Superior and Reversible Lithium Storage of SnO$_2$/Graphene Composites by Silicon Doping and Carbon Sealing

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ABSTRACT: The poor cycle stability and reversibility seriously hinder the widespread application of SnO$_2$ materials as anodes for lithium-ion batteries (LIBs). A novel sandwich-architecture composite of Si-doped SnO$_2$ nanorods and reduced graphene oxide with carbon sealing (Si-SnO$_2$@G@C) is engineered and fabricated by a facile two-step hydrothermal process and subsequent annealing treatment, which exhibit not only extraordinary rate performance and ultrahigh reversible capacity but also excellent cycle stability and high electrical conductivity as the anode of LIBs. The Si-doped SnO$_2$ nanoparticles on the surface of graphene were firmly wrapped in the C-coating and formed a porous sandwich structure, which can efficiently prevent the Sn nanoparticles from aggregation and provide more extra space for accommodating the volume variations and more active sites for reactions. The carbon layer also blocks the direct contact of the SnO$_2$ nanorods with electrolyte and prevents the graphene nanosheets from the restacking. More importantly, the reversibility of lithiation/delithiation reactions can be remarkably improved by the doping silicon. The doped Si not only accelerates the diffusion of Li$^+$ but also brings a significant increase in the specific capacity. As a consequence, the Si-SnO$_2$@G@C nanocomposite can maintain a high capacity of 654 mAh/g at 2 A/g even after 1200 cycles with negligible capacity loss and excellent reversibility with a Coulombic efficiency retention over 99%, which can be capable of the alternative to commercial graphite anodes. This work provides a new strategy for the reasonable design of advanced anode materials with superior and reversible lithium storage capacity.

KEYWORDS: SnO$_2$, silicon doping, graphene, carbon sealing, lithium-ion battery

1. INTRODUCTION

The invention of lithium-ion battery (LIBs) opens the process of electronic device portability. Compared with other conventional secondary batteries, lithium-ion batteries are increasingly showing advantages, such as small size, light weight, long life span, excellent environmental protection, and high energy density. Owing to the above characteristics, LIBs are widely applied in power tools, electric vehicles, military equipment, aerospace, and many other fields. Nevertheless, one of the major challenges that restrict its development is to seek alternative electrode materials with high specific capacity to replace the commercial graphite anodes. It has a limited specific capacity of 372 mAh/g and poor rate performance. In recent years, great efforts have been devoted to build hybrid architectures using the materials with high specific capacity for LIB anode, such as metal oxides. As an alternative anode material, SnO$_2$ with high theoretical capacity (ca. 1493 mAh/g), low cost, and environmental benignity has attracted many explorations on its lithium storage mechanism and practical application. Although it has quite high specific capacity, the drastic capacity fading during the charge/discharge process cannot be neglected, which is due to the huge volume variation (~300%) and the aggregation of tin particles during the lithiation/delithiation reaction. Moreover, the poor reversibility is also an important factor that hinders its extensive application in the anode materials for LIBs. Therefore, great efforts should be made to overcome these challenges of SnO$_2$-based materials for their practical applications.

It was reported that constructing nanostructure and compositing with carbon materials could effectively promote the electrochemical performance of SnO$_2$ materials by buffering the volume expansion and alleviating the diffusion-induced strains during the charge/discharge processes.

There have been many successful cases of synthesizing the composites of a carbonaceous matrix, especially graphene, and SnO$_2$ nanoparticles to overcome the shortcomings of SnO$_2$ as anode materials of LIBs, such as graphene networks...
encapsulating hollow SnO$_2$ nanostructures, an ultrafine SnO$_2$/graphene nanocomposite, skeleton-structured SnO$_2$/graphene composite spheres, a sandwiched spherical graphene wrapping SnO$_2$ nanoparticle composite, and so on. Nevertheless, it still needs further amelioration, as the weak interaction and nonintimate contact between graphene nanosheets and SnO$_2$ nanoparticles are insufficient to restrain the aggregation of Sn particles in the electrode. Besides, driven by van der Waals forces, the graphene nanosheets can easily restack during the drying process, which results in a large charge transfer resistance at the interface. In addition, in some composites, the SnO$_2$ particles are directly exposed to the electrolyte, which brings about undesirable side reactions and an unstable interface between SnO$_2$ and the electrolyte. Therefore, it is necessary to design a more subtle structure or introduce other elements to further enhance the energy storage properties of SnO$_2$–graphene nanostructures.

As we know, among the alternative electrode materials, Si with the highest theoretical capacity of 4200 mAh/g has been studied extensively. However, similar to SnO$_2$, the large volume change (~400%) caused by the pulverization of silicon particles and thick solid electrolyte interface (SEI) restrict its applications in LIBs. To alleviate these weaknesses, it has attracted extensive attention to fabricate various material structures, such as nanostructured Si materials, nanocomposites, and nanosilicon films, to restrain the volume change of Si during the charge/discharge processes. Nevertheless, there have been few reports on improving the electrochemical performances of SnO$_2$–graphene composites as anode materials of LIBs by doping silicon, which should be a feasible strategy due to the inherent performance advantages of silicon materials. In recent years, several reports have demonstrated that the multiple effects of Si and SnO$_2$ are beneficial for the lithium storage performance. For instance, Zhou et al. constructed a novel Si@SnO$_2$ core–shell heterostructure by facile self-assembly of SnO$_2$ nanowires on silicon hollow nanospheres, which exhibit remarkable synergy in large and reversible lithium storage by the synergy of silicon hollow nanospheres and SnO$_2$ nanowires. Ma et al. also designed a novel hollow structured SnO$_2$@Si nanosphere, which not only demonstrates high volumetric capacity as anode of LIBs but also prevents aggregation of Sn and confines solid electrolyte interphase thickening. These Si-based anode materials show excellent electrochemical performance; however, they still have some shortcomings like poor cycle stability and electrical conductivity.

