# Surface Oxidation Layer-Mediated Conformal Carbon Coating on Si Nanoparticles for Enhanced Lithium Storage

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**ABSTRACT:** Si is a well-known high-capacity lithium-ion battery anode material; however, it suffers from conductivity and volume expansion issues. Herein, we develop a "surface oxidation" strategy to introduce a SiO<sub>x</sub> layer on Si nanoparticles for subsequent carbon coating. It is found that the surface SiO<sub>x</sub> layer could facilitate the conformal resin coating process through strong interactions with phenolic resin, and well-defined core@double-shell-structured Si@SiO<sub>x</sub>@C can be obtained after further carbonization. Without the surface SiO<sub>x</sub> layer, only a negligible fraction of Si nanoparticles can be encapsulated into the carbon matrix. With enhanced conductivity and confined volume change, Si@SiO<sub>x</sub>@C demonstrates high reversible capacity as well as long-term durability.

KEYWORDS: silicon, silicon oxide, conformal carbon coating, core@double-shell structure, volume expansion

## 1. INTRODUCTION

Lithium-ion batteries (LIBs) have played significant roles in the modern society since 1990s owing to their high energy density and durability.<sup>1–8</sup> Currently, commercialized LIBs generally employ  $Li_4Ti_5O_{12}$  or graphite in the anode. Nevertheless, the performances of such batteries cannot meet the ever-increasing requirements partly due to the unsatisfactory capacity and high working potential of  $Li_4Ti_5O_{12}^{9}$  as well as the safety issue of graphite.<sup>10</sup> This situation necessitates novel anode materials with high capacity, suitable working potential, and better safety.<sup>11,12</sup>

Si is a promising LIB anode material,<sup>8,13–19</sup> not only because of its abundance and low cost but also due to its high theoretical capacity.<sup>20–24</sup> In addition, the suitable Li<sup>+</sup> insertion/extraction potential of Si greatly alleviates the formation of Li dendrites.<sup>25</sup> Nevertheless, the widespread application of Si is faced with low conductivity<sup>26,27</sup> and a large volume change,<sup>28–30</sup> leading to active material pulverization, detachment from the current collector, and repeated generation and rupture of the solid electrolyte interface (SEI) film.<sup>31–33</sup> These limitations eventually give rise to poor cycling and rate behaviors, seriously restricting the practical applications.

Encapsulating nanosized Si in a highly conductive carbon matrix has been employed to boost the conductivity and to mitigate the volume change of Si.<sup>13,34–43</sup> As a result, rationally designed Si/C composites usually demonstrate enhanced cyclability and rate capability compared with bare Si. However, the conformal coating of carbon onto Si is difficult owing to its relatively inert surface. Herein, we develop a "surface oxidation" method to introduce a SiO<sub>x</sub> layer on Si nanoparticles through annealing in air to facilitate the subsequent conformal carbon coating. Through strong hydrogen-bonding interactions, phenolic resin can be easily coated onto the SiO<sub>x</sub>-modified Si nanoparticles and then converted into a conformal carbon

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Figure 1. Schematic illustration for synthesizing core@double-shell-structured Si@SiO<sub>x</sub>@C and Si/C.



Figure 2. (a) SEM, (b, c) TEM, (d) HAADF-STEM images, (e) EDS spectra, and (f-j) EDS mappings of Si@SiO<sub>x</sub>@C (corresponding to d).

coating shell. The obtained material  $(Si@SiO_x@C)$  possesses a well-defined core@double-shell structure with enhanced conductivity and structural stability. As expected,  $Si@SiO_x@C$  demonstrates high reversible capacity as well as long-term durability.

# 2. EXPERIMENTAL SECTION

**Synthesis of Materials.** SiO<sub>x</sub>-modified Si nanoparticles (denoted as Si@SiO<sub>x</sub>) were synthesized by calcinating pristine Si nanoparticles at 600 °C for 4 h in air. The conformal coating of Si@SiO<sub>x</sub> with carbon was realized through a facile self-catalyzed polymerization approach. Typically, 0.2 g of Si@SiO<sub>x</sub> was first dispersed in 50 mL of deionized

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Figure 3. (a) XRD patterns of Si@SiO<sub>x</sub>@C, Si@SiO<sub>x</sub>, and Si; (b) Raman spectra of Si@SiO<sub>x</sub>@C and Si@SiO<sub>x</sub>; (c) TGA curves of Si@SiO<sub>x</sub>@C, Si/C, Si@SiO<sub>x</sub>, and Si; and (d) high-resolution Si2p XPS spectra of Si@SiO<sub>x</sub>@C, Si@SiO<sub>x</sub>, and Si.

water. Then, 0.16 g of 3-aminophenol and 0.2 g of hexamethylenetetramine (HMTA) were added. The dispersion was then heated to 85 °C and kept at 85 °C for 24 h under constant stirring. The collected intermediate (Si@SiO<sub>x</sub>@resin) was annealed at 800 °C for 4 h in Ar to obtain Si@SiO<sub>x</sub>@C. Si/C was synthesized by replacing Si@SiO<sub>x</sub> with bare Si under the same conditions. Pure carbon microspheres (CSs) were obtained by the same method without adding Si@SiO<sub>x</sub>. Si@ SiO<sub>x</sub>@C with a lower carbon content was prepared by increasing the Si@SiO<sub>x</sub> feeding amount to 0.4 g.

