A Low-Cost and High-Capacity SiO$_x$/C@graphite Hybrid as an Advanced Anode for High-Power Lithium-Ion Batteries

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ABSTRACT: Silicon suboxide (SiO$_x$) is one of the most promising anodes for the next-generation high-power lithium-ion batteries because of its higher lithium storage capacity than current commercial graphite, relatively smaller volume variations than pure silicon, and appropriate working potential. However, the high cost, poor cycling stability, and rate capability hampered its industrial applications due to its complex production process, volume changes during Li$^+$ insertion/extraction, and low conductivity. Herein, a low-cost and high-capacity SiO$_x$/C@graphite (SCG) hybrid was designed and synthesized by a facile one-pot carbonization/hydrogen reduction process of the rice husk and graphite. As an advanced anode for lithium-ion batteries, the SiO$_x$/C@graphite hybrid delivers a high reversible capacity with significantly enhanced cycling stability (842 mAh g$^{-1}$ after 300 cycles at 0.5 A g$^{-1}$) and rate capability (562 mAh g$^{-1}$ after 300 cycles at 1 A g$^{-1}$). The great improvement in performances could be attributed to the positive synergistic effect of SiO$_x$ nanoparticles as lithium storage active materials, the in-situ formed carbon matrix network derived from biomass functioning as an efficient three-dimensional conductive network and spacer to improve the rate capability and buffer the volume changes, and graphite as a conductor to further improve the rate capabilities and cycling stability by increasing the conductivity. The low-cost and high-capacity SCG derived from rice husk synthesized by a facile, scalable synthetic method turns out to be a promising anode for the next-generation high-power lithium-ion batteries.

1. INTRODUCTION

With high energy density, power density, and operating voltage, as well as their long cycle life, low rates of self-discharge, and low environmental pollution, as being an effective energy storage device, lithium-ion batteries (LIBs) have been widely applied in various fields.\textsuperscript{1–6} With the mass production of electric vehicles and the iterative update of portable electronic devices, there is a higher demand for the capacity and endurance of LIBs.\textsuperscript{7–12} However, the graphite, as the mainstream anode material currently used in the commercialization of LIBs, is close to its theoretical capacity (372 mAh g$^{-1}$) and cannot meet the application requirements of high-performance batteries.\textsuperscript{8,13–16} Therefore, the development of emerging anode materials with high specific capacity has become an irresistible trend.\textsuperscript{17}

Among the proposed emerging negative materials for LIBs, silicon is considered to be the best candidate for replacing graphite because of its ultrahigh theoretical capacity (4200 mAh g$^{-1}$), rich content in the earth’s crust, and environmentally friendly features.\textsuperscript{18–23} However, the silicon material has a large volume change (\~{}300%) during the repeated insertion and extraction of lithium ions, eventually leading to a sharp decline in capacity. In addition, the repeated buildup of the solid electrolyte interphase (SEI) caused by the cracking of the electrode would consume more Li$^+$, resulting in low Coulombic efficiency and poor calendar life of LIBs.\textsuperscript{19,24–31} To solve those disadvantages, SiO$_x$-based anode materials have received more and more attention. Compared with Si-based materials, SiO$_x$-based anodes are prone to achieve excellent cycling performance because of the in situ formation of Li$_2$O and lithium silicates during the lithiation process, which could contribute to establish a stable SEI layer and accommodate the volume variation of SiO$_x$.\textsuperscript{32–35} However, SiO$_x$ anodes still have shortcomings such as volume change (\~{}200%) and low electrical conductivity (\~{}6.7 \times 10^{-4} \text{ cm}^{-1}), resulting in the unexpected electrochemical performances.\textsuperscript{36}

Based on the experience of previous silicon-based anodes, the carbon doping is considered to be the most promising means of addressing the inherent defects of SiO$_x$-based anodes.\textsuperscript{37,38} It is well known that the carbon material has a high electrical conductivity and stable structure, which can inhibit or accommodate the volume expansion of the SiO$_x$-based anode material during the charging/discharging cycles. Therefore, it is a commercially preferred strategy to combine a SiO$_x$-based anode material with carbon to obtain a high-capacity, stable-resistant hybrid. However, the development of a simple, low-cost, and environmentally friendly method for preparing SiO$_x$ materials remains a big challenge.\textsuperscript{39–42}