Herein, according to the above discussion, a novel sandwich-architecture composite of Si-doped SnO$_2$ nanorods and reduced graphene oxide with carbon sealing (Si-SnO$_2$@G@C) is designed and fabricated by a two-step hydrothermal process and subsequent annealing treatment. The electrochemical performance of Si-SnO$_2$@G@C has been significantly enhanced by doping silicon and sealing carbon layer. The Si-doped SnO$_2$ nanoparticles on the surface of graphene were firmly wrapped in the C-coating and formed a sandwich structure, which can efficiently prevent the Sn nanoparticles from aggregation by obstructing the diffusion of Sn atoms. The carbon layer also blocks the direct contact of the SnO$_2$ nanorods with electrolyte and prevents the graphene nanosheets from restacking. What is more, the reversibility of lithiation/delithiation reactions is remarkably improved by doping silicon. Additionally, the doped Si not only generates Li$^+$ conductive Li$_2$SiO$_4$ during lithiation process but also decreases the defects in the carbon matrix and indeed accelerates the diffusion of Li$^+$. Besides, the doped Si can make the structure more wrinkled and porous, providing more extra space for accommodating the volume variations and more active sites for reactions. Therefore, it can lift the specific capacity due to the adsorption of extra lithium ions in the more wrinkled structure. As a consequence, the Si-SnO$_2$@G@C nanocomposite exhibits extraordinary rate performance, ultra-high-specific capacity, excellent cycle stability, and high electrical conductivity as the anode of LIBs.

2. EXPERIMENTAL SECTION

Materials Preparation. Si-SnO$_2$@G@C was prepared via a two-step hydrothermal process and subsequent annealing treatment. Graphene oxide (GO) was synthesized by using a modified Hummers’ method from graphite nanosheets. Typically, SnCl$_4$·5H$_2$O (0.01 M) was dissolved in a 50 mL GO colloidal solution under magnetic stirring. Then 50 µL of tetraethyl orthosilicate (TEOS) was dispersed in the above pseudo-solution by stirring for another 30 min and ultrasonic treatment for 1 h. 10 mL of urea solution (2.5 M) and 5 mL of HCl were added to the mixture by dropwise addition and quick transfer, respectively. Next, the uniform and stable colloidal solution in chocolate color was transferred into a 100 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 200 °C for 24 h. After cooling to room temperature, 0.03 mol of glucose was added to the autoclave for the second hydrothermal reaction, which was kept at 180 °C for 1 h. The black product was collected, washed with DI water and ethanol by centrifugation for several times, and dried at 80 °C overnight. Finally, the Si-SnO$_2$@G@C was obtained after annealing in Ar at 600 °C for 2 h. The Si-SnO$_2$@G was gained without the second step hydrothermal treatment. In addition, SnO$_2$@G and SnO$_2$@G@C samples were also produced for comparison using the above method without the addition of TEOS only. Also, the Si-SnO$_2$@G@C composites with 10, 100, and 200 µL of TEOS were prepared and named Si-SnO$_2$@G@C-1, Si-SnO$_2$@G@C-2, and Si-SnO$_2$@G@C-3, respectively.

Materials Characterization. Scanning electron microscopy (SEM) images were obtained from a PHILIPS XL30TMP. The high-resolution transmission electron microscopy (HRTEM) and elemental mapping studies were measured by using a TALOS F200X at an accelerating voltage of 200 kV. X-ray diffraction (XRD) analyses were performed on a high-resolution powder X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) over a 2θ range from 10° to 80°. Raman spectra were conducted on a Jobin-Yvon LabRAM HR Evolution spectrometer equipped with a 532 nm laser. X-ray photoelectron spectroscopy (XPS) was characterized by using a RBD upgraded PHI-5000 ESCA system (PerkinElmer) with Mg Kα radiation (hv = 1253.6 eV). Thermogravimetric analysis (TGA) was performed in air with a heating rate of 10 °C/min over a temperature range from 30 to 900 °C.

Electrochemical Measurement. The coin-type 2025 cells were employed for the electrochemical performance test. The electrodes were fabricated via a conventional slurry based method using an N-methyl-2-pyrrolidone (NMP) slurry with 70 wt % active materials, 20 wt % acetylene black, and 10 wt % poly(vinylidene fluoride) (PVDF) binder. The homogeneous slurry was poured onto a clean copper foil and dried at 80 °C overnight in a vacuum oven. The mass loading of active material in electrode was about 0.8–1.2 mg/cm$^2$. The coin cells were assembled in an Ar-filled glovebox with metallic lithium as counter electrode and Celgard 2400 polypropylene film as separator. The electrolyte was formulated in a solution of LiPF$_6$ (1 M) in a 1:1:1 in volume ratio of ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The galvanostatic discharge–charge (GCD) measurements were performed on a Land CT 2001A battery tester in a voltage window of 0.01–3 V (vs Li/Li$^+$). The cyclic voltammetry (CV) test and electrochemical impedance spectroscopy (EIS) were examined by using a CHI-660D electrochemical workstation.
3. RESULTS AND DISCUSSION

Figure 1 graphically demonstrated the integrated synthetic routes of sandwich-architecture Si-SnO$_2$@G@C and SnO$_2$@G@C. First, the GO nanosheets obtained through Hummers’ method were dispersed into single layer nanosheets by ultrasonic treatment. The SnCl$_4$·5H$_2$O and TEOS were used as tin and silicon precursors, which were attracted to the GO surface by hydrogen bonding or π−π interactions with functional groups by stirring and ultrasound. During the first step hydrothermal process, the Si-SnO$_2$ (SnO$_2$) nanorods were obtained and attached to the surface of the reduced graphene oxide (rGO) nanosheets. Meanwhile, the GO was reduced to rGO. Then, the glucose was used as carbon precursor to conduct the carbon coating process. The conditions of 180 $^\circ$C and 1 h are necessary to form a uniform and ultrathin carbon layer, which can cover the upper and lower surfaces of the Si-SnO$_2$@G (SnO$_2$@G) composite. The final sandwich-architecture Si-SnO$_2$@G@C (SnO$_2$@G@C) was produced after the annealing process, which reduced the defects inside the composite and made the crystallization more favorable and the structure more stable. The C-coated sandwich structure can efficiently prevent aggregation of Sn nanoparticles and restacking of graphene nanosheets as well as block the direct contact of the SnO$_2$ nanorods with electrolyte.