## 3. RESULTS AND DISCUSSION

The construction of core@double-shell-structured Si@SiO<sub>x</sub>@C generally involves three steps-surface oxidation, conformal resin coating, and carbonization (Figure 1). Specifically, the pristine Si nanoparticles are first calcined in air to introduce a surface SiO<sub>r</sub> layer on Si. Then, the 3-aminophenol-formaldehyde resin is coated conformally onto Si@SiO<sub>x</sub> through a self-catalyzed polymerization reaction, leading to the formation of Si@SiO<sub>x</sub>@resin. Finally, the Si@SiO<sub>x</sub>@resin is carbonized at 800 °C in Ar, and the core@double-shell-structured Si@SiO<sub>x</sub>@ C can be obtained. It should be mentioned that the introduction of a surface  $SiO_r$  layer is beneficial for the subsequent successful conformal carbon coating due to the strong interactions between the surface  $SiO_x$  and functional groups (-OH and  $-NH_2$ ) of the 3-aminophenol-formaldehyde resin. Without such a surface SiO<sub>x</sub> layer, only a small fraction of the pristine Si nanoparticles can be encapsulated into the carbon spheres, leading to a mixture of bare Si nanoparticles, carbon spheres, and carbon-coated Si (Si@C), and the sample is designated as Si/C.

Bare Si nanoparticles are generally round in shape with an average size of around 100 nm (Figure S1). Calcination of Si nanoparticles in air at 600 °C does not alter the overall morphology and size obviously (Figure S2a,b). However, one can notice that the sample after calcination presents an obvious core@shell structure in a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image

(Figure S2c). The core shows a brighter contrast, whereas the shell shows a darker contrast. The thickness of the shell is ~15 nm. Energy-dispersive X-ray spectroscopy (EDS) mappings clearly demonstrate that the core region consists of pure Si, while the shell region consists of both Si and O. These HAADF-STEM image and EDS mappings suggest that the calcination of Si nanoparticles in air introduces a uniform SiO<sub>x</sub> shell on their surface, and thus the sample after calcination is designated as Si@SiO<sub>x</sub>.

Si@SiO<sub>x</sub>@C obtained after coating Si@SiO<sub>x</sub> with the resin and carbonization is composed of irregularly shaped submicron particles with sizes of 200–400 nm (Figure 2a,b). The obvious increase in the particle size suggests the coating of carbon on  $Si@SiO_x$ . A small fraction of submicron spheres, which may be pure carbon spheres, can also be observed in Si@SiO<sub>x</sub>@C (Figure 2a, indicated by red arrows). Transmission electron microscopy (TEM) images clearly show the successful envelop of Si@SiO<sub>x</sub> nanoparticles with a darker contrast in the carbon matrix with a brighter contrast (Figure 2b,c). As displayed in Figure 2d, the conformal carbon coating presents a uniform thickness of ~100 nm. EDS spectra (Figure 2e) are obtained at the core and shell regions of a single Si@SiO<sub>x</sub>@C particle. The EDS spectra reveal that the core and shell consist of  $Si@SiO_r$ and N-doped carbon, respectively. The HAADF-STEM image (Figure 2d) and its corresponding EDS mappings (Figure 2f-j) further confirm the successful conformal coating of N-doped carbon on Si@SiO<sub>x</sub>. HAADF-STEM and EDS mappings are conducted on a few particles, and all of the results confirm the Si@SiO<sub>x</sub>@C core@double-shell structure of the products (Figure S3). To further demonstrate the uniform carbon coating, the Si@SiO<sub>x</sub>@C particles are subjected to HF etching, which selectively removes  $Si@SiO_r$  but leaves the carbon. Hollow carbon particles with a uniform shell thickness of  $\sim 100$ nm can be obtained (Figure S4) after HF etching, confirming the successful conformal coating. The conformal coating of www.acsami.org



**Figure 4.** (a) CV profiles and (b) representative GCD profiles of Si@SiO<sub>x</sub>@C; cycling performances of Si@SiO<sub>x</sub>@C and Si/C at (c) 200 mA g<sup>-1</sup> and (d) 500 mA g<sup>-1</sup>; and (e) rate performances of Si@SiO<sub>x</sub>@C and Si/C. For (d), the samples are activated at 200 mA g<sup>-1</sup> for 5 cycles and then cycled at 500 mA g<sup>-1</sup>.

carbon on Si $@SiO_x$  can be attributed to the introduction of a SiO<sub>x</sub> intermediate layer, which provides strong interactions with the 3-aminophenol-formaldehyde resin (carbon precursor) through hydrogen bonding. When applied in lithium storage, the SiO<sub>x</sub> intermediate layer and conformal N-doped carbon shell are highly beneficial for alleviating the volume variation of Si nanoparticles and improving the ionic/electrical conductivity.

