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Dynamics of Electrochemical Lithiation/ Delithiation of Graphene-Encapsulated Silicon Nanoparticles Studied by *In-situ* TEM

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The incorporation of nanostructured carbon has been recently reported as an effective approach to improve the cycling stability when Si is used as high-capacity anodes for the next generation Li-ion battery. However, the mechanism of such notable improvement remains unclear. Herein, we report *in-situ* transmission electron microscopy (TEM) studies to directly observe the dynamic electrochemical lithiation/delithiation processes of crumpled graphene-encapsulated Si nanoparticles to understand their physical and chemical transformations. Unexpectedly, in the first lithiation process, crystalline Si nanoparticles undergo an isotropic to anisotropic transition, which is not observed in pure crystalline and amorphous Si nanoparticles. Such a surprising phenomenon arises from the uniformly distributed localized voltage around the Si nanoparticles due to the highly conductive graphene sheets. It is observed that the intimate contact between graphene and Si is maintained during volume expansion/contraction. Electrochemical sintering process where small Si nanoparticles react and merge together to form large agglomerates following spikes in localized electric current is another problem for batteries. *In-situ* TEM shows that graphene sheets help maintain the capacity even in the course of electrochemical sintering. Such *in-situ* TEM observations provide valuable phenomenological insights into electrochemical phenomena, which may help optimize the configuration for further improved performance.

Si is a promising candidate anode material for the next generation Li-ion battery because of its high capacity, which is up to ten times as that of graphite anodes¹. However, Si inherently suffers from its large volume change (~300%) when alloyed with Li during the typical charge/discharge cycles, which degrades battery performance and causes potential safety issues. Several strategies have been employed to accommodate this dramatic volume change focusing on tailoring specific nanostructures of Si^{2–4} or incorporating with carbon-based materials^{5–10}. However, fundamental understandings of chemical and physical changes during electrochemical lithiation/de-lithiation are vital to design new and efficient electrode materials and to understand the degradation mechanism. The emerging *in-situ* transmission electron microscopy (TEM) techniques with localized electrical measurement capabilities provide a practical platform for investigating electrochemical reactions in Li-ion battery materials by building a full or half “nano-cell” inside the TEM specimen chamber^{11,12}. Such real-time observations of dynamic composition and microstructural evolution in the electrochemical reaction have provided many novel clues to understand the lithiation/de-lithiation mechanisms at nano- or even atomic-scale for several novel anode materials¹³.

Recently, microstructural evolution of pure Si in the electrochemical lithiation/delithiation reaction has been studied^{14–20}. Crystalline Si undergoes a two-phase process upon the first lithiation, with an interface between amorphous Li_xSi phase that is formed during the alloying reaction of Si and Li, and the remainder (unreacted) crystalline Si in the center. This lithiation process is anisotropic and dominated by the alloying reaction at the interface^{14,15,20–23}. At the end of the first lithiation, it has been observed that while amorphous Li_xSi is formed in pure Si nanowire, crystalline Li₁₅Si₄ (capacity of 3579 mAh·g^{−1}) is the final product in carbon coated and P-doped Si nanowires with better electric conductivity thus higher charging rate¹⁹. The phase transformation from amorphous Li_xSi to crystalline Li₁₅Si₄ at the first lithiation could thus be taken as a potent signature of fast and full lithiation process. Biaxial compression stress formed in the amorphous layer is considered as the cause of

mechanical deformation and further damage evolution²⁴. For spherical Si nanoparticles, a critical size of ~ 150 nm has been proposed to be the threshold below which no strain-induced fractures will be generated in Si nanoparticles in the lithiation/delithiation cycles²². Unexpectedly, the lithiation of amorphous Si has similar two-phase process, where the interface is defined between Li-poor core and Li-rich shell regions²⁵. It is noticeable that there is no fracture generated in the amorphous Si nanoparticles with a diameter up to 870 nm, implying the critical threshold for amorphous Si nanoparticles can be much higher than that of the crystalline ones¹⁶.