The morphology and the microstructure of the four samples were characterized by using the SEM and TEM images, as shown in Figures 2a and 2b (Figures S1 and S2), respectively. All the four samples exhibit visible nanosheet structures. The surface of the SnO$_2$@G is the smoothest of the four composites; however, the Si-SnO$_2$@G@C shows the most conspicuous laminated structure. Upon comparison of Figure 2a with Figure 2c or Figure 2b with Figure 2d, it can be inferred that the doped Si makes the structure more wrinkled and porous. Because of the flexible peculiarity of graphene and their strong π−π interaction, the samples without Si doping are easy to be crumpled into large particles (Figure 2a,b and Figure S1a–h). It is reported that the doped Si can improve the mechanical rigidity of the SnO$_2$@G nanosheets. Therefore, the nanosheets can readily interconnect with each other without aggregation, which can result in more wrinkled and porous three-dimensional (3D) structure. Besides, the effect of the doped Si on the morphology is more obvious from Figure 2a,c. The surface of SnO$_2$@G is smooth with visible grains, while clear folds can be seen on the surface of Si-SnO$_2$@G without granular sensation. The folds can act as electrolyte reservoir to reduce ion transport resistance. In addition, Figure 2d shows that the ultrathin nanosheets are interconnected with each other to form 3D porous structure with carbon coating. However, the structure is not distinct for the samples without carbon coating due to the restacking of graphene nanosheets during drying and annealing. The carbon coating inhibits the volume expansion of Si-SnO$_2$ nanorods and ensures the stability of the composite structure during the cycling. Therefore, it can be concluded that the stable porous sandwich structure must be achieved by the synergy of silicon doping and carbon coating. This favorable 3D porous microstructure of the Si-SnO$_2$@G@C provides more extra space for accommodating the volume variations and more active sites for reactions. Besides, it can improve the interfacial contact and promote the diffusion of Li$^+$. To further reveal the details and the inner nanostructures of the Si-SnO$_2$@G@C nanocomposite, TEM and HRTEM characterizations have been
conducted. Figure 3 and Figure S2 present the rice-granular Si-
SnO$_2$ nanorods with a length of 10$^{-20}$ nm and a diameter of
around 5 nm evenly and densely distributed on the graphene
nanosheet. From Figure 3c,d the graphene and the ultrathin C-
coating layer can be clearly distinguished, which indicate the
sandwich architecture of the Si-SnO$_2$@G@C. The HRTEM
images in Figure 3d and Figure S2f further reveal that the well-
dispersed nanocrystallites have nonuniform shapes, and the
observed lattice spacing of 0.334 nm corresponds to the (110)
planes of tetragonal SnO$_2$. The STEM image and its
corresponding EDS elemental mapping are exhibited in Figure
3e to further demonstrate the distribution of SnO$_2$
nanoparticles and silicon element. Figure 3f indicates that
the tin element is completely crystallized to form SnO$_2$
nanorods, which are sealed in the carbon layer. The
distributions of oxygen and silicon are similar to that of tin,
which suggests that the silicon is doped in the SnO$_2$
nanoparticles forming Si-SnO$_2$ nanorods.

X-ray diﬀraction (XRD) analysis was employed to study the
crystal structures and phase transformation of the four samples.
The results are exhibited and compared in Figure 4a. For all
the four samples, the typical diffraction peaks at 2$\theta$
$= 26.8^\circ$, $33.9^\circ$, $37.9^\circ$, $39.1^\circ$, $51.8^\circ$, $54.7^\circ$, $57.9^\circ$, $61.9^\circ$, $64.8^\circ$, $66.0^\circ$,
$71.3^\circ$, and $78.7^\circ$ could be indexed to the (110), (101), (200),
(111), (211), (220), (002), (310), (112), (301), (202), and
(321) diﬀraction planes of the tetragonal SnO$_2$ with a P42/
mm space group (JCPDS No. 41-1445), respectively. As for
SnO$_2$@G, all the diffraction peaks can correspond to them. For
other three samples, however, the weak diffraction peaks at 2$\theta$
$= 30.6^\circ$, $32.0^\circ$, $43.9^\circ$, $44.9^\circ$, $55.3^\circ$, $62.5^\circ$, $63.8^\circ$, $64.6^\circ$, $72.4^\circ$,
$73.1^\circ$ and $79.5^\circ$ could be indexed to the (200), (101), (220),
(111), (301), (112), (400), (321), (420), (411), and (312)
diffraction planes of cubic phase Sn (JCPDS No. 65-2631),
respectively. These results demonstrate that the Sn$^{4+}$ is
crystallized to form rutile-type SnO$_2$ crystals after the
hydrothermal treatment. The appearance of the Sn peaks
may be due to the fact that a very small amount of SnO$_2$
is reduced to Sn during the annealing process. The effect on the
entire composite can be negligible. It should be pointed out
that there are no peaks indexed to Si or SiO$_x$, which can be
ascribed to the formation of amorphous SiO$_2$ and the low
content of doped Si. Additionally, to investigate the change in
the carbon matrix by doping Si, Raman spectroscopy using a
532 nm laser as the excitation source was adopted. As shown in
Figure 4b, two obvious peaks corresponding to the D-band (k-
point phonons of A$_{1g}$ symmetry) and the G-band (E$_{2g}$ phonon
of C sp$^2$ atoms) of carbon material can be found in the Raman
spectra of all the four composites at 1342 and 1597 cm$^{-1}$,
respectively. As for Si-SnO$_2$@G and Si-SnO$_2$@G@C, there is
a sharp peak at 478 cm$^{-1}$, which can be indexed to the
amorphous SiO$_2$ with a phonon confinement effect or a
masking effect of the graphene and C-coating. It is well-
known that the ratio of the intensities of the D-band to the G-
band ($I_D/I_G$) is an indicator of the degree of graphitic disorder.
The $I_D/I_G$ values of Si-SnO$_2$@G and Si-SnO$_2$@G@C were calculated to be 0.99 and 1.03, respectively, which are lower than the composites without the Si doping. Also, the values of the samples with C-coating are lower, indicating that the defects of carbon matrices decrease on account of the doped Si and the introduction of partially graphitizing mesoporous carbon around the graphene nanosheets. It can thereby accelerate the diffusion of the lithium ions.

