge potential, low cost, high natural abundance, and environmental benignity, which make it highly attractive to the lithium ion battery industry. However, it has been difficult to develop a practical Si anode since significant structure and volume changes (around 270%) occur during the lithiation/delithiation process, resulting in poor cycle life and low coulombic efficiency. To improve electrochemical performance of Si anodes, various nano-structured Si anodes, including Si nanowires, Si nanotubes, hollow Si nanospheres, and carbon-coated yolk-shell structured Si composites, were developed. Recently, graphene has been used in Si anodes to...
buffer the volume changes and improve electronic conductivities due to its unique properties, such as superior electrical conductivity, high surface area (2600 m² g⁻¹), excellent chemical stability, and strong mechanical strength.[7–9] The most common method to prepare nano-Si/graphene composites is filtering of an aqueous nano-Si and graphene oxide (GO) suspension followed by reduction treatment or a one-step aerosol spray of aqueous nano-Si and GO suspension.[10–14] However, due to the tendency for aggregation of Si nanoparticles in GO suspension, it is challenging to synthesize a uniform Si/graphene composite, which is critical to achieve long cycling life of Si/graphene anodes. If Si nanoparticles can be well dispersed and bonded to GO in the Si-GO suspension, a uniform Si/graphene composite can be obtained by either a two-step filtering/annealing process or one-step aerosol spray.

In this paper, aminopropyltrimethoxysilane (APS) functionalized Si nanoparticles with strong bonds to micro-sized graphene shells were synthesized by a scalable aerosol method (Scheme 1). APS is a special compound with a trimethoxysilane group on one end and amino group on the other. Firstly, Si nanoparticles were uniformly dispersed in an aqueous solution (Scheme 1a). The trimethoxysilane group reacts with SiO₂ on the Si nanoparticle surface (Scheme 1b) to functionalize the Si surface. When mixing with GO suspension, the amino group on the other end of APS interacts with the carboxylic group on GO to form a strong bond between GO and Si (Scheme 1c). The APS groups can also provide great steric hindering between Si nanoparticles to prevent them from aggregation in the suspension solution. The uniform aerosol dispersion of GO sheets and Si nanoparticles was nebulized to form aerosol droplets (Scheme 1d) and passed through a preheated tube furnace by N₂ as carrier gas (Scheme 1e). In the aerosol spray process, water was quickly evaporated and GO was partially reduced resulting in a uniform graphene bonded and encapsulated nano-Si composite (Scheme 1f). For electrode preparation, sodium alginate was utilized to replace carboxymethyl cellulose (CMC) to further improve the interaction between the graphene-bonded-and-encapsulated-Si groups and current collector (Scheme 1g). The optimized design of anode exhibited superior cycling stability and rate capability.

2. Result and Discussion

2.1. Materials Characterization

Figure 1a shows the SEM images of APS functionalized Si@graphene (APS-Si-G) and Figure 1b is the magnified view of the green square in Figure 1a. Figure 1c shows the bare Si@graphene (Si-G). The Si nanoparticles in both Si-G and APS-Si-G samples were well wrapped by graphene. Unwrapped Si nanoparticles were not observed, suggesting high yield of graphene-encapsulated Si composite in the aerosol process. The amount of Si nanoparticles wrapped by each graphene sheet in the APS-Si-G sample (Figure 1a) is much less than that in Si-G sample (Figure 1c) although the ratio of graphene to Si is the same for both samples. This is because the functional groups on the APS-Si surface provide steric hindering between Si nanoparticles thus preventing Si nanoparticles from aggregation. This unique nano-structure of APS-Si-G not only improves the electronic conductivity of active materials, but also provides void space to accommodate the volume change of Si nanoparticles during lithiation, maintaining high electronic conductivity of the composite. The defects on graphene sheets generated during oxidation and reduction provide Li diffusion channels[15,16] and the open ends of the graphene shell (Figure 1a,d) allow electrolyte to penetrate into the graphene shell and electrochemically react with the Si nanoparticles inside the shell during charge/discharge.