Carbon based materials have been incorporated with Si as matrix², coating/shell⁶ or simply mixture⁷ to improve the cyclic performance of the Li-ion battery. However, the underlying mechanisms which are crucial to design electrode materials for better performance have not yet been revealed experimentally. Graphene as a novel carbon materials with an array of unique properties has also been utilized to modify the Si anodes⁸. A recent first-principles study²⁶ on the lithiation of Si/Graphene composite shows a significant enhancement of Li mobility at the interface of Si/graphene. Herein, we have studied the electrochemical reactions of Si nanoparticles encapsulated by graphene sheets using *in-situ* transmission electron microscopy (TEM) to understand the effect of graphene sheets on phase transformation and concomitant volume change of embedded Si nanoparticles. Although pure Si nanoparticles (<150 nm) are fracture-free during lithiation/delithiation process, big particles can be formed by the small ones due to the electrochemical sintering and grain growth whenever there are localized spikes in electric current in the charge/discharge cycles. We observed such *in-situ* electrochemical sintering and formation of large Si particles. Surprisingly, the graphene sheets help to hold the sintered and large Si nanoparticles thus retain capacity and cyclability in the course of electrochemical sintering.

Since Si nanoparticles are encapsulated in graphene sheets, lithiation of the graphene sheets is the first process before the lithium ions can penetrate into and react with Si. Because that graphene is a good conductor of both electron and lithium ions, the microstructural change in graphene sheets is too rapid to detect at the beginning of electrochemical lithiation, even after the amorphous Li_xSi layer can be identified (about ~ 10 nm as shown in Fig. 1a). The lithiated graphene sheets did show thicker and thicker fringes along with the lithiation process as shown in Fig. 1b–d. For example, after 253 seconds, the fringe of the lithiated graphene sheets became ~ 6.7 nm in the thickness (Fig. 1d). This increase in the layer thickness is attributed to the formation of LiC_x phase²⁵, though in the current study the sheets are too thin to collect useful electron diffraction or other measurements to identify the structure unambiguously.

The lithiation of crystalline Si nanoparticles encapsulated by the graphene sheets showed many similarities to the pure crystalline Si nanoparticles. Upon first lithiation, a core-shell structure with crystalline Si core and amorphous Li_xSi shell is formed. As shown in Fig. 1e, the interface between amorphous Li_xSi and crystalline Si is clearly seen in the high-resolution TEM image of a partially lithiated Si nanoparticle in the first lithiation cycle. The electron energy loss filtered TEM image in Fig. 1f also clearly indicates that Li is mainly distributed in the outer shell of the Si nanoparticles; which is also an indication that the lithiation process is dominated by the interface reaction. The kinetics of first lithiation of Si/Graphene nanoparticles is similar to that happens in pure crystalline Si nanoparticles. As seen in Fig. 2a–d, an interphase interface forms quickly after applying the biasing voltage, separating the amorphous Li_xSi phase from the crystalline Si core; which shows darker contrast in the images (the corresponding *in-situ* video clip is contained in the Supplementary Movie 1). As the lithiation proceeds, the crystalline Si core shrinks and disappears completely when the first lithiation is complete. By measuring the thickness of lithiated Li_xSi shell as a function of time, the kinetics of the lithiation of Si/Graphene is plotted in Fig. 2e which

shows a parabolic growth behavior. This observation is similar to that of pure crystalline Si nanoparticles without graphene sheets. Here we observed also the slowing of reaction front as it progresses into the particles (e.g. after about 120 seconds), a similar phenomenon observed in pure crystalline Si nanoparticles¹⁵. As shown above, the lithiation behavior of Si/Graphene is similar with pure Si although in principal the Li diffusion can be significantly enhanced by incorporating graphene. The diffusivity of Li in Si is in the order of $\sim 10^{-12} \text{ cm}^2\text{s}^{-1}$ which is orders of magnitude slower than that on graphene (which is $\sim 10^{-6}$ to $10^{-7} \text{ cm}^2\text{s}^{-1}$)⁹. This enhancement of Li mobility is due to the presence of an electric field, which attracts Li cations while repelling Si anions; thereby resulting in a distinct alternative Li–Si layered structure near graphene²⁶. However, the lithiation kinetics could not be dramatically promoted by higher mobility of Li ions since the interface reaction plays a more significant role. It has been gradually recognized that the lithiation is limited by the rate of the reaction at the interface (e.g. the break of Si–Si bond), rather than by the diffusion of lithium through the amorphous phase¹⁵. This explains why the kinetics of Si/Graphene nanoparticles lithiation is similar to that of the pure Si nanoparticles. And the stress field induced by volumetric expansion also largely determines the reaction-rate during lithiation which should be accommodated by elastic deformation of lithiated Si¹⁷. Both of the above two factors contribute to the parabolic growth behavior of the lithiation of crystalline Si. Atomistically, the lithiation kinetics are controlled by the migration of the interface, which occurs through a ledge mechanism involving the lateral movement of ledges on the close-packed $\langle 111 \rangle$ atomic planes¹³. Hence, the lithiation should proceed anisotropically along the preferred growth direction which has been reported to be $\langle 110 \rangle$ ²¹.