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On the other hand, silicon exists in the form of amorphous silica in plants, for example, rice husks, reed leaves, oat husks, etc.13−14 Chu et al. reported a silicon/carbon composite by the one-pot carbonization/magnesiothermic reduction process of the rice husk.27 Being applied as an anodic material, it delivered a high reversible capacity of 560 mAh g−1 as cycled at a current density of 100 mA g−1 over 180 cycles with good structural stability.27,44 Gao et al. also synthesized the SiOx/C composite material derived directly from agricultural rice husk byproducts, which delivered a reversible capacity of nearly 600 mAh g−1 at a current density of 100 mA g−1 after 100 cycles.45 Peng et al. used grapefruit peel to successfully prepare SiOx-modified biocarbon anode materials through the microwave-assisted hydrothermal reaction. After 100 cycles, a specific discharge capacity of 745 mAh g−1 could be obtained at a current density of 0.358 A g−1.47 Guo et al. synthesized a high-performance SiOx/C composite by exfoliating and repairing the structure of artificial graphite to load SiOx particles between the inside and the surface of silica. The synergy of multicomponent carbon materials could effectively solve the disadvantages of SiOx-based anodes in high-performance LIBs, especially in terms of promoting the formation of stable SEI layers. The resultant SiOx/C anodes demonstrated high reversible capacities (645 mAh g−1), excellent cycling stability (∼90% capacity retention for 500 cycles), and superior rate capabilities.36 Although these hybrids as anode materials delivered a high capacity, the cycling stability and rate capabilities could not meet the expected results. If we add another carbon conductor to the hybrid, it maybe can increase the cycling performances and rate capabilities. Based on above considerations, we want to mix graphite with SiOx/carbon derived from rice husk to improve the conductivity and cycling performances of the electrode hybrid for practical applications. To our knowledge, there is no report about the design and synthesis of a hybrid consisting of graphite and SiOx/C derived from rice husk for high-power LIBs.

Herein, we will report a low-cost and high-capacity SiOx/C@graphite (SCG) hybrid designed and synthesized by a facile one-pot carbonization/hydrogen reduction process of the rice husk and graphite. The positive synergistic effect of SiOx nanoparticles as lithium storage active materials, the in situ-formed carbon matrix network derived from biomass functioning as an efficient three-dimensional conductive network and spacer to improve the rate capability and buffer the volume changes, and graphite as a conductor could further improve the rate capabilities and cycling stability of SiOx/C@graphite as the anode for LIBs. As an anode for lithium-ion batteries, the porous SiOx/C@graphite nanocomposite could be expected to deliver a high reversible capacity with significantly enhanced cycling stability and rate capability.

2. RESULTS AND DISCUSSION

As described in the Experimental Section, Scheme 1 illuminates the fabrication process of the SiOx/C@graphite (SCG) hybrid. First, the recovered natural rice husk is immersed in hydrochloric acid to remove metal impurities and then precarbonized to obtain the precursor material by thermally decomposing the organic matter. The precursor material and graphite are mechanically ball-milled according to a mass ratio of 1:1. Herein, ball milling was adopted to achieve the homogeneous dispersion of SiOx/C and graphite. The ball-milled product is reduced at an argon/hydrogen (Ar/H2) atmosphere to form the SiOx/C@graphite (SCG) hybrid at different temperatures.