To further study the morphology of the material, transmission electron microscopy (TEM) was used to analyze the material. Figure 2a shows the TEM image of a single graphene capsule. A limited number (∼10) of Si nanoparticles

![Scheme 1. Schematic procedure for the synthesis of graphene bonded and encapsulated nano-Si composite.](image-url)
are wrapped in the graphene shell. The Si particles are separated from each other and there are large spaces among the particles. The magnified view of the spot marked in blue square in Figure 2a is given in Figure 2b. The zoomed in image identifies clear graphene layer on the surface of Si particles, confirming encapsulation. The high resolution TEM (HRTEM) image (Figure 2c) provides clear view of fine Si lattice, silica layer and graphene shell. The thickness of silica layer is around 7 nm. The graphene shell is in multiple layers with a thickness of about 8 nm.

Figure 2d shows the TEM bright field image of a graphene capsule with the energy dispersive X-ray spectroscopy (EDS) element mapping of Si and carbon (C) given in Figure 2e and f. The TEM bright field image (Figure 2d) shows good dispersion of Si nanoparticles. The element mapping (Figure 2e,f) demonstrated uniform distribution of Si and C elements. Element mapping for Si (Figure 2e) shows distinct Si nanoparticles, implying good Si dispersion with free space within the graphene shell.

The composition of APS-Si-G sample was determined using thermogravimetric analysis (TGA). Figure 3a shows the TGA curve of APS-Si-G sample. The 28% of mass loss below 500 °C corresponds to the oxidation of graphene in the sample. Si particles are stable up to 600 °C. The gradually regained mass above 600 °C is attributed to oxidation of the Si core. The overall percentage of Si in APS-Si-G sample is determined to be 72 wt%. The bonding effect between the Si and graphene shell was characterized by using Fourier transform infrared spectroscopy (FTIR). Figure 3b shows FTIR spectra for APS-Si, GO and APS-Si-G composites. In the FTIR of GO, the O-H (broad coupling $\nu$ O⎯H) at $\sim$3200 cm$^{-1}$ and the carbonyl stretch ($\nu$ C = O) at $\sim$1700 cm$^{-1}$ are generated by the carboxylic group on the surface of GO. This data is consistent with the reported GO FTIR curve.$^{[17,18]}$ In the APS-Si spectrum, the existence of amino groups is evidenced by the NH$_2$ stretch ($\nu$ NH$_2$) at $\sim$3000 cm$^{-1}$, the $\delta$NH$_2$ absorption (δ NH$_2$) at $\sim$1600 cm$^{-1}$ and the characteristic peaks of amino groups ($\chi$ NH$_2$) at 900 cm$^{-1}$–650 cm$^{-1}$, which demonstrates well functionalization of Si. The O⎯H peak (broad coupling $\nu$ O⎯H) centered at $\sim$3200 cm$^{-1}$, existing in GO, disappears in the APS-Si-G sample, which
indicates bonds formation between two components. For the FTIR spectrum of APS-Si-G samples, new peak appearing at \( \sim 3600 \text{ cm}^{-1} \) is resulted from the N—H stretch (\( \nu \text{N—H} \)) and the sharp doublet at \( \sim 3000 \text{ cm}^{-1} \) is generated by the N—H stretch overtone. C=O (\( \nu \text{C=O} \)) peak at \( \sim 1700 \text{ cm}^{-1} \) and C=N (\( \nu \text{C=N} \)) peak at \( \sim 1450 \text{ cm}^{-1} \) are also evidence of formation of amide groups.

### 2.2. Electrochemical Performance

The first three lithiation/delithiation cycling behavior of the APS-Si-G sample were characterized using cyclic voltammetry (CV) as shown in Figure 4a. The broad peak between 1.7 V and 0.5 V (vs. Li/Li\(^+\)) in the first cathodic scan is attributed to the formation of solid electrolyte interphase (SEI) film on graphene and Si. SEI film formation leads to irreversible capacity and low coulombic efficiency of the first cycle.\(^{[19,20]} \)