Indeed, such anisotropic lithiation has been observed for pure crystalline Si nanoparticles in the first lithiation²². However, we observed isotropic lithiation in the beginning and then anisotropic lithiation in the later stage (when Li_xSi depth reaches ~ 40 nm) for Si nanoparticles uniformly encapsulated by graphene sheets under investigation. As shown in Fig. 3a–f (the corresponding video is in the Supplementary Movie 2) and the illustration in Fig. 3g, the reaction interface between the core (crystalline Si) and shell (amorphous Li_xSi) changes from isotropic to anisotropic as the lithiation proceeds. The Si nanoparticle is consumed isotropically at the beginning and maintains a spherical geometry; but it then gradually develops hexagonal facets; which is a clear sign of anisotropic growth in the later stage of lithiation. We have employed a recently developed kinetic model by Zhao²⁴ to understand this surprising observation:

$$\Delta G = \Delta G_r - e\Phi + \frac{1}{x}(\sigma_m^{\text{Si}}\Omega^{\text{Si}} - \sigma_m^{\text{Li}_x\text{Si}}\Omega^{\text{Li}_x\text{Si}}), \quad (1)$$

where ΔG_r is the free energy of the reaction of $\text{Li} + \frac{1}{x}\text{Si} = \frac{1}{x}\text{Li}_x\text{Si}$; $e\Phi$ is the work done to the nanoparticle by external voltage (Φ is the localized voltage applied to the nanoparticle, and e is the elementary charge); the third term presents the work difference (noted as ΔG_σ) done by stress in crystalline Si and amorphous Li_xSi during the lithiation, σ_m^{Si} and $\sigma_m^{\text{Li}_x\text{Si}}$ are the mean stresses in crystalline Si and amorphous Li_xSi at the reaction front, and Ω^{Si} and $\Omega^{\text{Li}_x\text{Si}}$ are the volume per crystalline Si and amorphous Li_xSi atom. In the case of pure Si nanoparticles undergoing a chemical lithiation (where there is no an external voltage applied and thus external work is this zero)²², the reaction is mainly controlled by the free energy of reaction ΔG_r from the very beginning, which leads to clear isotropic lithiation. In the case of pure Si nanoparticles undergoing an electrochemical lithiation where there an external work applies²², anisotropic lithiation is observed as well, implying the ΔG_r is still the dominant factor. In both cases, however, the energy change related to the stress ΔG_σ is not the dominant factor, although it plays an important role in the formation of fractures²² and slowing down the

Figure 1 | The first lithiation of a graphene sheets encapsulated Si nanoparticle for (a) 43 second; (b) 147 second; (c) 201 second and (d) 253 seconds, respectively. The crystalline Si core and the amorphous Li_xSi shell can be seen and marked in (d). The graphene sheets have very low contrast (too thin to be observed) in (a). They gradually became thicker and thicker as shown from (b) to (d), caused by graphite lithiation. (e) HREM image of the reaction interface between the crystalline Si core and the amorphous Li_xSi shell. (f) Li map of the partially lithiated Si/Graphene nanoparticle closed to the $\text{Li}_2\text{O}/\text{Li}$ probe (as the reference) studied by EELS energy filtered TEM.

lithiation reaction¹⁵. If ΔG_σ became dominant, this would have led to isotropic lithiation because the stress should be the same across the spherical reaction front.

For the graphene sheets encapsulated Si nanoparticles, the graphene sheets might generate an additional compressive stress in the reaction front at the beginning of lithiation, due to the large difference in volume change of graphite and Si when reacted with lithium. This surely will prompt isotropic lithiation. However, such contribution is minor since the graphene layers are quite thin; they are also expandable and shrinkable along with the Si nanoparticles. Meanwhile, the stress formed in $\text{Li}_x\text{Si}/\text{Si}$ increases with the progress of lithiation²⁴, which will quickly put the contribution of the graphene to ΔG_σ in the shadow.