Figure 1 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of different samples. The SEM images of pure SC (SiOx/C) directly derived from rice husk without the addition of graphite show a block structure with uneven size (Figure 1a), while the SCG-1100 show a relatively homogeneous structure (Figure 1b). It may be because that the presence of graphite during the process of ball milling could reduce the friction between the grinding ball and the precursor and accelerate the movement of the grinding ball, which can make the ball milling process more complete. The SEM images of SCG-900 and SCG-1300 were also characterized, as shown in Figure S1. Compared with the SEM of Figure 1b, it can be easily seen that the morphologies of the SCG products do not much change with different temperatures, showing that the high temperature does not affect the morphologies of the products. The TEM images of the pure SC and SCG-1100 are presented in Figure 1c,d, respectively. The main component of the darker matrix is the SiOx/C, and the lighter color region is graphite. It can be seen in Figure 1c that the SiOx/C (SC) composite is exposed without any buffer layer because of the absence of graphite during the process of ball milling. In contrast, the SCG-1100 sample was mixed with graphite mechanical ball milling. As shown in Figure 1d, it can be easily seen that the SiOx/C matrix is tightly bound to the graphite. This structure could help to alleviate the volume effect of the SiOx and Si nanoparticles. The EDS mapping results (Figure 1e−h) show the distribution of carbon, oxygen, and silicon elements in the SCG-1100 sample. It can be seen that the distribution of carbon and oxygen is uniform, but the distribution of silicon is uneven. It may be because that the SiOx in rice husk is mainly distributed on the upper and lower epidermis of rice husks, while organic carbon is mainly distributed in the vascular bundles of rice husks in the form of lignin and cellulose.

To further study the microstructure of the rice husk-derived SiOx/C composite, X-ray diffraction (XRD) and Raman spectroscopy were also conducted. As shown in Figure 2a, the XRD pattern of SCG-1100 shows a high intensity peak, corresponding to graphite at 26.6°. When the characteristic peak of graphite is removed from the SCG-1100 sample, the remaining peaks (inset of Figure 2a) correspond to the characteristic peaks of Si and SiOx, indicating that the part of the SiOx component in the rice husk precursor is reduced by hydrogen to SiOx particles containing low valence Si. The XRD patterns of SCG-900 (Figure S2) and SCG-1300 (Figure S3) samples also have similar results. While the XRD pattern of the pure SC shows broad peaks at 22 and 43°, which can be assigned to the crystallographic planes of (002) and (100) in the disordered carbon structure (Figure S4), respectively. In Raman spectra (Figure 2b), two detached characteristic peaks at ~1360 and ~1580 cm−1 can be assigned to typical D and G bands, respectively. It is well known that the intensity ratio of the ID/IG reflects the graphitization degree of carbonaceous materials and the defect density. The value of ID/IG for the SCG-1100 hybrid was calculated as 1.02, which illustrates that the type of carbon in the SCG-1100 is mainly disordered carbon with some defects.
Furthermore, the SiO$_x$ content of the pure SC material can be determined by TG measurement in air (Figure 2c). It is interesting that the TG curve of pure SC showed that the weight increased at 200−350 °C, indicating the presence of Si elements in the pure SC. It is due to the fact that the Si could react with O elements in air to form SiO$_2$, resulting in the increase in weight. The TG results show that the SiO$_x$ content in pure SC at 1100 °C is about 45%. Thus, the SiO$_x$ content in the SCG-1100 material was calculated to be about 22.5 wt %. The N$_2$ adsorption/desorption isotherm in Figure 2d exhibits the BET surface area and the pore structure of the SCG-1100. The BET analysis shows that the surface area of SCG-1100 (213.97 m$^2$ g$^{-1}$) is lower than that of pure SC (296.82 m$^2$ g$^{-1}$, Figure S5). This result indicates that a dense carbon layer is built around the SiO$_x$ particles by mixing with graphite ball milling, which is consistent with the results of TEM observation. The pore size distribution of SCG-1100 indicates that the SCG-1100 sample mainly contains mesopores, which help to transport Li$^+$, resulting in the improvement of lithium storage capacity.

Figure 1. SEM images of the (a) pure SC and (b) SCG-1100 anode material. TEM images of the (c) pure SC and (d) SCG-1100 anode material. (e–h) Elemental energy-dispersive X-ray spectroscopy (EDS) mapping of the SCG-1100 sample, showing the distribution of carbon, oxygen, and silicon.