The control samples are also characterized by scanning electron microscopy (SEM) and TEM. The CSs derived from the self-polymerization of 3-aminophenol and HMTA are composed of uniform carbon spheres with diameters of ~1  $\mu$ m (Figure S5). Without the surface SiO<sub>x</sub> layer, only a very small fraction of Si nanoparticles can be encapsulated into the carbon matrix, and a mixture of Si nanoparticles, carbon spheres, and Si@C is obtained (Figure S6).

Figure 3a displays the X-ray diffraction (XRD) data of Si@  $SiO_x @C, Si@SiO_x$  and pure Si. All three samples present peaks at  $2\theta$  = 28.4, 47.3, 56.1, 69.1, and 76.4°, which are characteristics of crystalline Si. The N-doped carbon shows an amorphous feature, as evidenced by the absence of diffractions for carbon in the XRD pattern of Si@SiO, @C. Si@SiO, @C and Si@SiO, present a sharp band at  $\sim 506$  cm<sup>-1</sup> and a weak one at 928 cm<sup>-1</sup> in Raman spectra (Figure 3b), corresponding to the Si-Si stretching.<sup>44,45</sup> In addition, Si@SiO<sub>x</sub>@C presents a broad D band (1338 cm<sup>-1</sup>) and a G band (1588 cm<sup>-1</sup>), which are characteristics of carbon. The comparable D and G band intensities confirm the amorphous characteristic of carbon. Thermogravimetric analysis (TGA) is conducted to monitor the carbon contents of samples (Figure 3c). Compared to pure Si,  $Si@SiO_x$  shows a lower weight gain at temperatures above 800 °C, which originates from the preoxidation of Si to  $SiO_x$ . For Si@SiO<sub>x</sub>@C, the combustion of amorphous carbon causes a sharp weight loss at ~550 °C, and the carbon accounts for ~62.7 wt % of the total weight. N2 sorption is employed to determine the surface area (Figure S7). Si@SiO<sub>x</sub> shows a smaller surface area  $(3.0 \text{ m}^2 \text{ g}^{-1})$  than Si@SiO<sub>x</sub>@C  $(146.1 \text{ m}^2 \text{ g}^{-1})$ .

The surface composition and valence states are characterized by X-ray photoelectron spectroscopy (XPS). Considering that the effective detecting depth of XPS is less than 10 nm, Si@  $SiO_{r} @C$  is subjected to  $Ar^{+}$  etching before measurement. The survey spectrum of Si@SiO<sub>x</sub>@C exhibits a stronger C 1s signal than those of Si@SiO<sub>r</sub> and Si (Figure S8). The Si 2p core-level spectra (Figure 3d) of all three samples show five Si components:  $Si^{4+}$  (103.9 eV),  $Si^{3+}$  (102.8 eV),  $Si^{2+}$  (101.6 eV),  $Si^{+}$  (100.1 eV), and  $Si^{0}$  (98.7 eV).<sup>46</sup> The average Si-valence states of Si, Si@SiO<sub>x</sub>, and Si@SiO<sub>x</sub>@C are calculated to be 0.74, 1.83, and 1.72, respectively. In detail, the surface of Si is dominated by Si<sup>0</sup> as expected; after surface oxidation, the Si<sup>3+</sup> component increases sharply. After further resin coating and carbonization, the  $Si^{4+}$ ,  $Si^{2+}$ , and  $Si^+$  species increase obviously, which may be caused by the disproportionation of Si<sup>3+</sup> during carbonization. The C 1s spectrum of Si@SiO<sub>x</sub>@C (Figure S8b) can be deconvoluted into sp<sup>2</sup>-bonded C (C=C), C-O or C-N bond, and C=O bond.<sup>47</sup> The N 1s core-level spectrum (Figure S8c) is dominated by quaternary N, pyrrolic N, and pyridinic N<sup>48</sup>, indicating that the amorphous carbon is doped by nitrogen. The O 1s spectrum (Figure S8d) is dominated by Si–O–Si, C– O-C, and Si-O-C.

Figure 4a presents the cyclic voltammetry (CV) profiles of  $Si@SiO_x@C$ . Two reduction peaks are observed at 1.34 and 0.60 V of the first cathodic process. Both peaks disappear in the subsequent cycles, suggesting that such peaks originate from the decomposition of the fluoroethylene carbonate (FEC) and/or carbonic ester-based electrolyte. As for the subsequent cycles, the redox peaks can be ascribed to the alloying/dealloying reaction (Si + x Li<sup>+</sup> + x e<sup>-</sup>  $\leftrightarrow$  Li<sub>x</sub>Si). The overlapping CV curves since the second cycle indicate the good electrochemical reversibility of Si@SiO<sub>x</sub>@C.