However, for the graphene sheets encapsulated Si nanoparticles, the localized external work $e\Phi$ can be efficiently and uniformly applied to the testing nanoparticles owing to the existence of the highly conductive graphene layers. The reaction is mainly controlled by the external work $e\Phi$ in the initial stage of lithiation (equation 1), which leads to isotropic lithiation. Fig. 1 a–d shows another example of how the external work may have impact on the first lithiation. When a $\text{Li}_2\text{O}/\text{Li}$ probe is directly contact with the Si/Graphene nanoparticle (Fig. 1), the localized external voltage is asymmetrically applied to the nanoparticle due to the damage of the graphene layer on the surface. Such an asymmetric external voltage/work led to the formation of asymmetric lithiated Si, i.e. the Li_xSi layer in the right which is closed to the probe is thicker than that formed in the left in

Figure 2 | The first lithiation of a cluster of graphene sheet encapsulated Si nanoparticles with lithiation time of (a) 9, (b) 66, (c) 247 and (d) 704 seconds. (e) The plot of thickness of lithiated shell as a function of time which shows a parabolic growth behavior, which is not diffusion controlled (as shown by the dotted line).

Figure 3 | The first lithiation of a single graphene sheet encapsulated Si nanoparticles with lithiation time of (a) 0 s, (b) 100 s, (c) 140 s, (d) 200 s, (e) 600 s and (f) 800 s; (g) schematic of isotropic to anisotropic lithiation of crystalline Si nanoparticle. The magnitude of localized external voltage/work applied at the Si/Li_xSi interface (reaction front) decreases along with the lithiation as indicated by read arrows.

Fig. 1d. In the Si/Graphene nanoparticle (Fig. 3a), the localized external voltage is uniformly and almost spherically applied since the Li₂O/Li probe has no direct contact with it. This leads to the isotropic lithiation because the external work $e\Phi$ is uniformly and isotropically applied. Along with the lithiation, a large part of external work $e\Phi$ has been consumed by the lithiated Si layer due to large resistance of Li_xSi. The contribution of the external work $e\Phi$ at the reaction front thus decreases along with the lithiation. In the later stage of lithiation, the reaction is then dominated by its own free energy change (*i.e.* energy difference between breaking of Si-Si bond and formation of Si-Li bond), and there are different reaction rates at different crystalline planes which leads to anisotropic consumption of crystalline Si and formation of facets with projected hexagonal symmetry as seen in Fig. 3f. Therefore, the transition from isotropic to anisotropic growth behavior is attributed to the evolution of localized external work in the reaction front during the lithiation process. The phenomenon is easily observed in Si/Graphene nanoparticles because that graphene layers have much higher electronic and ionic conductivity than those of Si. The external work in the reaction front of the Si/Graphene nanoparticles are efficiently and uniformly applied to the electrode materials due to the existence of the graphene layers with high conductivity. By assuming that the volume of amorphous Li_xSi is the same before the isotropic to anisotropic transition, the critical diameter of Si nanoparticle is estimated at about 67 nm, below which such a transition will not occur. Unlike pure crystalline Si nanoparticle, the lithiation of Si/Graphene nanoparticle is isotropic at the beginning. This could lead to a more uniformly distributed stress in the nanoparticle thus improvement in cycling stability, similar to that with amorphous Si nanoparticles¹⁶.

Loss of necessary intimate physical contact due to large volume change is the other major problem with pure Si nanoparticles in the charge/discharge cycling, which results in fading capacity. Graphene sheets encapsulated Si nanoparticle, on the other hand, show good capacity retention²⁷. Here, our *in-situ* TEM observation show that the graphene sheets always attach to the Si nanoparticles in the lithiation and de-lithiation process. Supplementary Fig. 2a shows the graphene sheets attach to- and grown with- Si nanoparticle while lithiation. Supplementary Fig. 2b shows the morphology of multiple crystalline Si nanoparticles after several lithiation/de-lithiation cycles still remain still covered by and attached to graphene sheets (the

corresponding *in-situ* video clip showing the delithiation process of Si/Graphene nanoparticles is contained in the Supplementary Movie 3). These observations indicate that the graphene sheets help maintain the integrity of multiple Si nanoparticles and maintain electronic and lithium ionic diffusion pathways during charge/discharge cycles. In the case of multiple nanoparticles (see Fig. 2a–d and the corresponding video in the Supplementary Movie 1 and 3), it was observed that Si nanoparticles remain encapsulated in (crumpled) graphene sheets through-out the whole lithiation/delithiation process even if they were confined by the near neighbor nanoparticles. These observations shed considerable light on the real conditions of crystalline Si nanoparticles' reaction during cycling, and offer guidance to better design nanostructured Si and other anode materials involving inevitable large volume expansion. It could be inferred from these observations that the multilayer graphene sheets protect and accommodate large volume expansion during lithiation, and thus help to maintain a fast charge-discharge rate in cycling.

