Bowl-like 3C-SiC Nanoshells Encapsulated in Hollow Graphitic Carbon Spheres for High-Rate Lithium-Ion Batteries

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ABSTRACT: Searching for new electrode materials with high capacities and excellent rate performance is crucial for the development of next-generation lithium-ion batteries (LIBs). Silicon carbide (SiC), which is traditionally considered to be electrochemically inert toward lithiation, has recently been demonstrated to be a potential high-performance anode material upon activation by surface graphitization. Despite the great potential, it remains a grand challenge to synthesize SiC nanostructures with precisely controlled morphologies and surface properties, due to the rather high reaction temperatures (>1200 °C) typically required for SiC crystallization. Herein, we designed and synthesized a novel type of SiC nanostructures in which bowl-like, ultrathin SiC nanoshells were encapsulated in hollow graphitic carbon spheres (designated as SiC@HGSs), which exhibited unexpectedly high electrochemical performance when used as LIB anodes. SiC@HGSs retained a stable capacity of 1345 mAh g⁻¹ at a current density of 0.6 A g⁻¹ after 600 cycles and 742 mAh g⁻¹ at 3 A g⁻¹ after 1000 cycles. Even at a high current density of 6 A g⁻¹, SiC@HGSs could still deliver a capacity of ~400 mAh g⁻¹. The superior high-rate performance is attributable to the unique architecture and exceptional structural durability of SiC@HGSs.

INTRODUCTION

The growing demand for portable electronic devices and electrical vehicles has stimulated significant interest in developing lithium-ion batteries (LIBs) with high energy and power densities.¹ sla Progress in LIBs lies in large part on the performance of electrodes. Currently, the dominant anode material in commercial LIBs is graphite; however, its low capacity (~370 mAh g⁻¹) and poor high-rate capability can hardly meet the stringent requirements for next-generation LIBs. Consequently, tremendous efforts have been focused on high-capacity anode materials such as Si,⁶ Sn,⁶–⁹ SnO₂¹⁰–¹² and transition metal oxides¹¹–¹⁵ over the past few years. Despite the great promise, these materials typically suffer from drastic volumetric changes caused by repeated lithium insertion and extraction, which can lead to fast capacity decay and poor rate performance.¹⁶ While these problems could, in principle, be partially addressed by a number of strategies, such as nanostructuring,¹⁷–¹⁹ carbon coating,²₀ and structural design,²¹–²⁴ several issues still exist in implementing the aforementioned anodes within commercialized batteries. Therefore, there is still an urgent need for searching for alternative anode materials with high capacities, long-term cycling stabilities, and excellent rate capabilities.

Silicon carbide (SiC), as a conventional wide band gap semiconductor, has been widely implemented in high-temperature semiconducting devices,²⁵,²⁶ and graphene growth substrates,²⁷,²⁸ due to its low thermal expansion coefficient, chemical inertness, and mechanical durability. In terms of LIB applications, unfortunately, SiC was traditionally considered to be electrochemically inert,²⁹,³⁰ such that it has been mainly used as a structural reinforcement agent to couple with high-capacity materials such as Si and SnO₂ for forming composite anodes.³¹–³³ Thanks to the recent extensive research in Si-based anodes, a number of studies have shown that lithium ions can intercalate into the lattices of SiC upon appropriate structural design and surface modification,³⁴–³⁷ suggesting that SiC could be electrochemically active toward lithium storage. Indeed, several groups have reported the use of SiC as anode materials for LIBs. For instance, Xu et al. demonstrated that SiC thin films exhibited a good cycling stability up to 60 cycles.³⁶ Kumar et al. reported that 3C-SiC nanoparticles could deliver a reversible capacity of ~1200 mAh g⁻¹ at a low current density of 23 mA g⁻¹.³⁸ Although it is becoming increasingly
evident that SiC could be used as an active material for LIB anodes, the battery performance currently achievable is far inferior to that of the well-known anode materials mentioned above.

More recently, Hersam et al.\textsuperscript{39} reported that the lithium-storage capacity of SiC substrates could be increased by an order of magnitude upon the growth of an epitaxial layer of graphene. The enhanced performance is mainly attributed to the graphene layer, which not only improves electrical conductivity but also inhibits the oxidation of SiC, thereby facilitating the intercalation of lithium ions into SiC lattices. This result strongly suggests that the lithium-storage properties of SiC could be further substantially improved by surface graphitization, which combined with deliberate structural design may lead to high-performance SiC anodes. However, graphitization, which not only improves electrical conductivity but also inhibits the oxidation of SiC, thereby enhancing performance, is mainly attributed to the graphene layer, which not only improves electrical conductivity but also inhibits the oxidation of SiC, thereby facilitating the intercalation of lithium ions into SiC lattices.