In addition, Figure 4c shows the thermogravimetric analysis (TGA) curves to determine the contents of C for the four samples. Because the content of SiO$_2$ and Sn reduced by SnO$_2$ is very low, the influence of the oxidation of SiO$_2$ and Sn can be neglected. The graphene approximately accounts for 26.8 wt % of Si-SnO$_2$@G and 29.2 wt % of SnO$_2$@G. As for Si-SnO$_2$@G@C and SnO$_2$@G@C, the total contents of C are estimated as 32.1 and 38.1 wt %. Thus, the contents of C-coating can be roughly estimated as 5.3 and 8.9 wt %.

Figure 3. (a−c) TEM and (d) HRTEM images of Si-SnO$_2$@G@C. (e) STEM image of Si-SnO$_2$@G@C composite and the corresponding elemental mapping images of (f) Sn + HAADF, (g) C, (h) O, (i) Sn, and (j) Si.
Figure 4. (a) XRD patterns, (b) Raman spectra, and (c) TGA curves of the as-prepared SnO$_2$@G, SnO$_2$@G@C, Si-SnO$_2$@G, and Si-SnO$_2$@G@C. (d) N$_2$ adsorption–desorption isotherms of Si-SnO$_2$@G@C composite; the inset shows the corresponding pore size distribution curve.

Figure 5. (a) Rate performance of the four composite electrodes at various current densities. (b) GCD profiles of Si-SnO$_2$@G@C at the increasing discharge current density from 0.1 to 5.0 A/g. Cycling performance and Coulombic efficiency of the as-prepared samples cycled at (c) 0.5 A/g for 200 cycles and (d) 2 A/g for 1200 cycles, at 0.1 A/g for the first five cycles.
respectively. Moreover, nitrogen adsorption–desorption isotherms were measured for all the four samples, and the results of the Si-SnO$_2$@G@C composite are shown in Figure 4d. A mesoporous structure is confirmed, and it shows a type IV adsorption–desorption pattern. The corresponding pore size distribution curve shown in the inset indicates that the micropores are uniformly distributed around 3.7 nm, which is in accordance with the SEM and TEM results. The Brunauer–Emmett–Teller (BET) surface area and the total volume in pores of SnO$_2$@G, Si-SnO$_2$@G, SnO$_2$@G@C, and Si-SnO$_2$@G@C are 204.4 m$^2$/g, 198.7 m$^2$/g, 203.7 m$^2$/g, 0.2516 cm$^3$ g$^{-1}$, 216.9 m$^2$/g, 0.2303 cm$^3$ g$^{-1}$, and 169.1 m$^2$/g, 0.2161 cm$^3$ g$^{-1}$, respectively. All the samples have quite large BET surface area and relatively large total volume in pores (Figure S3), which can competitively buffer the tremendous volume expansion of SnO$_2$ nanorods during the lithiation/delithiation process. The BET surface is evidently reduced by the synergistic effect of C-coating and Si doping, which could reduce the consumption of electrolyte caused by surface reactions.

To further analyze the composition and the valence state of the Si-SnO$_2$@G@C composite, X-ray photoelectron spectroscopy (XPS) was performed. Four typical peaks at 284.8, 497.4, 495.8, and 531.3 eV can be observed in the XPS overall spectra (Figure S4a), which correspond to C 1s, Sn 3d$_{3/2}$, Sn 3d$_{1/2}$, and O 1s, respectively. However there are no obvious peaks related to Sn 3d$^{3/2}$ and Sn 3d$^{1/2}$, respectively. It is found by the fitting analysis that the peaks entirely belong to the Sn$^{4+}$, which is a further proof of the SnO$_2$ cladding. It is because the sandwich structure cannot be removed, and it shows a type IV adsorption isotherm with a H3 hysteresis loop in the inset, indicating that the improvement in rate performance relies on the combination of silicon doping and carbon cladding. Additionally, the pulsed discharge and charge curve for all the samples show no obvious hysteresis, indicating that the SnO$_2$ nanorods will directly contact with the electrolyte and the graphene nanosheets will restack during the discharging process. Thereby, the structure will be instability during the lithiation/delithiation reactions, resulting in the capacity reduction especially at high current densities. To further analyze its rate performance, the charge–discharge curves of the Si-SnO$_2$@G@C electrode at different current density are displayed in Figure 5b. There is no obvious hysteresis growth in charge–discharge plateaus even at a high current density of 5 A/g, which proves its superlative electronic/ionic transport characteristics. To further characterize the role of Si in the Si-SnO$_2$@G@C electrode, the electrochemical performance of the composite electrodes with different silicon content is also evaluated by GCD measurements in half-cells. The rate performance of the composite electrodes is shown in Figure S5, indicating that the doping amount of silicon (50 μL of TEOS) for the Si-SnO$_2$@G@C electrode has the optimum rate performance. It is found that the skimpy silicon doping (Si-SnO$_2$@G@C-1 with 10 μL of TEOS added) cannot increase the specific capacity of SnO$_2$@G@C. That may be because the introduction of trace impurities does not show the beneficial effect of silicon but will destroy the properties of the original composite. The excessive silicon doping (Si-SnO$_2$@G@C-3 with 200 μL of TEOS added) can increase the initial capacity of SnO$_2$@G@C. However, the specific capacity is decreased significantly as the excessive silicon doping exacerbate the volume change during cycling. The 100 μL TEOS addition can slightly improve the rate performance, which means the beneficial effect of the doped Si on the electrochemical performance of SnO$_2@G@C$ anode. However, the capacities of Si-SnO$_2$@G@C-2 and Si-SnO$_2$@G@C-3 are much smaller than that of Si-SnO$_2$@G@C, which is because excessive silicon doping can make the mechanical rigidity of the nanosheets too strong to form an optimal porous structure.