The phase transformation of Si in the *in-situ* lithiation/delithiation reactions has been studied by electron diffraction. As shown in Supplementary Fig. 3a, the diffraction pattern taken from a partially lithiated Si/Graphene nanoparticles consists of diffraction spots from crystalline Si (core) and diffuse diffraction rings from amorphous Li_xSi shell. At the late stage of the first lithiation, a phase transformation from amorphous Li_xSi to nano-sized crystal Li₁₅Si₄ can be identified, as shown in Supplementary Fig. 3b, a nano-beam diffraction taken by a small electron probe of ~40 nm. The single crystal like pattern can be indexed using Li₁₅Si₄ lattice structure and a simulated pattern is shown in Supplementary Fig. 3c for comparison. Such a phase transformation in Si during lithiation is consistent with those observed in the carbon coated and P-doped Si nanowires¹⁹ and pure Si nanoparticles^{12,28}. After the first lithiation, the Si remains amorphous in the subsequent delithiation and lithiation cycles²⁹.

Although the stress in the reaction interface can be altered by the graphene sheets, the graphene sheets are too thin to avoid fractures when there is a large volume expansion in Si nanoparticle in lithiation. As shown in Supplementary Fig. 4 and Supplementary Movie 4, a small crack starts to form at the surface of the Si/Graphene nanoparticle when the lithiation depth is only ~65 nm. The existence of thin graphene sheets does not alter the stress distribution in the late

stage of lithiation; and thus has little contribution to the formation of crack and propagation of fracture path.

One strategy to prevent fracture and pulverization of Si particles during charge/discharge cycling is to use nanostructured Si, *e.g.* Si nanoparticles less than 150 nm seem remain fracture-free²². However, electrochemical sintering process caused by localized spikes in current/voltage often degrades the performance of these nanostructured Si anodes. The lithiation-induced neck flattening of two a-Li_xSi particles has been reported on the crystalline Si particles with a size of ~ 100 nm³⁰. Although electrochemical sintering is not common in commercial batteries where electrodes are made of bulk materials, it has been demonstrated as a cause of capacity degradation in electrodes made of nanomaterials^{32–36}. In our experiments, an abrupt electrochemical sintering process is observed for graphene encapsulated crystalline Si nanoparticles. Fig. 4a shows a group of crystalline Si nanoparticles with an average size of a few tens of nanometers wrapped in crumpled graphene which are connected with Li₂O/Li through a carbon nanotube (used to provide good contact). When there is a sudden spike in current caused by the instant connection of the carbon nanotube and the particles cluster, the crystalline Si nanoparticles instantly sinter together and fill the capsule of the graphene sheets as shown in Fig. 4b (and the Supplementary Movie 5). When the contact formed, the electric current could jumped to 1 mA which was the limit set by the holder and last for only few seconds, while the electric current is normally less than 100 nA when -3 V bias is applied. Surprisingly, the large sintered Si nanoparticles encapsulated inside the graphene sheets functioned quite well in the subsequent lithiation/delithiation cycles, enduring large volume changes as shown in Fig. 4c–h. The lithiation/delithiation rate afterward the electrochemical sintering is high, due to a high carbon/Si mass ratio in the observed nanoparticles and a good electric conductor formed by sintering. The abnormal abrupt electrochemical sintering was caused by abrupt contact between the graphene and the carbon nanotube in this specific experiment but is highly possible in the real battery electrode materials where local contacts of nanostructures having large volume variation in charge/discharge cycling. This observation demonstrates that small

crystalline Si nanoparticles alone may not be stable under external voltage and could not maintain their original morphology in the charge/discharge cycling. On the other hand, it shows that the graphene sheets can act as a stronghold to confine the sintering process in the capsule and a “cushion” to hold the large particles formed, which may contribute to maintaining the high capacity in charge/discharge cycling. Similar observations were reported with the emphasis on the contribution of the voids formed by graphene layers³¹. Such *in-situ* TEM observation gives us insights into the dynamics during charge/discharge process and helps to highlight the role of the graphene sheets in nanostructured Si anode. A reasonable mass ratio between graphene and Si nanoparticles is important to keep high capacity and cycling stability in the event of electrochemical sintering. When there is too little graphene, it will be too fragile to hold the products. On the other hand, the capacity will be low if there are too many graphene layers.