Representative galvanostatic charge/discharge (GCD) profiles of Si@SiO<sub>x</sub>@C are displayed in Figure 4b. Si@SiO<sub>x</sub>@C manifests a relatively low first-cycle Coulombic efficiency (CE) of 64.4%, which is attributed to irreversible Li<sup>+</sup> consumption,



Figure 5. Schematic illustrations showing the structure evolution of (a) Si@SiO<sub>x</sub>@C and (b) pristine Si nanoparticles during cycling.

such as SEI formation and lithium trapping in the active material. To meet the requirements of practical uses, the low first-cycle CE issue can be improved through prelithiation strategies.<sup>50-52</sup>

Figure 4c compares the cycling performances at 200 mA g<sup>-1</sup>. Although Si/C possesses a higher first discharge capacity, the capacity declines quickly upon cycling. On the contrary, Si@ $SiO_x$ @C demonstrates a much better cyclability, maintaining 770 mAh g<sup>-1</sup> after 50 cycles. For comparison, the cycling performances and representative GCD profiles of the bare Si, Si@SiO<sub>x</sub>, and CSs are provided in Figures S9 and S10. The much-improved cycling stability of Si@SiO<sub>x</sub>@C compared to the control samples verifies the important role of conformal N-doped carbon coating in alleviating the volume variation. The long-term cycling performances are presented in Figure 4d. After 500 cycles, the Si@SiO<sub>x</sub>@C still keeps a high capacity (739 mAh g<sup>-1</sup>); the capacity retention is 94.4% to the sixth cycle. In contrast, the retained capacity of Si/C is just 284 mAh g<sup>-1</sup>, and the retention is only 46.7% to the sixth cycle.

Besides high capacity and improved cyclability,  $Si@SiO_x@C$  also manifests an ideal rate capability. The  $Si@SiO_x@C$  delivers a capacity of 343 mAh  $g^{-1}$  at 5 A  $g^{-1}$  (Figures 4e and S11). Furthermore, the capacity can be restored to 849 mAh  $g^{-1}$  when the current density shifts back to 200 mA  $g^{-1}$ . Compared to previous reports (Table S1),  $Si@SiO_x@C$  exhibits competitive lithium storage properties.  $Si@SiO_x@C$  with a lower carbon content is also synthesized. Although the  $Si@SiO_x@C$  with a lower carbon content presents a higher capacity, its cyclability is not as good as the  $Si@SiO_x@C$  with a higher carbon content (Figure S12).

Figure S13 presents the electrochemical impedance spectra (EIS) plots, from where the Warburg impedance (*W*) and charge-transfer resistance ( $R_{ct}$ ) can be determined.<sup>53</sup> Before cycling (Figure S13a), Si@SiO<sub>x</sub>@C shows an  $R_{ct}$  value of 41.2  $\Omega$ ; after 100 cycles (Figure S13b), the  $R_{ct}$  increases slightly to 57.7  $\Omega$ . On the contrary, the  $R_{ct}$  of Si@SiO<sub>x</sub> increases quickly from 79.8 to 185.0  $\Omega$ . The EIS results verify the vital role of the N-doped carbon coating in enhancing the conductivity.

The large volume variation and unsatisfactory structural stability represent significant challenges for alloying-type anode materials. The structural stability is studied by ex situ SEM (Figures S14 and S15) and TEM (Figure S16). Severe cracking could be observed for the Si@SiOx-based electrode after 100 cycles (Figure S14b). In addition, the electrode thickness increases sharply from 17.4 to 24.8  $\mu$ m, and the thickness expansion ratio reaches 42.5% (Figure S15b). In contrast, the Si@SiO<sub>x</sub>@C-based electrode shows excellent structural integrity (Figure S14d). After 100 cycles, the thickness of the electrode increases slightly from 14.5 to 15.4  $\mu$ m, corresponding to an alleviated thickness expansion of 6.2% (Figure S15d). The HAADF-STEM image and EDS mappings of Si@SiO, @C after cycling are provided in Figure S16. The core@double-shell structure is well maintained after 100 deep discharge-charge cycles, verifying its ideal structural integrity. The ex situ SEM and TEM reveal the important role of carbon coating in suppressing the volume expansion and maintaining the structural integrity, which are responsible for the boosted cycling stability of Si@ SiO"@C.

The structure evolution of  $Si@SiO_x@C$  and bare Si nanoparticles during cycling is schematically presented in Figure 5. For  $Si@SiO_x@C$ , although the volume change of Si is unavoidable, the  $SiO_x$  layer and carbon shell could suppress the huge volume variation of Si and improve its structural stability. Consequently, stable cycling can be achieved. However, for bare Si nanoparticles, the repeated volume variation/contraction unavoidably leads to pulverization and an unstable SEI film. As a result, the bare Si nanoparticles suffer from poor cyclability. Considering the fact that most of the Si nanoparticles in Si/C have not been coated with carbon, it is not surprising that Si/C exhibits unsatisfactory cycling stability.