The electrochemical performance of the four composites as anode materials for a lithium-ion battery is first evaluated by galvanostatic charge/discharge (GCD) measurements in half-cells. The rate capacity and cycle stability of the sample electrodes were tested in the voltage range of 0.01–3.0 V (vs Li$^+$/Li$^-$) as shown in Figure 5. Figure 5a illustrates the rate capacity of the five sample electrodes at different current densities from 0.1 to 5 A/g and then back to 0.1 and 1 A/g, respectively. It can be seen that the rate performance of the Si-SnO$_2$@G@C electrode shows a significant improvement compared to other three samples, which exhibits both higher reversible capacity and higher capacity retention. The Si-SnO$_2$@G@C electrode delivers reversible capacity of 1127, 968, 851, 780, 704, and 564 mAh/g at 0.1, 0.2, 0.5, 1, 2, and 5 A/g, respectively. After 50 cycles, it returns back to 913 mAh/g at 0.1 A/g. Also, it remains at 670 mAh/g even after the next 50 cycles at 1 A/g, demonstrating its outstanding reversibility and cycle stability. Moreover, the Si-SnO$_2$@G@C electrode has a tremendously high initial discharge capacity up to 1981 mAh/g at 0.1 A/g, which is much higher than the theoretical capacity of SnO$_2$ and most previous reports in SnO$_2$-based materials as anode materials of LIBs. Besides, the rate capacities of other three electrodes are not much different, which indicates that the improvement in rate performance must rely on the combination of silicon doping and carbon cladding. It is because the sandwich structure cannot be wrinkled and porous without the doped Si, which can provide more extra space for accommodating the volume variations and more active sites for reactions. Without the carbon layer, however, the SnO$_2$ nanorods will directly contact with the electrolyte and the graphene nanosheets will restack during the discharging process. Thereby, the structure will be instability during the lithiation/delithiation reactions, resulting in the capacity reduction especially at high current densities. To further analyze its rate performance, the charge–discharge curves of the Si-SnO$_2$@G@C electrode at different current density are displayed in Figure 5b. There is no obvious hysteresis growth in charge–discharge plateaus even at a high current density of 5 A/g, which proves its superlative electronic/ionic transport characteristics. To further characterize the role of Si in the Si-SnO$_2$@G@C electrode, the electrochemical performance of the composite electrodes with different silicon content is also evaluated by GCD measurements in half-cells. The rate performance of the composite electrodes is shown in Figure S5, indicating that the doping amount of silicon (50 μL of TEOS) for the Si-SnO$_2$@G@C electrode has the optimum rate performance. It is found that the skimpy silicon doping (Si-SnO$_2$@G@C-1 with 10 μL of TEOS added) cannot increase the specific capacity of SnO$_2$@G@C. That may be because the introduction of trace impurities does not show the beneficial effect of silicon but will destroy the properties of the original composite. The excessive silicon doping (Si-SnO$_2$@G@C-3 with 200 μL of TEOS added) can increase the initial capacity of SnO$_2@G@C$. However, the specific capacity is decreased significantly as the excessive silicon doping exacerbate the volume change during cycling. The 100 μL TEOS addition can slightly improve the rate performance, which means the beneficial effect of the doped Si on the electrochemical performance of SnO$_2@G@C$ anode. However, the capacities of Si-SnO$_2$@G@C-2 and Si-SnO$_2$@G@C-3 are much smaller than that of Si-SnO$_2$@G@C, which is because excessive silicon doping can make the mechanical rigidity of the nanosheets too strong to form an optimal porous structure.

The stabilities of the four anode materials during the charge/discharge process at different current densities are compared in Figure S5c,d. Figure 5c shows the galvanostatic cyclability at 0.5A/g in the voltage range of 0.01–3.0 V (vs Li$^+$/Li$^-$) for 200 cycles. The four samples show a capacity decline within the
first 40 cycles as a result of the SEI fluctuation and electrolyte decomposition. For Si-SnO$_2$@G@C, the specific capacity starts to increase after 60 cycles, which can be attributed to the excellent pseudocapacitive effect. However, the capacities of the other three samples remain steady in the 40–200 cycles. The samples with Si doping have notably more capacity fading than the other two, which can be ascribed to the thicker solid electrolyte interface. However, with carbon coating and synergistic effect of Si and C, a discharge capacity of 772 mAh/g is retained after 200 cycles for the Si-SnO$_2$@G@C, which is much higher than other samples. In addition, the curves of the SnO$_2$@G@C and SnO$_2$@G electrode are almost same, further proving the synergistic effect of Si and C on electrochemical performance. Furthermore, the Coulombic efficiency of the Si-SnO$_2$@G@C electrode is the highest of the four samples at 0.5A/g, which is 60.2% initially and increases to 91.7% at the second cycle and then maintains over 97% after 15 cycles. To further investigate the long-term cycling performance of the four electrodes, another galvanostatic cyclability test was conducted at a high current density of 2 A/g (0.1 A/g for the first five cycles), as shown in Figure 5d. Unsurprisingly, the Si-SnO$_2$@G@C electrode shows an optimal cyclability and a highest capacity of 654 mAh/g even after 1200 cycles, which shows a 93.4% retention of the initial capacity and a Coulombic efficiency retention over 99%. The Capacity fading in the first several cycles. However, the initial discharge capacity and Coulombic efficiency of Si-SnO$_2$@G are higher than those of SnO$_2$@G, as shown in Figure 5a,c,d. It can be demonstrated that the Si doping has a positive effect on the electrochemical performance.