The peaks at 0.2 V and 0.05 V showing in the second and third cathodic sweeps correspond to lithium insertion to form different phases of Li-Si alloy. Peaks showing in the anodic sweep at 0.3 V and 0.5 V are attributed to the delithiation of Li-Si alloy. This figure exhibits the typical Si lithiation/delithiation behavior and is consistent with reported CV curves for Si-carbon composite.\(^{[21,22]} \)
The cycling stability of APS-Si-G and Si-G samples during charge/discharge between 0.002 V–1.5 V (vs. Li/Li\(^+\)) at 500 mA g\(^{-1}\) is shown in Figure 4b. All the specific capacity is calculated based on the total mass of Si and graphene. Capacity of Si-G without APS decreased quickly from initially 1000 mAh g\(^{-1}\) to 160 mAh g\(^{-1}\) after 100 cycles. This is due to the disconnection between graphene and Si nanoparticles and the inter-particle crush effect caused by volume expansion/shrinkage. Since the Si particles inside graphene are aggregated and no bonds between the two components exist, the large volume change may affect the structure stability and cause detachment of Si from graphene, resulting in disconnection to the current collector. Different from the Si-G sample, the APS-Si-G sample contains bonds between Si and graphene and larger void space between Si nanoparticles in each graphene shell. This unique morphology greatly improves the structure stability, thus contributes to superior cycling stability. SEM images of APS-Si-G after 100 charge/discharge cycles are provided in Figure S1, which show good graphene encapsulated Si structure, demonstrating good structure retention after cycles. The capacity of APS-Si-G retains a specific charge capacity of 760 mAh g\(^{-1}\) after 100 cycles and 656 mAh g\(^{-1}\) even after 200 cycles which reveal the superior cycling ability (inset of Figure 4b). The coulombic efficiency of ASP-Si-G reaches around 100% after 15 cycles and remains stable during the subsequent charge/discharge cycles. Figure 4c shows the charge/discharge curves for the APS-Si-G sample at the 2\(^{nd}\) cycle, 20\(^{th}\) cycle, 50\(^{th}\) cycle and 100\(^{th}\) cycle, respectively. The plateau appearing at 0.1 V and 0.2 V during the discharge process and at 0.4 V on the charge process correspond to Li-Si alloy and dealloy processes.

The capacity contributed by Si in APS-Si-G composite was calculated by extracting the capacity of graphene measured at the same current. The specific capacity of graphene at 500 mA g\(^{-1}\) charging/discharging rate is 180 mAh g\(^{-1}\). For an initial capacity of ~1000 mAh g\(^{-1}\) for the APS-Si-G sample, the capacity of Si is around 1318 mAh g\(^{-1}\), which is much lower than theoretical capacity of 3589 mAh g\(^{-1}\). The low utilization of Si may be attributed to insufficient binding of ASP-Si-G particles to ASP-Si-G particles and ASP-Si-G particles to current collector. To further increase the utilization of Si nanoparticles in APS-Si-G sample, sodium alginate (SA) was used as an alternative binder. It has been revealed that SA can provide more uniform binder coverage than CMC binder due to higher concentration and more uniform distribution of carboxylic groups. Besides, SA can also stabilize SEI film and provide fast Li ion transport.\(^{[23]}\)

**Figure 5a** shows the comparison of cycling stability for APS-Si-G sample using CMC and SA binders. Although the APS-Si-G samples show sustainable cycling stability with both CMC and SA binders, the utilization of Si in the APS-Si-G sample with SA binder is much higher than that with CMC binder. As shown in Figure 5a, the APS-Si-G sample using SA binder can deliver a specific charge capacity above 1800 mAh g\(^{-1}\) with the above 2422 mAh g\(^{-1}\) on Si, which is much higher than the APS-Si-G sample with CMC binder. For the APS-Si-G electrode using SA binder, a specific charge capacity of 1500 mAh g\(^{-1}\) can be achieved even after 120 full charge/discharge cycles. Also, the 1\(^{st}\) cycle coulombic efficiency for the APS-Si-G sample with SA binder is 60% which is much higher than the sample with CMC binder (~30%). Moreover, compared to the slow activation process of the APS-Si-G sample with CMC, the coulombic efficiency for APS-Si-G with SA binder quickly reached 100% after first 5 cycles.