Figure 2. (a) Powder XRD patterns of the SCG-1100. (b) Raman spectra of the SCG-1100. (c) TG curves of pure SC in an air atmosphere. (d) Nitrogen adsorption/desorption isotherm curve and corresponding BJH pore size distribution of SCG-1100.
Element analysis of the SCG-1100 was carried out using X-ray photoelectron spectroscopy. It can be seen from Figure 3a that the XPS results confirmed the presence of silicon, carbon, and oxygen elements in the sample. The carbon element is derived from carbonized rice husks and graphite. The high-resolution spectrum of the Si (2p) region shows three peaks located at 103.5, 104.1, and 104.5 eV (Figure 3b), belonging to Si+, Si2+, and Si3+ of the amorphous SiOx, respectively. Figure 3c presents the spectrum of the C (1s) region where three peaks at about 283.8, 284.6, and 287.7 eV are observed, corresponding to...
the C=\text{C}, C=\text{O}, and C=\text{O} structures in the hybrid, respectively. A single highly symmetric peak centered at 532.7 eV is seen in the spectrum of the O (1s) region (Figure 3d), which is mainly originated from the rice husk-derived SiO₂/C hybrid. For comparison, the high-resolution spectra of the Si (2p) region of SCG-900 and SCG-1300 samples are also shown in Figures S6 and S7, respectively. The analysis results of the proportion of Si⁺, Si²⁺, and Si³⁺ in different samples are exhibited in Table S1. It is clearly found that more Si⁺ exists in the SCG-1100 sample than SCG-900 and SCG-1300. Thus, it would be expected that the SCG-1100 sample could provide more lithium storage capacity than SCG-900 and SCG-1300.

Figure 4a shows the cyclic voltammetry curves of the SCG-1100 for the initial three cycles at a scan rate of 0.1 mV s⁻¹ over a potential window of 0.01−3.0 V versus Li/Li⁺. A broad cathodic peak at ~0.75 V could be observed in the first discharge process and disappeared in the subsequent cycles. This peak is related to the formation of the solid electrolyte interphase (SEI), resulting in low Coulombic efficiency and the loss of the irreversible capacity in the first cycle. The cathodic peak at 0.16 V could be assigned to alloying of Li,Si, while the anodic peaks ranging at 0.12−0.16 V should be mainly attributed to dealloying of Li,Si.⁴⁷,⁴¹ These peaks are overlapped in the subsequent cycles, which suggest the excellent reversibility of SCG-1100 for the insertion and extraction of Li⁺.⁴⁹ The anodic peak of graphite at 0.24 V corresponds to the deintercalation process of the Li/C composite. The discharge/charge curves of SCG-1100 for the 1st, 2nd, 3rd, 100th, and 200th cycles at a current density of 0.5 A g⁻¹ are shown in Figure 4b. The first discharge/charge specific capacity was 2151.5/793.7 mAh g⁻¹ with an initial Coulombic efficiency of 36.89%. It can be clearly found that there is a large capacity loss in this process, being consistent with the test results of the first cycle of the CV. The large capacity loss is ascribed to the formation of the solid electrolyte interphase (SEI) film as well as amorphous Li₂O and lithium silicate and the decomposition of electrolyte in the first cycle.⁴⁹,⁵⁰