By coupling with the LiFePO<sub>4</sub> cathode materials, Si@SiO<sub>x</sub>@ C//LiFePO<sub>4</sub> and Si/C//LiFePO<sub>4</sub> full-cells are assembled. The commercial LiFePO<sub>4</sub> cathode material exhibits a discharge plateau at 3.4 V with very stable cycling (Figure S17). The Si@ SiO<sub>x</sub>@C//LiFePO<sub>4</sub> full-cell inherits the ideal cycling stability of LiFePO<sub>4</sub> (Figure 6). However, the voltage plateau of the full-cell

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Figure 6. (a) Representative GCD profiles and (b) cycling performance of the Si@SiO<sub>x</sub>@C//LiFePO<sub>4</sub> full-cell at 0.2 C (1 C = 170 mA g<sup>-1</sup>).

is lowered to around 3.1 V. Based on the weight of LiFePO<sub>4</sub>, the Si@SiO<sub>x</sub>(@C//LiFePO<sub>4</sub> full-cell manifests a high reversible capacity (143.2 mAh g<sup>-1</sup>) and maintains 131.9 mAh g<sup>-1</sup> after 100 cycles. In contrast, the Si/C//LiFePO<sub>4</sub> full-cell demonstrates very poor cyclability (Figure S18). Its capacity decays to only 25 mAh g<sup>-1</sup> after 100 cycles, which is due to the pulverization of Si.

#### 4. CONCLUSIONS

In conclusion, a surface oxidation strategy has been developed to optimize the subsequent carbon encapsulation process and thus lithium storage performance of Si nanoparticles. The surface  $SiO_x$  layer facilitates the conformal coating of resin, which is then converted into N-doped carbon, through hydrogen bonding. Without the surface  $SiO_x$  layer, only a very small fraction of Si nanoparticles can be encapsulated into carbon. The N-doped carbon coating improves the conductivity as well as the structural integrity of  $Si@SiO_x$ . As a consequence, the core@ double-shell-structured  $Si@SiO_x@C$  demonstrates significantly improved cycling stability. This contribution highlights the significant role of interactions between active materials and carbon precursors in fabrication of high-performance carbon-coated electrode materials.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c19673.

SEM, TEM, HAADF-STEM images and EDS mappings of Si nanoparticles, Si@SiO<sub>x</sub>, Si@SiO<sub>x</sub>@C, Si/C; TEM images of the hollow carbon particles; N<sub>2</sub> adsorption/ desorption isotherms; XPS survey spectra; cycling performances and selected GCD profiles; charge– discharge curves of Si@SiO<sub>x</sub>@C at various current densities; lithium storage performances of various Sibased anode materials; and electrochemical impedance spectroscopy plots (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Dunn, B.; Kamath, H.; Tarascon, J. M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334*, 928–935.

(2) Yang, Z.; Zhang, J.; Kintner Meyer, M. C.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **2011**, *111*, 3577–3613.

(3) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. J. Am. Chem. Soc. **2013**, 135, 1167–1176.

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(4) Sun, Y.; Liu, N.; Cui, Y. Promises and Challenges of Nanomaterials for Lithium-Based Rechargeable Batteries. *Nat. Energy* **2016**, *1*, No. 16071.

(5) Choi, J. W.; Aurbach, D. Promise and Reality of Post-Lithium-Ion Batteries with High Energy Densities. *Nat. Rev. Mater.* **2016**, *1*, No. 16013.

(6) Liu, Z.; Yu, Q.; Zhao, Y.; He, R.; Xu, M.; Feng, S.; Li, S.; Zhou, L.; Mai, L. Silicon Oxides: A Promising Family of Anode Materials for Lithium-Ion Batteries. *Chem. Soc. Rev.* **2019**, *48*, 285–309.

(7) Liu, Z.; Zhao, Y.; He, R.; Luo, W.; Meng, J.; Yu, Q.; Zhao, D.; Zhou, L.; Mai, L. Yolk@Shell SiO<sub>x</sub>/C Microspheres with Semi-Graphitic Carbon Coating on the Exterior and Interior Surfaces for Durable Lithium Storage. *Energy Storage Mater.* **2019**, *19*, 299–305.

(8) Zhang, Y.; Hu, G.; Yu, Q.; Liu, Z.; Yu, C.; Wu, L.; Zhou, L.; Mai, L. Polydopamine Sacrificial Layer Mediated SiO<sub>x</sub>/C@C Yolk@Shell Structure for Durable Lithium Storage. *Mater. Chem. Front.* **2020**, *4*, 1656–1663.