RESULTS AND DISCUSSION

Synthesis of Poly(methylacrylic acid) (PMAA) Spheres. Mono-disperse PMAA spheres with a mean diameter of 220 nm were synthesized by distillation precipitation polymerization of methacrylic acid (MMA), with 1,1'-methylene bis(acrylamide) (MBA) and azodisobutyronitrile (AIBN) as the cross-linker and the initiator, respectively. Typically, 3 mL of MMA, 750 mg of MBA, and 75 mg of AIBN were dispersed in 300 mL of acetonitrile under sonication in a dried sealed round-bottomed flask, equipped with a fractionation column, a condenser, and a receiver. The reaction mixture was heated from room temperature to the boiling state within 30 min, and the reaction was completed after distilling off 150 mL of acetonitrile within 1 h. The resultant PMAA spheres were collected by centrifugation and washed with ethanol three times to remove unreacted monomers and oligomers.

Synthesis of PMAA@SiO\textsubscript{2}@RF Spheres. PMAA spheres were sequentially coated with SiO\textsubscript{2} and resorcinol-formaldehyde (RF) shells through a two-step sol–gel process, resulting into PMAA@SiO\textsubscript{2}@RF double-shelled spheres. In a typical synthesis, 400 mg of PMAA spheres was dispersed in 80 mL of ethanol, into which 5.3 mL of aqueous ammonia solution (25 wt %) and 16 mL of tetraethoxysilane (TEOS) solution (10 vol % in ethanol) were sequentially added under stirring. After 12 h, 12 mL of deionized water, 2.7 mL of aqueous ammonia solution (25 wt %), 600 mg of resorcinol, and 0.84 mL of formaldehyde solution were added. The reaction mixture was stirred for 24 h at room temperature and then transferred to a 150 mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 160 °C under argon, during which the PMAA core decomposed to afford a hollow structure. In the meantime, the outer RF shells were carbonized into highly graphitic carbon, which simultaneously reacted with the inner SiO\textsubscript{2} shells, converting them into SiC with a bowl-like morphology. Figure 1b shows the TEM image of 220 nm (±15 nm) PMAA spheres used in this work, which were synthesized by distillation precipitation polymerization. By the conventional Stöber method,\textsuperscript{46-47} the negatively charged PMAA spheres could be easily coated with a uniform SiO\textsubscript{2} shell with a thickness of 25 nm (±3 nm) to afford PMAA@SiO\textsubscript{2} spheres (Figure 1c). Without purification, the resulting PMAA@SiO\textsubscript{2} spheres were then coated with a RF sequentially coated with SiO\textsubscript{2} and RF shells by a two-step sol–gel process.

Synthesis of SiC@HGSs. In a typical procedure to synthesize SiC@HGSs, 2 g of dried PMAA@SiO\textsubscript{2}@RF spheres were placed in a graphite crucible, which was then heated in a tube furnace 1600 °C under Ar for 6 h. Characterization. Scanning electron microscopy (SEM) images were taken on a Zeiss-Ultra55 scanning electron microscope operated at 3 kV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and high-angle annular dark-field, scanning TEM (HAADF-STEM) images and elemental mapping were obtained using a Tecnai G2 20 TWIN microscope operated at 200 kV. Raman spectra were recorded on an XploRA Raman system. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA instrument at a heating rate of 20 °C min\textsuperscript{-1} in air. Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D4 X-ray diffractometer over a scan range 10°–80°.