**Figure 5b** compares the rate capability of the APS-Si-G sample using CMC and SA binders. APS-Si-G sample with CMC binder shows good rate capability up to 8C (current density = 8000 mA g\(^{-1}\)) while the APS-Si-G with SA binder shows superior performance up to 12C (12 000 mA g\(^{-1}\)). The strong mechanical strength of graphene shells ensures electronic conductivity of Si nanoparticles when undergoing volume expansion and contraction. At the same time, the open ends of graphene shells ensure the sufficient transfer of lithium ions even at high C rates. In Figure 5b, the capacity retains ~84% at 1C (1000 mA g\(^{-1}\)), 50% at 8C as in 0.1C (100 mA g\(^{-1}\)) in sample with SA binder, while retention for sample with CMC binder is 76% at 1C and 44% at 8C. The sample with SA binder cycled at high rate (12C) provides similar capacity (700 mAh g\(^{-1}\) based on total mass) as that...
of the sample with CMC at a comparatively low charging/discharging rate (4C, 4000 mA g⁻¹), demonstrating that SA binder enhanced the performance of APS-Si-G anode sample.

The great improvement of electrochemical performance by SA binder could be attributed to the high concentration of carboxylic groups in SA. It was reported that the ester-like bond resulting from reaction between hydroxyl groups on the active material and carboxylic groups in SA would have more opportunity to generate ester-like bonds between binder and GO shells, thus providing better interaction within the electrode. The morphology of APS-Si-G with SA binder is highly favored in Si composite anode, since the bonding between graphene and Si ensures sufficient conductivity when Si undergoes the lithiation/delithiation process, and at the same time, SA will improve the conductivity between graphene shells and current collector to enhance the utilization of active material.

3. Conclusion

In this paper, we have successfully synthesized a unique graphene bonded and encapsulated Si anode using a one-step scalable aerosol spray method. The high electronic conductivity and mechanical strength of the open-end graphene shells, the strong chemical bonding between Si nanoparticles and graphene, and the strong binding among ASP-Si-G particles and between ASP-Si-G and current collector generated by SA binder contribute to exceptionally high capacity, superior cycling stability, and good rate capability. The composite with SA binder can deliver a specific charge capacity of 2250 mAh g⁻¹ (total mass of Si and graphene) at 0.1C, 1900 mAh g⁻¹ at 1C, 700 mAh g⁻¹ at 12C, and retains 76% of initial capacity after 120 charge/discharge cycles at 1C.

4. Experimental Section

Graphene Oxide (GO) Synthesis: Graphite oxide was synthesized through a modified Hummer’s method. Graphite powder (1 g, synthetic, 99.999%, Sigma Aldrich) and NaNO₃ (0.5 g, reagent plus, Sigma Aldrich) were mixed up with concentrated sulphuric acid (95%–98%, ACS reagent, Sigma Aldrich). Then KMnO₄ (3 g, ACS reagent, Sigma Aldrich) was added into the mixture while stirring in an ice bath, with the temperature maintained below 20 °C. After 10 min, the temperature was brought up to 35 °C and maintained at certain temperature in oil bath. A brown paste was obtained after 30 min. Distilled water (46 mL) was then added into the mixture to dilute the paste and the temperature was increased to 98 °C and held for 15 min. Warm water (140 mL) was further added for dilution and H₂O₂ (20 mL, 30 wt% in H₂O, Sigma Aldrich) was then added into the liquid mixture. Liquid turned golden while adding. Then the resulting mixture was filtered out while hot and the solid (graphite oxide) was carefully dried out.

The fore-mentioned graphite oxide was then dispersed in distilled water and the mixture was sonicated for 30 min using a horn sonicator, followed by another 2 h of sonication in a water bath sonicator, resulting in GO suspension.