(9) Liu, J.; Pang, W. K.; Zhou, T.; Chen, L.; Wang, Y.; Peterson, V. K.; Yang, Z.; Guo, Z.; Xia, Y. Li<sub>2</sub>TiSiO<sub>5</sub>: A Low Potential and Large Capacity Ti-Based Anode Material for Li-Ion Batteries. *Energy Environ. Sci.* **2017**, *10*, 1456–1464.

(10) Zhang, Y.; Du, F.; Yan, X.; Jin, Y.; Zhu, K.; Wang, X.; Li, H.; Chen, G.; Wang, C.; Wei, Y. Improvements in the Electrochemical Kinetic Properties and Rate Capability of Anatase Titanium Dioxide Nanoparticles by Nitrogen Doping. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4458–4465.

(11) Hu, G.; Zhong, K.; Yu, R.; Liu, Z.; Zhang, Y.; Wu, J.; Zhou, L.; Mai, L. Enveloping  $SiO_x$  in N-Doped Carbon for Durable Lithium Storage Via an Eco-Friendly Solvent-Free Approach. *J. Mater. Chem. A* **2020**, *8*, 13285–13291.

(12) Dunn, J.; Gaines, L.; Kelly, J.; James, C.; Gallagher, K. The Significance of Li-Ion Batteries in Electric Vehicle Life-Cycle Energy and Emissions and Recycling's Role in Its Reduction. *Energy Environ. Sci.* **2015**, *8*, 158–168.

(13) Xie, C.; Xu, Q.; Sari, H. M. K.; Li, X. Elastic Buffer Structured Si/ C Microsphere Anodes Via Polymerization-Induced Colloid Aggregation. *Chem. Commun.* **2020**, *56*, 6770–6773.

(14) Wang, J.; Liao, L.; Lee, H. R.; Shi, F.; Huang, W.; Zhao, J.; Pei, A.; Tang, J.; Zheng, X.; Chen, W.; et al. Surface-Engineered Mesoporous Silicon Microparticles as High-Coulombic-Efficiency Anodes for Lithium-Ion Batteries. *Nano Energy* **2019**, *61*, 404–410.

(15) Hu, Y.-S.; Demir-Cakan, R.; Titirici, M.-M.; Müller, J.-O.; Schlögl, R.; Antonietti, M.; Maier, J. Superior Storage Performance of a Si@SiO<sub>x</sub>/C Nanocomposite as Anode Material for Lithium-Ion Batteries. *Angew. Chem., Int. Ed.* **2008**, 47, 1645–1649.

(16) Tao, H.-C.; Huang, M.; Fan, L.-Z.; Qu, X. Interweaved  $Si@SiO_x/C$  Nanoporous Spheres as Anode Materials for Li-Ion Batteries. *Solid State Ionics* **2012**, 220, 1–6.

(17) Lee, J. K.; Oh, C.; Kim, N.; Hwang, J.-Y.; Sun, Y.-K. Rational Design of Silicon-Based Composites for High-Energy Storage Devices. *J. Mater. Chem. A* **2016**, *4*, 5366–5384.

(18) Luo, W.; Chen, X.; Xia, Y.; Chen, M.; Wang, L.; Wang, Q.; Li, W.; Yang, J. Surface and Interface Engineering of Silicon-Based Anode Materials for Lithium-Ion Batteries. *Adv. Energy Mater.* **2017**, *7*, No. 1701083.

(19) Yang, J.; Wang, Y.; Li, W.; Wang, L.; Fan, Y.; Jiang, W.; Luo, W.; Wang, Y.; Kong, B.; Selomulya, C. Amorphous  $TiO_2$  Shells: A Vital Elastic Buffering Layer on Silicon Nanoparticles for High-Performance and Safe Lithium Storage. *Adv. Mater.* **2017**, *29*, No. 1700523.

(20) Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G. Li-Ion Battery Materials: Present and Future. *Mater. Today* **2015**, *18*, 252–264.

(21) Obrovac, M.; Krause, L. Reversible Cycling of Crystalline Silicon Powder. J. Electrochem. Soc. **2007**, *154*, A103–A108.

(22) Wang, D.; Gao, M.; Pan, H.; Wang, J.; Liu, Y. High Performance Amorphous-Si $@SiO_x/C$  Composite Anode Materials for Li-Ion Batteries Derived from Ball-Milling and in Situ Carbonization. *J. Power Sources* **2014**, 256, 190–199.

(23) Jiang, B.; Zeng, S.; Wang, H.; Liu, D.; Qian, J.; Cao, Y.; Yang, H.; Ai, X. Dual Core-Shell Structured Si@SiO<sub>x</sub>@C Nanocomposite Synthesized Via a One-Step Pyrolysis Method as a Highly Stable Anode Material for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31611–31616.