Electrochemical Measurements. Electrochemical properties of SiC@HGSs were evaluated using coin-type half cells (2016R), which were assembled in an argon-filled glovebox (Unilab from mBraun). The working electrodes were prepared by a slurry coating procedure. The slurry consisted of SiC@HGSs, acetylene black, and polyvinylidene fluoride (PVDF) binder with a mass ratio of 7:2:1 dissolved in N-methyl-2-pyrrolidinone. This slurry was spread on a copper foil, which acted as a current collector. The electrodes were dried at 90 °C for 4 h in air, and then at 90 °C in vacuum for another 12 h. Lithium metal foil was used as the counter electrode. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (Autolab 204 N). Galvanostatic measurements were performed on a Neware cell test instrument (Shenzhen Neware Electronic Co., Ltd. China), which was cycled between 0.01 and 3.0 V (vs Li/Li\textsuperscript{+}) at various current densities.
shell by *in situ* polymerization of resorcinol and formaldehyde, yielding PMAA@SiO2@RF spheres (Figure 1d). The RF shell thickness was tunable in the range 40–95 nm by varying the concentration of resorcinol (*Figure S1*, Supporting Information). Interestingly, the inner PMMA core collapsed upon the sequential growth of SiO2 and RF shells (Figure 1d and Figure S1), probably caused by the partial dissolution of PMAA during the two-step overcoating process. Nonetheless, the spherical morphology and size monodispersity of the original PMAA spheres were well-preserved in PMAA@SiO2@RF spheres.

To enable SiC@HGSs, PMAA@SiO2@RF spheres were simply heated at 1600 °C under argon for 6 h. The RF shell thickness was found to have a profound influence on the formation of SiC@HGSs. Thermal treatment of PMAA@SiO2@RF spheres having a RF shell thickness of 40 nm (±3 nm) yielded irregular particles (*Figure S2a*), the crystal structure of which was ascribed to low-cristobalite (JCPDF 99-0039) as indicated by XRD (*Figure 2b*). The formation of low-cristobalite suggested that the amount of pyrolytic carbon derived from 40 nm RF shells was insufficient to convert SiO2 into SiC. SiC@HGSs could be obtained only when the RF shell was thicker than 50 nm (±4 nm) (*Figure S2c–e*). Shown in *Figure 2a–c* are TEM images of SiC@HGSs derived from PMAA@SiO2@RF spheres having an RF shell thickness of 50, 75, and 95 nm, respectively, indicating that all three samples exhibited a hollow structure containing SiC (*Figure 1d*), with an outer shell thickness of 8 (±1.5) and 45 (±2.1) nm, respectively. HAADF-STEM and elemental mapping further confirmed the existence of SiC within hollow spheres (*Figure 2d*), while the close contact between SiC and the outer graphitic shell could be clearly observed by HRTEM (*Figure 2e*). The lattice fringes with an interplanar spacing of 0.217 nm (±0.02 nm) could be well indexed to the (200) plane of 3C-SiC (*Figure 2e*), which possessed a high single-crystallinity as indicated by selected-area electron diffraction (SAED, *Figure 2e*, inset).

Further structural characterization was carried out using XRD. As shown in *Figure 3a*, all three SiC@HGS samples showed major peaks indexed to 3C-SiC (JCPDS 29-1129). Notably, a small peak at 34° (indicated by the arrow) that was attributed to the (101) reflection of 6H-SiC (JCPDS 75-1541) was also observed in all cases, indicating the coexistence of 6H-SiC as a minor phase with 3C-SiC. Importantly, the diffraction peaks of low-cristobalite were not observed in the XRD patterns of all SiC@HGS samples, implying the complete conversion of SiO2 into SiC. The diffraction peak located at 26° was ascribed to the (002) plane of graphite, suggesting that the outer graphitic shells possessed a high graphitization degree, which was corroborated by HRTEM (*Figure 2e*) and Raman spectroscopy (*Figure 3b*), as evidenced by the well-separated D and G bands as well as the well-resolved 2D band at ∼2700 cm−1.48–50 The sharp D band was indicative of the presence of a significant amount of disordered carbon,49,50 which could be attributed to the structural defects arising from the spherical curvature of carbon shells. As indicated by TGA (*Figure 3c*), the carbon content of SiC@HGSs with a graphitic shell thickness of 8, 28, and 45 nm was determined to be ∼22% (±2.7%), 44% (±1.9%), and 70% (±1.1%), respectively. For simplicity, SiC@HGSs with a carbon content of X% were denoted as SiC@G-X. SEM and TEM established that the residual SiC species after TGA measurements possessed a bowl-like morphology with a thickness of 20 nm (±1.3 nm) (*Figure 3d*), which was slightly thinner than that of the original SiO2 shells (∼25 ± 3 nm).