Silicon Dispersion and Functionalization: To form a uniform SiO₂ layer on the surface of Si nanoparticles, Si nanoparticles were first oxidized in a mixture of sulphuric acid and hydrogen peroxide. These oxidized Si nanoparticles were then dispersed into distilled water and sonicated for 10 min using a horn sonicator, followed by another 1 h sonication in a water bath sonicator to create a homogenous suspension of Si nanoparticles. 10 wt% aminopropyltrimethoxysilane (APS) (97%, Sigma Aldrich) was added to the Si suspension to functionalize the Si surface, resulting in APS-Si. The mechanism of the reaction involved is shown below.

\[
\text{H}_2\text{SiO}_3 + 2\text{H}_2\text{O} + \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{Si}(\text{CH}_3)_2\text{NH}_2 + 3\text{H}_2\text{O}
\]

Homogenous APS-Si-GO Suspension: Homogenous APS-Si-GO suspension was obtained by slowly adding the aqueous APS-Si suspension into the GO suspension while stirring at room temperature. Terminal NH₃ groups on APS-Si reacts with COOH groups on GO to form an amide bond. Mechanism of reaction involved is shown below.

\[
\text{Si-O} + \text{H}_2\text{COOH} + \text{NH}_3 \rightarrow \text{Si} - \text{COO}\text{H} + \text{NH}_3 \text{O}^-
\]

APS-Si-G Synthesis Using Aerosol Spray Process: Graphene-encapsulated Si (APS-Si-G) powder sample was further synthesized by one-step aerosol technique. The suspension of graphene bonded Si nanoparticles was nebulized by an ultrasonic atomizer. The resulting aerosol droplets were carried by N₂ gas at a flow rate of 1 L/min to flow through a preheated horizontal tube at 700 °C. The bonds between Si nanoparticles and GO, and the rapid solvent evaporation at 700 °C force single-layered graphene to wrap up Si nanoparticles quickly. The resulting graphene encapsulated Si composite was collected by a PTFE membrane. Since the reaction time in the furnace is short (<3 s), GO was partially reduced, and part of the amide bond would survive. This unique structure provides sufficient connection between the two components and good conductivity as well. The resulting APS-Si-G composite appeared as black powder. Graphene-encapsulated Si anode without functionalization was also prepared by similar method.

Materials Characterization: The morphology of the graphene-encapsulated Si was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in the University of Maryland Nanocenter. The percentage of graphene in the composite was determined by thermogravimetric analysis (TGA). Powder sample was loaded into the TGA equipment (CAHN TG 2131, USA) with control bucket. The sample was heated from 200 °C to 750 °C in air atmosphere at a heating rate of 10 °C per min. The APS-Si, GO, and APS-Si-graphene composite samples were characterized by Fourier transform infrared spectroscopy (FTIR) on a high resolution infrared spectrometer (Model 670, Thermo Nicolet,
USA. Powder samples were pressed into pellets and scanned from 4000 cm$^{-1}$ to 650 cm$^{-1}$ in air.

**Electrochemical Testing:** Graphene-encapsulated Si electrodes were prepared by the slurry coating method. The active material was mixed with 10 wt% binder (CMC or sodium alginate) and milled for 30 minutes to form a slurry. Then, the obtained slurry was cast on copper foil and dried in a vacuum oven at 100 °C overnight. The loading amount of active material was 0.5 mg cm$^{-2}$. Coin cells, consisting of a graphene-encapsulated Si working electrode, a lithium metal counter electrode, Celgard 3501 separator, and 1.0 M LiPF$_6$ in dimethyl carbonate (DMC): fluoroethylene carbonate (FEC) (1:1) co-solvent liquid electrolyte, were assembled in an argon-filled glove box for electrochemical tests.

Galvanostatic charge/discharge was performed using an Arbin test station. Cells were cycled between 0.002 V and 1.5 V at different currents. After the cell reached the cut off voltages, it was relaxed for 10 mins before subsequent charge or discharge. Cyclic voltammetry (CV) test with voltage ranging from 0 V to 3 V was performed at a scan rate of 0.1 mV s$^{-1}$ using a Solatron 1260/1287 Electrochemical Interface (Solatron Metrology, UK).

For the rate capability tests, cells were pre-cycled for 20 cycles for activation and then charged-discharged at various C rates between 0.002 V and 1.5 V. The capacity is calculated based on the overall mass of Si and graphene.

**Supporting Information**

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

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