To further study the effect of silicon doping on lithium ion diffusion, an electrochemical impedance spectroscopy (EIS) measurement was performed with the new cells, the cells after the rate test for 100 cycles, and the cells after 200 galvanostatic charge/discharge cycles at the current density of 0.5 A/g for SnO$_2$@G@C and Si-SnO$_2$@G@C. As shown in Figure 6a,b, the Nyquist plots contain a semicircle in the high-frequency region connected with the transfer resistance of the lithium ion through the SEI film ($R_0$). Another semicircle in the medium-frequency region is related to the charge transfer resistance ($R_1$) at the electrode interface and a slope in the low-frequency region. It can be assigned to the Warburg impedance ($Z_w$), which is related to diffusion process of lithium ion. The EIS spectra could be well fitted by using the equivalent circuit in Figure 6c, where $R_w$ is regarded as the internal resistance and leads to the intercept of the high-frequency semicircle on the $Z’$-axis. The fitting values of $R_w$, $R_0$, and $R_1$, are shown in Table S1. Before cycling, the fitting values of $R_w$, $R_0$, and $R_1$ of Si-SnO$_2$@G@C are 52.0 and 29.9 Ω, respectively, which are both smaller than that of SnO$_2$@G@C (127.3/81.4 Ω). It means that the transfer of a lithium ion and an electron at the electrode/electrolyte interface is much faster for Si-SnO$_2$@G@C. The values of $R_t$ and $R_{ct}$ of the two composites significantly decrease after 100 cycles due to the ultrafine nanocrystals formed during the cycling. After 200 cycles, however, the values of the fitted $R_t$ and $R_{ct}$ increase slightly for SnO$_2$@G@C. Nevertheless, they do not considerably change for Si-SnO$_2$@G@C. It further demonstrates that the doped Si can efficiently improve the stability of internal structure and electrochemical performance.
described as $Z' = R_{ct} + R_{el} + \sigma \omega^{1/2}$, where $R_{ct}$, $R_{el}$, and $\omega$ are the charge transfer resistance, electrolyte resistance, and angular frequency, respectively. The parameter $\sigma$ is the Warburg factor corresponding to the slope of the curve in Figure 6d, which is related to the lithium ion diffusion coefficient.\textsuperscript{37} According to the results, the initial value of $\omega$ for Si-SnO\textsubscript{2}@G@C is smaller than that of SnO\textsubscript{2}@G@C, which increases slightly after 200 cycles. It can be inferred that Si-SnO\textsubscript{2}@G@C has a higher lithium ion diffusion coefficient, and the diffusion of Li$^+$ is hindered slightly during the charge/discharge cycles as compared to the case of SnO\textsubscript{2}@G@C.

Cyclic voltammetry (CV) was used to explore the electrochemical reaction in detail and confirm the effect on the lithiation/delithiation reaction of Si addition at a sweep rate of 0.5 mV/s from 0.01 to 3.0 V vs Li/Li$^+$. Figure 7a,b illustrates the first five cycles of the CV curves of Si-SnO\textsubscript{2}@G@C and SnO\textsubscript{2}@G@C, respectively. For the initial cathodic (lithium insertion) scan, a quite distinct reduction peak at around 0.75 V can be found for both the two electrodes, corresponding to the formation of Li$_2$O. It disappears in the subsequent cycles as a result of the formation of the SEI layer on the surface of the active material.\textsuperscript{42} The peak of Si-SnO\textsubscript{2}@G@C is much sharper than that of SnO\textsubscript{2}@G@C, suggesting an increase of the initial capacity for doping Si to the SnO\textsubscript{2}@G@C. It can be attributed to the reaction of SiO\textsubscript{2} with Li$^+$ (SiO\textsubscript{2} + Li$^+$ + e$^-$ → Si + Li$_2$O + Li$_4$SiO$_4$)\textsuperscript{38} and the enhancement of the reduction of SnO\textsubscript{2} to Sn (SnO\textsubscript{2} + 4Li$^+$ + 4e$^-$ → Sn + 2Li$_2$O). Also, the peak near 0 V in the CV curves of the two samples corresponds to the formation of Li$_4$Sn alloys (Sn + 4.4Li$^+$ + 4.4e$^-$ ↔ Li$_4$Sn).\textsuperscript{43} In the second to the fifth cycle, the visible peak is divided into two peaks at around 0.11 and 0.34 V, which represent the alloying reaction of Li$_x$Sn. Besides, there are another two weak peaks at about 1.14 and 0.86 V, which can be linked with the conversion of SnO\textsubscript{2} to SnO/Li$_2$O and SnO to Sn/Li$_2$O, respectively. All of the four reduction peaks can correspond to the oxidation peaks in anodic (lithium deintercalation) scan, revealing the reversibility of the two electrodes. Besides, the broad peak at 0.57 V and the small peak at 0.64 V can be related to the multiple dealloying reaction of Li$_x$Sn for Li ion extraction in the SnO\textsubscript{2}@G@C electrode. However, the two oxidation peaks also appear and are sharper in the Si-SnO\textsubscript{2}@G@C electrode than in the SnO\textsubscript{2}@G@C electrode, which may be due to the overlap of oxidation peaks corresponding to the formation of the Li–Si alloy (Si + Li$^+$ + e$^-$ ↔ Li$_x$Si) and the Li–Si alloy (Sn + Li$^+$ + e$^-$ ↔ Li$_x$Sn). It further demonstrates that the lithium storage capacity of Si-SnO\textsubscript{2}@G@C could be enhanced by the doped Si. Nevertheless, the two weak peaks at 1.26 and 1.87 V match with the oxidation of Sn to SnO and SnO to SnO$_2$, respectively. Additionally, the CV curves of the two electrodes in the second to fifth cycle are highly coincident, demonstrating that the electrochemical reactions in both the