(24) Zhang, F.; Zhu, G.; Wang, K.; Qian, X.; Zhao, Y.; Luo, W.; Yang, J. Boosting the Initial Coulombic Efficiency in Silicon Anodes through Interfacial Incorporation of Metal Nanocrystals. *J. Mater. Chem. A* **2019**, *7*, 17426–17434.

(25) Chandrasekaran, R.; Magasinski, A.; Yushin, G.; Fuller, T. F. Analysis of Lithium Insertion/Deinsertion in a Silicon Electrode Particle at Room Temperature. *J. Electrochem. Soc.* **2010**, *157*, A1139–A1151.

(26) Pollak, E.; Salitra, G.; Baranchugov, V.; Aurbach, D. In Situ Conductivity, Impedance Spectroscopy, and Ex Situ Raman Spectra of Amorphous Silicon During the Insertion/Extraction of Lithium. *J. Phys. Chem.* C **2007**, *111*, 11437–11444.

(27) Zhou, S.; Fang, C.; Song, X.; Liu, G. The Influence of Compact and Ordered Carbon Coating on Solid-State Behaviors of Silicon During Electrochemical Processes. *Carbon Energy* **2020**, *2*, 143–150.

(28) McDowell, M. T.; Lee, S. W.; Harris, J. T.; Korgel, B. A.; Wang, C.; Nix, W. D.; Cui, Y. In Situ Tem of Two-Phase Lithiation of Amorphous Silicon Nanospheres. *Nano Lett.* **2013**, *13*, 758–764.

(29) McDowell, M. T.; Lee, S. W.; Nix, W. D.; Cui, Y. 25<sup>th</sup> Anniversary Article: Understanding the Lithiation of Silicon and Other Alloying Anodes for Lithium-Ion Batteries. *Adv. Mater.* **2013**, *25*, 4966–4985.

(30) Zhang, Y.; Mu, Z.; Lai, J.; Chao, Y.; Yang, Y.; Zhou, P.; Li, Y.; Yang, W.; Xia, Z.; Guo, S. Mxene/Si@SiO<sub>x</sub>@C Layer-by-Layer Superstructure with Autoadjustable Function for Superior Stable Lithium Storage. *ACS Nano* **2019**, *13*, 2167–2175.

(31) Wu, J.; Cao, Y.; Zhao, H.; Mao, J.; Guo, Z. The Critical Role of Carbon in Marrying Silicon and Graphite Anodes for High-Energy Lithium-Ion Batteries. *Carbon Energy* **2019**, *1*, 57–76.

(32) Yim, C.-H.; Courtel, F. M.; Abu-Lebdeh, Y. A High Capacity Silicon-Graphite Composite as Anode for Lithium-Ion Batteries Using Low Content Amorphous Silicon and Compatible Binders. *J. Mater. Chem. A* **2013**, *1*, 8234–8243.

(33) Zhu, G.; Zhang, F.; Li, X.; Luo, W.; Li, L.; Zhang, H.; Wang, L.; Wang, Y.; Jiang, W.; Liu, H. K.; Dou, S.; Yang, J. Engineering the Distribution of Carbon in Silicon Oxide Nanospheres at the Atomic Level for Highly Stable Anodes. *Angew. Chem., Int. Ed.* **2019**, *58*, 6669– 6673.

(34) Tao, H.-C.; Fan, L.-Z.; Qu, X. Facile Synthesis of Ordered Porous Si@C Nanorods as Anode Materials for Li-Ion Batteries. *Electrochim. Acta* **2012**, *71*, 194–200.

(35) Wu, H.; Yu, G.; Pan, L.; Liu, N.; McDowell, M. T.; Bao, Z.; Cui, Y. Stable Li-Ion Battery Anodes by in-Situ Polymerization of Conducting Hydrogel to Conformally Coat Silicon Nanoparticles. *Nat. Commun.* **2013**, *4*, No. 1943.

(36) Ko, M.; Chae, S.; Ma, J.; Kim, N.; Lee, H.-W.; Cui, Y.; Cho, J. Scalable Synthesis of Silicon-Nanolayer-Embedded Graphite for High-Energy Lithium-Ion Batteries. *Nat. Energy* **2016**, *1*, No. 16113.

(37) Xu, Q.; Li, J. Y.; Sun, J. K.; Yin, Y. X.; Wan, L. J.; Guo, Y. G. Watermelon-Inspired Si/C Microspheres with Hierarchical Buffer Structures for Densely Compacted Lithium-Ion Battery Anodes. *Adv. Energy Mater.* **2017**, *7*, No. 1601481.

(38) Son, Y.; Ma, J.; Kim, N.; Lee, T.; Lee, Y.; Sung, J.; Choi, S. H.; Nam, G.; Cho, H.; Yoo, Y.; et al. Quantification of Pseudocapacitive Contribution in Nanocage-Shaped Silicon-Carbon Composite Anode. *Adv. Energy Mater.* **2019**, *9*, No. 1803480.