Presumably, SiC was formed through a carbothermic reduction reaction between SiO2 and carbon occurring at 1600 °C. The overall reaction can be written as follows:

\[
\text{SiO}_2(s, l) + 3\text{C}(s) \rightarrow \text{SiC}(s) + 2\text{CO}(g)
\]

As has been proposed previously,42,51 the overall carbothermal reaction was a result of two consecutive reactions involving a gaseous intermediate identified as silicon monoxide (SiO). Namely, SiO2 reacted with carbon through a solid–solid or solid–liquid reaction in the first step, producing gaseous SiO and CO:

\[
\text{SiO}_2(s, l) + \text{C}(s) \rightarrow \text{SiO}(g) + \text{CO}(g)
\]

The resulting SiO species then reacted with carbon in the second step, yielding solid SiC and CO:

\[
\text{SiO}(g) + 2\text{C}(s) \rightarrow \text{SiC}(s) + \text{CO}(g)
\]

We speculate that the original spherical SiO2 shells collapsed during the carbothermic reduction process due to the gaseous SiO and CO species generated, giving rise to the observed bowl-like SiC nanoshells.

To investigate electrochemical performance, SiC@HGSs with various carbon contents (i.e., SiC@G-X) were tested as anode materials for LIBs, which were cycled on the basis of a half-cell configuration. For comparison, the carbon-coated commercial 3C-SiC nanoparticles with a diameter of ∼20 nm and a carbon content of 20% (denoted as Com-SiC@C) were also tested under identical conditions (*Figure S3*). *Figure 4a* shows the cyclic voltammograms (CVs) of SiC@G-22 anodes for the initial 3 cycles in the potential range of 0–3.0 V (vs Li+/Li−). The irreversible peak at ∼0.70 V was attributed to the formation of solid–electrolyte interphase (SEI)42–54 in accordance with that of Com-SiC@C (*Figure S4*) and...
previously reported SiC anodes. As shown in the galvanostatic charge/discharge voltage profiles (Figure S5a), SiC@G-22 anodes delivered the initial discharge and charge capacities of 1944 and 700 mAh g\(^{-1}\), respectively, at a current density of 0.6 A g\(^{-1}\). In addition, no obvious voltage plateaus were observed in the first discharge process, indicative of no resemblance to that of silicon\(^{55}\) or carbon,\(^{56}\) consistent with Com-SiC@C anodes (Figure S5b). The second-cycle discharge capacity of SiC@G-22 anodes was 792 mAh g\(^{-1}\) (with a Coulombic efficiency of 79.2%, Figure S5a), corresponding to 40.7% of the initial discharge capacity. The reduced capacity and relatively low first-cycle Coulombic efficiency was mainly due to graphitic shells present in SiC@G-22 as well as the irreversible SEI formation.\(^{57,58}\)

The rate capability of SiC@G-22 anodes was evaluated at various current densities ranging from 0.06 to 6 A g\(^{-1}\), as shown in Figure 4b. Surprisingly, SiC@G-22 anodes delivered a stable capacity of 1068, 595, and 395 mAh g\(^{-1}\) at current densities of 1.2, 3, and 6 A g\(^{-1}\), respectively, demonstrating superior high-rate performance. In addition, a capacity over 1370 mAh g\(^{-1}\) could be recovered when the current density was switched back to 0.6 A g\(^{-1}\). The long-term cycling performance of SiC@G-22 anodes was tested at a current density of 0.6 A g\(^{-1}\), as presented in Figure 4c. It is interesting to note that the specific capacity of SiC@G-22 anodes initially decayed until 40 cycles and then started to increase gradually, retaining a highly stable capacity of 1345 mAh g\(^{-1}\) after 600 cycles. In comparison, although the capacity of Com-SiC@C anodes also continuously increased after the initial 50 cycles, the specific capacity after 600 cycles was only 350 mAh g\(^{-1}\), much lower than that of SiC@G-22 anodes (Figure 4c, black curve). The capacity increase, which has been commonly observed previously in metal-oxide anodes,\(^{65-72}\) could be attributed to the activation of electrode materials\(^{65-68}\) or side reactions involving the reversible growth of polymeric gel-like films.\(^{69-72}\) Recently, Jie Lian and co-workers have reported that the high-rate lithiation-induced reconstruction could favor the formation of a stable SEI layer, which might explain the observed capacity increase commonly observed in metal-oxide anodes.\(^{73}\) In terms of SiC, as has been proposed previously,\(^{39}\) the capacity of SiC could be activated upon the growth of an epitaxial layer of graphene, while the native oxide layer at SiC surface was detrimental for capacity activation. We hypothesize that, in the current case, the intimate contact between SiC and graphitic shells greatly facilitates electronic and ionic transport while effectively suppressing the oxidation of SiC, which combined with the possible high-rate lithiation-induced reactivation improves the capacity retention of SiC@G-22 anodes upon extended cycling.