Figure 7. CV curves of (a) Si-SnO\textsubscript{2}@G@C electrode and (b) SnO\textsubscript{2}@G@C electrode at a scan rate of 0.5 mV/s in the range of 0.01–3.0 V vs Li/Li$^+$. The GDC profiles of (c) Si-SnO\textsubscript{2}@G@C and (d) SnO\textsubscript{2}@G@C for the 1st, 2nd, 3rd, 10th, 50th, 100th, and 200th cycles at 0.5 A/g. The differential charge capacity curves of (e) Si-SnO\textsubscript{2}@G@C and (f) SnO\textsubscript{2}@G@C at the 1st, 2nd, 10th, 50th, 100th, and 200th cycles at 0.5 A/g.
Si-SnO$_2$@G@C and SnO$_2$@G@C electrodes are greatly reversible. What is more important, as compared to the SnO$_2$@G@C electrode, all the redox peaks of Si-SnO$_2$@G@C are more distinct, confirming the improvement of the reversibility during the lithiation/delithiation process by the doped Si.

The electrochemical reactions found in CV curves are consistent with the plateaus in galvanostatic voltage–capacity curves at a current density of 0.5 A/g (Figure 7c,d). It can be observed that the 1st to 3rd and the 50th to 200th charge–discharge curves show good superposition, especially for Sn-SnO$_2$@G@C. It further reveals the favorable cycle stability of Si-SnO$_2$@G@C. To intuitively analyze the durability differences of conversion reaction between these two composites, the differential charge capacity plots (DCPs) are displayed in Figure 7e,f. Four typical peaks at 0.57, 0.64, 1.26, and 1.87 V correspond to the multiple dealloying reaction of Li$_x$Sn, oxidation reactions of Sn and SnO$_x$, consistent with the CV results exactly. The peaks of Si-SnO$_2$@G@C are obviously sharper than that of SnO$_2$@G@C, especially for the dealloying peaks in 0.5–0.7 V. This could be attributed to the overlap of the oxidation peaks, which are responsible for the dealloying reaction of Li$_x$Sn and Li$_x$Si (Si + xLi$^+$ + xe$^-$ $\rightarrow$ Li$_x$Si). It demonstrates the extra lithium storage capacity induced by the doped Si. Moreover, the intensity of the peaks gradually decreases with increasing the cycle times, indicating that the reversibility of the conversion reaction reduces during the cycle process. In addition, it is well-known that Li$_4$SiO$_4$ is a fast conductor of Li$^+$, and the diffusion of lithium ions in Si-SnO$_2$@G@C composite is accelerated by the Li$_4$SiO$_4$ produced from activation of SiO$_x$. As a consequence, the lithiation/delithiation of Li–Sn became more reversible by the doped Si.

Note that the reversible capacity of the Si-SnO$_2$@G@C electrode has exceeded the theoretical value, which could be attributed to the capacitive mechanism for energy storage, including diffusion-control capacity and surface pseudocapacitance. Figure 8 shows the CV analysis at various scan rates from 0.1 to 1 mV/s, where the energy storage kinetics of the SnO$_2$@G@C electrode and the Si-SnO$_2$@G@C electrode are further investigated. In consideration of the high rate capacity and great lithium ion diffusion, it can be inferred that pseudocapacitance may dominate the charge transfer during charge–discharge process. The charge storage can be analyzed according to the power-law relationship $i = k_1
u^{1/2} + k_2 \nu = a\nu^b$, where $i$ and $\nu$ are the current and sweep rate, $a$ and $b$ are represented adjustable parameters, $k_1\nu^{1/2}$ is the diffusion-controlled contribution, and $k_2 \nu$ is the capacitive contribution. When the $b$ value approaches 0.5, it is a diffusion-controlled lithium storage process. While it is near 1.0, the electrochemical reactions are dominated by the surface capacitance. Figure 8c,d exhibits the log($i$)–log($\nu$) plots for the Si-SnO$_2$@G@C electrode and the SnO$_2$@G@C electrode to obtain the $b$ value. The $b$ values corresponding to the strongest reduction and oxidation peak currents of SnO$_2$@G@C and Si-SnO$_2$@G@C electrodes are fitted to be 0.83/0.89 and 0.81/0.90, respectively. It confirms the synergistic effect of the surface-controlled capacitive reaction and diffusion-controlled redox reaction. Note that the conversion process is capacitive-dominant and quite rapid. Besides, the $b$ values of the oxidation peaks are closer to 1, indicating that the charge transfer is faster in the delithiation process. Furthermore, there is no significant difference in the $b$ values of the two electrodes, which proves that the doped Si does not destroy the original lithium storage mechanism of the composite.

Consequently, the sandwich-architecture composite of Si-doped SnO$_2$ nanorods and reduced graphene oxide with C sealing (Si-SnO$_2$@G@C) shows improved electrochemical performance, as compared to the SnO$_2$@G, Sn-SnO$_2$@G, and SnO$_2$@G@C, which is desirable for high capacity and long
cycle life span LIBs. Moreover, the lithium storage property of the Si-SnO2@G@C electrode is in excess of most Sn-based anode materials because of the doped Si and the carbon sealing. The comparison of the rate and cycling performance of the Si-SnO2@G@C electrode and that of the reported Sn-based anode materials in recent years is summarized in Figure 9 and Table 1, respectively. Based on the above discussion, the

Table 1. Comparison of Cycling Performance the Si-SnO2@G@C Electrode and Previously Reported SnO2-Based Anode Materials