In summary, we have studied the lithiation and delithiation process of graphene encapsulated crystalline Si nanoparticles by *in-situ* TEM. In the first lithiation, the crystalline Si nanoparticles show a transition from isotropic to anisotropic lithiation presented by a spherical to a (projected) hexagonal faceted core along with the electrochemical reaction. It is largely attributed to the change in the localized external voltage/work applied in the reaction interface between amorphous Li_xSi shell and crystalline Si core. The highly conductive graphene sheets improve the efficiency of the external voltage/work applied to nanostructured electrode materials. The formation of the Li₁₅Si₄ phase in 1st lithiation is an indication that the lithiation/delithiation of the crumpled graphene encapsulated Si nanoparticle is fast and complete, due to high electronic and ionic conductivity of the graphene backbone. Meanwhile, the graphene sheets plays a significant role to maintain the integrity of the crystalline Si nanoparticles during the lithiation and delithiation process, *i.e.* they always attach to the surface of Si nanoparticles facilitating fast Li ion diffusion through their interface and accommodate volume/shape/stress changes. We also demonstrated that graphene can be used to effectively confine the electrochemical sintering of small crystalline Si nanoparticles and maintain the storage capacity

Figure 4 | The sintering process of small Si nanoparticles encapsulated by graphene sheets. (a) The pristine small Si nanoparticles encapsulated in graphene sheets; (b) sintered big Si particles encapsulated in graphene sheets; (c)–(e): lithiation process of the as-sintered Si particles, (f)–(h) delithiation process of the as-sintered Si particles. The scale bar is 200 nm. (i) Schematic of the electrochemical sintering and protection provided by graphene sheets.

even with ubiquitous spikes in charge/discharge processes. These findings offer guidance to designing of improved nanostructured Si materials as fast and large-capacity anode materials for lithium ion batteries.

Methods

The graphene-encapsulated Si nanoparticles (Si/Graphene) were synthesized by a rapid, one-step capillary-driven assembly route in aerosol droplets as reported²⁷. The *in-situ* TEM experiments were performed on a specified electrical probing TEM holder (Nanofactory Instrument AB). This holder has a dual-probe design as shown in Supplementary Fig. 1a (schematic) and Supplementary Fig. 1b (bright-field TEM image), i.e. one Au rod is used as the sample holder with a small amount of Si/Graphene dispersed on its tip; on the other side a STM tungsten (W) probe driven by Piezo-motor capable of 3-D positioning with a step-size of 1 nm is used to mount Li metal. The W probe tip was scratched by Li metal strip and then affixed on the TEM holder inside an Ar-filled glove box. With an airtight cover, the TEM holder was transferred to TEM column with limited exposure to air (~5 s), where a layer of lithium oxide was grown on the surface of Li metal and was acted as a solid electrolyte for the nano-cell Li-ion batteries. The lithium ion (Li^+) in Li_2O can be differentiated from the neutral Li atom (Li^0) in metallic Li by electron energy loss spectroscopy (EELS). We did EELS mappings on the sample to confirm that the Si/Graphene nanoparticles were directly touched merely the Li_2O as shown in Supplementary Fig. 1c–f. This was to ensure an electrochemical lithiation instead of chemical lithiation would happen when a biasing was applied. When the Au rod was negatively biased to -3 V, charging for Si/Graphene nanoparticles occurred, corresponding to the electrochemical lithiation of the nanoparticles. When a potential of positive $+3$ V was applied, it was discharging process which delithiation reaction of the nanoparticles would occur. The voltage is higher than that when the battery performance measurements was made²⁵. This was largely due to the onset potential for solid electrolyte Li_2O in the *in-situ* observations. While the Si/Graphene was directly approached by a thin layer of $\text{Li/Li}_2\text{O}$, we chose not to use such a directly connecting area to perform *in-situ* observations. This was to prevent the electron-beam sensitive $\text{Li/Li}_2\text{O}$ from disintegration which would lead to lose contact between the Si/Graphene nanoparticles and $\text{Li/Li}_2\text{O}$. In some cases, carbon nanotubes were also employed as the support of the Si/Graphene nanoparticles so that it was easy to make contact between the two electrodes (Fig. 4a). This could also prevent the chemical lithiation of Si/graphene nanoparticles which would happen when Li metal was directly in contact with the nanoparticles.

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Author contributions

L.L. and J.W. designed and executed the TEM experiments, analyzed data and wrote the manuscript with advice of V.P.D. J.L., J.H. synthesized the Si/Graphene samples and tested their performance as anode in Li-ion batteries. All the authors discussed the results and commented on the manuscript.

Additional information

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This Article contains an error in the order of the Supplementary Information movies. Supplementary Information “movie2” and “movie3” were published as “movie3” and “movie2”, respectively.

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