To understand the roles of graphite and the influence of temperature on the electrochemical properties, the pure SC, SCG-900, SCG-1100, and SCG-1300 as anodes were investigated at a current density of 0.5 A g⁻¹ (Figure 4c) and the corresponding Coulombic efficiency is shown in Figure S8. It can be easily seen that the pure SC delivers the lowest reversible capacity, showing that the graphite plays an important role in the improvement of the SiO₂-based hybrid. For the other three samples, the SCG-900, SCG-1100, and SCG-1300 delivered specific capacities of 702, 842, and 598 mAh g⁻¹ at the 300th cycle, respectively. It can be also clearly seen that the SCG-1100 delivers the highest capacity and has the best capacity retention. This could be ascribed to the more Si⁺ exists in the SCG-1100 sample than SCG-900 and SCG-1300, which have been proved by the XPS spectrum analysis results. For further probing the role of graphite, the cycling performances of pure SC and SCG-1100 electrode materials at a low current density of 0.1 A g⁻¹ were also tested. As shown in Figure S9, after 300 cycles, the pure SC shows a specific capacity of 693 mAh g⁻¹, and the SCG-1100 still provides a higher specific reversible capacity of 842 mAh g⁻¹. The specific capacity of the SCG-1100 electrode material is still higher than that of pure SC, indicating that the addition of graphite can effectively increase the specific capacity of the hybrid even in low current density. The comparison of the electrochemical properties between the samples in this work and other reported SiO₂-based electrode is shown in Table S2. It is interesting that the SCG-1100 hybrid as an advanced anode for LIBs is still superior to some previous reports. Figure 4d presents the rate capabilities of SCG-1100 at various current densities from 0.1 to 2 A g⁻¹. Ten cycles were performed at each current density to further evaluate its electrochemical performance. The average charge/discharge capacities of the SCG-1100 hybrid electrode are 1163/1185, 1065/1089, 731/752, 453/462, and 290/295 mAh g⁻¹ at current rates of 0.1, 0.2, 0.5C, 1, and 2 C, respectively. It can be easily found that the specific capacities decreased slightly with the increase in rate. It is worth noting that when the current density is reduced to 0.1 A g⁻¹ again, the specific capacity can be restored to 1200 mAh g⁻¹, showing the excellent rate performance of the SCG-1100. In addition, the SCG-1100 anode also shows satisfactory performance at large current densities. Figure 4e shows the cycling performances at a high current density of 1 A g⁻¹ from the fourth cycle. It can be found that the specific capacity of the SCG-1100 hybrid decays first in the first 30th cycle and then rises in the following cycles, which is very similar to previous reports.⁴⁹ The first decay is due to the volume expansion effect of silicon particles in the cycling process. The repetitive volume changes could fracture the SEI layers and result in a more extensive exposure of Si active sites during the lithiation process. The fresh active site could provide more sites to store charge, thereby increasing capacity.⁴⁹ The subsequent growth of capacity is ascribed to the high rate lithiation-induced reactivation, which could effectively restructure the porous microstructures and optimize the stable SEI.⁵⁰ With the stable SEI formation and structure refinement, the reactivated anode materials showed a high capacity and excellent cycling performance even in a long cycle at a high rate.⁴⁹ At the 200 cycles, its reversible capacity is stable at 575 mAh g⁻¹. After 300 cycles, the specific capacity of the SCG-1100 hybrid still retains 562 mAh g⁻¹, and the Coulombic efficiency is 99.37%, showing its good cycling stability at a high rate of 1 A g⁻¹. To further explore the electrochemical behaviors, electrochemical impedance spectroscopy (EIS) measurements were performed on pure SC and three SC hybrid batteries before cycling. As shown in Figure 4f, the Nyquist plots are composed of semicircles in the high- to medium-frequency region and straight lines in the low-frequency region. The diameter of the semicircle in the high-frequency region is related to the contact resistance (Rc) of the electrolyte and the electrode.⁵¹,⁵² The diameter of the oblate semicircle in the intermediate-frequency region corresponds to the SEI film impedance (RSEI) and the charge-transfer impedance at the interface between the electrode and the electrolyte (RCT), and the oblique part of the low-frequency region is related to the solid-phase diffusion (Zet) ability of lithium ions in the electrode also known as the Warburg impedance.⁵³,⁵⁴ It can be clearly discerned that the diameter of the semicircle of the SCG-1100 hybrid is the smallest than that of pure SC, SCG-900, and SCG-1300, showing that the charge-transfer resistance of SCG-1100 is the smallest. Therefore, it can be inferred that the addition of graphite can effectively increase the charge-transfer rate during the charge and discharge process, which is beneficial to the storage and release of Li⁺. Meanwhile, the SiO₂ in the sample has a negative effect on the conductivity. Combined with the XPS spectra, more SiO₂ is converted into low valence Si at 1100 °C. Thus, the SCG-1100 composite material has a lower electrical conductivity, which is in accordance with the result of cycling performance. In a word, the SCG-1100 as the anode for high-power LIBs shows improved lithium reversible capacities.
3. CONCLUSIONS