<table>
<thead>
<tr>
<th>SnO2-based materials</th>
<th>rate (A/g)</th>
<th>capacity (mAh/g)</th>
<th>cycles</th>
<th>year</th>
<th>ref</th>
</tr>
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<tbody>
<tr>
<td>W-SnO2@rGO</td>
<td>1</td>
<td>776</td>
<td>2000</td>
<td>2017</td>
<td>10</td>
</tr>
<tr>
<td>C-SnO2@3D-CNT</td>
<td>1</td>
<td>452</td>
<td>500</td>
<td>2019</td>
<td>12</td>
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<tr>
<td>SnO2/NSGS</td>
<td>2</td>
<td>480</td>
<td>2000</td>
<td>2018</td>
<td>16</td>
</tr>
<tr>
<td>C-graphene/SnO2</td>
<td>1</td>
<td>445</td>
<td>250</td>
<td>2018</td>
<td>18</td>
</tr>
<tr>
<td>SnO2-nanoparticles</td>
<td>2</td>
<td>700</td>
<td>1000</td>
<td>2017</td>
<td>19</td>
</tr>
<tr>
<td>SnO2/Co@C</td>
<td>5</td>
<td>400</td>
<td>1800</td>
<td>2017</td>
<td>20</td>
</tr>
<tr>
<td>hollow SnO2@GO</td>
<td>1</td>
<td>553</td>
<td>500</td>
<td>2017</td>
<td>21</td>
</tr>
<tr>
<td>SnO2/GS</td>
<td>2</td>
<td>564</td>
<td>200</td>
<td>2018</td>
<td>24</td>
</tr>
<tr>
<td>SnO2/Sn-rGO</td>
<td>1.6</td>
<td>449</td>
<td>400</td>
<td>2018</td>
<td>25</td>
</tr>
<tr>
<td>SnO2@C</td>
<td>1</td>
<td>668</td>
<td>200</td>
<td>2017</td>
<td>35</td>
</tr>
<tr>
<td>C@SnO2@rGO</td>
<td>2</td>
<td>525</td>
<td>1200</td>
<td>2019</td>
<td>39</td>
</tr>
<tr>
<td>SnO2@HPC@NC</td>
<td>1</td>
<td>767</td>
<td>500</td>
<td>2019</td>
<td>46</td>
</tr>
<tr>
<td>SnO2/NC</td>
<td>0.5</td>
<td>491</td>
<td>100</td>
<td>2016</td>
<td>47</td>
</tr>
<tr>
<td>h-SnO2 microspheres</td>
<td>5</td>
<td>404</td>
<td>600</td>
<td>2018</td>
<td>48</td>
</tr>
<tr>
<td>hollow SnO2/N-rGO</td>
<td>1</td>
<td>652</td>
<td>200</td>
<td>2018</td>
<td>49</td>
</tr>
<tr>
<td>C/SnO2/Sn</td>
<td>1</td>
<td>504</td>
<td>1000</td>
<td>2017</td>
<td>50</td>
</tr>
<tr>
<td>C@SnO2@C</td>
<td>5</td>
<td>400</td>
<td>10000</td>
<td>2019</td>
<td>51</td>
</tr>
<tr>
<td>SnO2/BGO</td>
<td>0.5</td>
<td>704</td>
<td>150</td>
<td>2019</td>
<td>52</td>
</tr>
<tr>
<td>SnO2@C@C/VO2</td>
<td>0.5</td>
<td>597</td>
<td>100</td>
<td>2017</td>
<td>53</td>
</tr>
<tr>
<td>Si-SnO2@G@C</td>
<td>0.5</td>
<td>772</td>
<td>200</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>

excellent electrochemical performance could be attributed to the synergistic effect of the carbon coating and the doped Si in the following four ways. (1) The sandwich structure that the C-coating tightly wraps the Si-doped SnO2 nanorods on the surface of graphene can block the diffusion of Sn atoms and efficiently reduce the aggregation of Sn nanoparticles. The carbon layer also blocks the direct contact of the SnO2 nanorods with electrolyte and prevents the graphene nanosheets from restacking, which can ensure the great cycling stability of the Si-SnO2@G@C electrode. (2) The doped Si can make the structure more wrinkled and porous, providing more extra space for accommodating the volume variations and more active sites for reactions. Therefore, since extra lithium ions can be adsorbed in more wrinkled structures, the specific capacity of the electrode can be significantly increased. (3) The reversibility of lithiation/delithiation reactions is remarkably improved by the doped Si, which contributes to the initial Coulombic efficiency. (4) The doped Si not only generates Li+ conductive Li4SiO4 during lithiation process but also decreases the defects in the carbon matrix. It indeed accelerates the diffusion of Li+. As a result, the rate performance and the electrical conductivity are improved.

4. CONCLUSIONS

A sandwich-architecture composite of Si-doped SnO2 nanorods and reduced graphene oxide with C sealing is fabricated by using a facile method of two-step hydrothermal reaction and subsequent thermal treatment, which improves the electrochemical performance of the SnO2-based anode materials. In the porous sandwich structure, the Si-doped SnO2 nanoparticles on the surface of graphene were firmly wrapped in the C-coating. It can efficiently prevent the Sn nanoparticles from aggregation and provide more extra space for accommodating the volume variations and more active sites for reactions. With the contribution of the synergistic effect of the carbon coating and the doped Si, the Si-SnO2@G@C nanocomposite exhibits extraordinary rate performance, ultra-high specific capacity, excellent cycle stability, and high electrical conductivity as the anode of LIBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsami.0c00073](https://pubs.acs.org/doi/10.1021/acsami.0c00073).

* SEM and TEM images of SnO2@G, SnO2@G@C, Si-SnO2@G, and Si-SnO2@G@C, N2 adsorption−desorption isotherms and BET surface area of SnO2@G, SnO2@G@C, and Si-SnO2@G; XPS general spectra and high-resolution spectra for Sn 3d, O 1s, C 1s, and Si 2p regions of Si-SnO2@G@C; rate performance of the composite electrodes with different silicon content at various current densities, the fitting values of Rct, Rp and Rf for the SnO2@G@C and Si-SnO2@G@C electrodes (PDF) *

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Notes

The authors declare no competing financial interest.

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