(39) Zhang, H.; Zhang, X.; Jin, H.; Zong, P.; Bai, Y.; Lian, K.; Xu, H.; Ma, F. A Robust Hierarchical 3D Si/CNTs Composite with Void and Carbon Shell as Li-Ion Battery Anodes. *Chem. Eng. J.* **2019**, *360*, 974– 981.

(40) Zhang, Y.-C.; You, Y.; Xin, S.; Yin, Y.-X.; Zhang, J.; Wang, P.; Zheng, X.-S.; Cao, F.-F.; Guo, Y.-G. Rice Husk-Derived Hierarchical Silicon/Nitrogen-Doped Carbon/Carbon Nanotube Spheres as Low-Cost and High-Capacity Anodes for Lithium-Ion Batteries. *Nano Energy* **2016**, *25*, 120–127.

(41) Gao, R.; Tang, J.; Yu, X.; Tang, S.; Ozawa, K.; Sasaki, T.; Qin, L.-C. In Situ Synthesis of MOF-Derived Carbon Shells for Silicon Anode

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with Improved Lithium-Ion Storage. Nano Energy 2020, 70, No. 104444.

(42) Yan, Z.; Jin, H.; Guo, J. Low-Temperature Synthesis of Graphitic Carbon-Coated Silicon Anode Materials. *Carbon Energy* **2019**, *1*, 246–252.

(43) Luo, W.; Wang, Y.; Chou, S.; Xu, Y.; Li, W.; Kong, B.; Dou, S. X.; Liu, H. K.; Yang, J. Critical Thickness of Phenolic Resin-Based Carbon Interfacial Layer for Improving Long Cycling Stability of Silicon Nanoparticle Anodes. *Nano Energy* **2016**, *27*, 255–264.

(44) Li, B.; Qi, R.; Zai, J.; Du, F.; Xue, C.; Jin, Y.; Jin, C.; Ma, Z.; Qian, X. Silica Wastes to High-Performance Lithium Storage Materials: A Rational Designed Al<sub>2</sub>O<sub>3</sub> Coating Assisted Magnesiothermic Process. *Small* **2016**, *12*, 5281–5287.

(45) Park, M.-H.; Kim, M. G.; Joo, J.; Kim, K.; Kim, J.; Ahn, S.; Cui, Y.; Cho, J. Silicon Nanotube Battery Anodes. *Nano Lett.* **2009**, *9*, 3844– 3847.

(46) Ren, Y.; Li, M. Facile Synthesis of SiO<sub>x</sub>@C Composite Nanorods as Anodes for Lithium Ion Batteries with Excellent Electrochemical Performance. J. Power Sources **2016**, 306, 459–466.

(47) Wang, J.; Liu, H.; Diao, J.; Gu, X.; Wang, H.; Rong, J.; Zong, B.; Su, D. Size-Controlled Nitrogen-Containing Mesoporous Carbon Nanospheres by One-Step Aqueous Self-Assembly Strategy. *J. Mater. Chem. A* **2015**, *3*, 2305–2313.

(48) Wickramaratne, N. P.; Xu, J.; Wang, M.; Zhu, L.; Dai, L.; Jaroniec, M. Nitrogen Enriched Porous Carbon Spheres: Attractive Materials for Supercapacitor Electrodes and CO<sub>2</sub> Adsorption. *Chem. Mater.* **2014**, *26*, 2820–2828.

(49) Xia, Q.; Wang, B.; Wu, Y.; Luo, H.; Zhao, S.; Van Ree, T. Phenyl Tris-2-Methoxydiethoxy Silane as an Additive to PC-Based Electrolytes for Lithium-Ion Batteries. *J. Power Sources* **2008**, *180*, 602–606.

(50) Liu, N.; Hu, L.; McDowell, M. T.; Jackson, A.; Cui, Y. Prelithiated Silicon Nanowires as an Anode for Lithium Ion Batteries. *ACS Nano* **2011**, *5*, 6487–6493.

(51) Forney, M. W.; Ganter, M. J.; Staub, J. W.; Ridgley, R. D.; Landi, B. J. Prelithiation of Silicon-Carbon Nanotube Anodes for Lithium Ion Batteries by Stabilized Lithium Metal Powder (SLMP). *Nano Lett.* **2013**, *13*, 4158–4163.

(52) Zhao, J.; Lu, Z.; Liu, N.; Lee, H.-W.; McDowell, M. T.; Cui, Y. Dry-Air-Stable Lithium Silicide-Lithium Oxide Core-Shell Nanoparticles as High-Capacity Prelithiation Reagents. *Nat. Commun.* **2014**, *5*, No. 5088.

(53) Cao, X.; Chuan, X.; Li, S.; Huang, D.; Cao, G. Hollow Silica Spheres Embedded in a Porous Carbon Matrix and Its Superior Performance as the Anode for Lithium-Ion Batteries. *Part. Part. Syst. Charact.* 2016, 33, 110–117.