To investigate the influence of the thickness of graphitic shells on the electrochemical performance, LIB anodes based on SiC@G-X were cycled at a high current density of 3 A g\(^{-1}\), as shown in Figure 4d. Similar to the case of SiC@G-22 anodes...
cycled at 0.6 A g\(^{-1}\), the initial specific capacity of both SiC@G-22 and SiC@G-44 decreased until 50 and 100 cycles, respectively, and then started to increase, retaining a reversible capacity of 742 and 589 mAh g\(^{-1}\) after 1000 cycles, respectively. In contrast, SiC@G-70 anodes maintained a relatively stable yet low capacity at 109 mAh g\(^{-1}\) for 500 cycles. Apparently, the relatively low capacity of SiC@G-44 and SiC@G-70 anodes was primarily attributed to the low weight percentage of SiC. In addition, one could also reasonably expect that the thicker graphitic shells in SiC@G-44 and SiC@G-70 could impede the intercalation and extraction of lithium ions at high current densities.

**Figure 4.** (a) Representative CVs of SiC@G-22 anodes at a scan rate of 0.2 mV s\(^{-1}\). (b) Rate capabilities of SiC@G-22 anodes at current densities ranging from 0.06 to 6 A g\(^{-1}\). (c) Cycling performance and the corresponding Coulombic efficiencies of SiC@G-22 and Com-SiC@C anodes at 0.6 A g\(^{-1}\). (d) Cycling performance of SiC@G-22, SiC@G-44, and SiC@G-70 anodes and the corresponding Coulombic efficiencies at 3 A g\(^{-1}\).

cycled at 0.6 A g\(^{-1}\) for 500 times. SEM indicated that SiC@G-22 distributed uniformly throughout the entire electrode after extended cycling (Figure 5b and Figure S7), while TEM revealed that the hollow structure of SiC@G-22 remained intact (Figure 5b, inset), although the outer shell thickness increased from 8 to 20 nm due to the SEI formation. As revealed by XRD (Figure 5c), SiC@G-22 anodes predominantly maintained a highly crystalline 3C-SiC structure under both lithiation and delithiation conditions, although the peak intensity slightly decreased in the lithiation state, presumably originating from the insertion of lithium ions into SiC lattices. As proposed previously, the intercalation of lithium ions in 3C-SiC is similar to the case of the lithium-implanted zinc blende III–V semiconductors, in which lithium ions occupy the two crystallographically independent sites at (\(1/4, 1/4, 1/4\)) and (\(1/2, 1/2, 1/2\)) with minor perturbation to the lattices, as depicted in Figure 5d. Despite the largely retained crystal structure, it should be noted that the small peak at 34° corresponding to 6H-SiC became more pronounced after cycling (Figure 5c). In addition, two new peaks at 23.5° and 37.9° emerged after cycling, which could be indexed to the (004) and (103) reflections of 6H-SiC, respectively. These results suggested that a small portion of 3C-SiC was transformed into 6H-SiC during cycling, in agreement with the previously reported results. Nonetheless, the minimal structural change upon extended cycling explains the exceptional structural durability and therefore excellent cycling stability of SiC@G-22 anodes.
CONCLUSION

In summary, monodisperse hollow graphitic carbon spheres containing ultrathin, bowl-like 3C-SiC nanoshells were designed and synthesized on the basis of a templating strategy coupled with a carbothermal reduction process. Owing to their unique architectures, SiC@HGSs displayed unexpectedly excellent high-rate performance, retaining a stable capacity of 1345 mAh g\(^{-1}\) at a current density of 0.6 A g\(^{-1}\) after 600 cycles and 742 mAh g\(^{-1}\) at 3 A g\(^{-1}\) after 1000 cycles, which combined with the low cost and environmental benignity of SiC strongly suggests the great potential of SiC@HGSs for high-performance LIB anodes. Our studies may shed light on the development of electrode materials and indicate that many traditionally inert materials such as SiC are worthy of reconsideration, and may display remarkably high lithium-storage properties upon deliberate structural design and surface modification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b04750.

TEM images, SEM images, XRD patterns, TGA curve, CVs, and galvanostatic charge/discharge voltage profiles (PDF)

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Notes

The authors declare no competing financial interest.

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