In summary, we have designed and synthesized a low-cost and high-capacity SiO$_x$/C@graphite (SCG) hybrid by a facile one-pot carbonization/hydrogen reduction process of the rice husk and graphite. As an anode material for lithium-ion batteries, the SiO$_x$/C@graphite hybrid delivers a high reversible capacity with significantly enhanced cycling stability (842 mAh g$^{-1}$ after 300 cycles at 0.5 A g$^{-1}$) and rate capability (562 mAh g$^{-1}$ after 300 cycles at 1 A g$^{-1}$). The great improvement in performances could be attributed to the positive synergistic effect of SiO$_x$ nanoparticles, the in situ-formed carbon matrix network, and graphite. The low-cost and high-capacity SCG derived from rice husk synthesized by a facile, scalable synthetic method turns out to be a promising anode for the next-generation high-power lithium-ion batteries.

4. EXPERIMENTAL SECTION

4.1. Preparation of SiO$_x$/C@graphite. In a typical procedure, the rice husks were soaked in a 2 M HCl solution at 60 °C for 8 h, then washed with deionized water until the solution was neutral, and dried at 60 °C overnight. Then, the rice husks were kept at 450 °C in a tube furnace under nitrogen for 1 h with a heating rate of 2 °C min$^{-1}$ to obtain the precursor.

The as-obtained precursor and graphite were mixed at a mass ratio of 1:1 and ball-milled for 5 h. For the pyrolysis process, 2 g of the ball-milled sample was loaded in a tube furnace and carbonized at 900 °C for 5 h under an argon/hydrogen (Ar/H$_2$) flow with a heating rate of 3 °C min$^{-1}$ to obtain SiO$_x$/C@graphite (denoted as SCG-900). For comparison, the ball-milled sample was heated at 1100 and 1300 °C to obtain SCG-1100 and SCG-1300, respectively. The precursor without graphite was kept at 1100 °C for 5 h under an argon/hydrogen (Ar/H$_2$) flow with a heating rate of 3 °C min$^{-1}$ to obtain SiO$_x$/C (denoted as pure SC).

4.2. Material Characterization. The as-synthesized products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα radiation), field emission scanning electron microscopy (FESEM, JEOL, JSM-6700F) with an energy-dispersive X-ray spectrometer, and TEM (FEI TF20 and JEM-2100F) from Shiyanjia Lab. The surface composition of the products was evaluated using XPS (Thermo ESCALAB 250XI). Thermogravimetric analysis (TG) was performed on a Pyris Diamond TG-DTA instrument under a nitrogen atmosphere. Raman analysis was performed on a Renishaw Raman spectrometer. The specific surface area and pore volume were estimated by nitrogen adsorption/desorption measurements at 77 K using a Micromeritics ASAP 2460 via the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

4.3. Electrochemical Measurements. Electrochemical performances were measured using the assembled 2032 coin-type half-cell. The working electrodes were composed of 60 wt % active materials, 30 wt % conductive additives, and 10 wt % poly(vinylidene difluoride) as the binder. N-Methyl-2-pyrrolidone (NMP) was used as the solvent. The mixed slurry was cast onto a piece of copper foil, dried in a vacuum oven at 60 °C for 12 h, and then cut into discs with a diameter of 13 mm. The loading mass of the as-prepared active materials on the electrode was 2.1 mg cm$^{-2}$. Lithium foil was used as the reference electrode. LiPF$_6$ (1 M) in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume) was used as the electrolyte. The galvanostatic charge/discharge tests were performed using a LAND CT-2001A (Wuhan, China) testing system at different current densities in the voltage range between 0.01 and 3.0 versus (Li/Li$^+$)/V. Cyclic voltammetry (CV) measurements were carried out on a CHI 760E (Chenhua Co., Ltd., China) electrochemical workstation between 0.01 and 3.0 versus (Li/Li$^+$)/V at a sweep rate of 0.1 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) tests were carried out on an electrochemical workstation (Autolab 302N) in a frequency range of 0.01–10$^5$ Hz with an ac amplitude of 10 mV.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00686.

Characterization of materials, SEM, TG, EDS, XPS, TEM, N$_2$ adsorption/desorption isotherms, pore size distribution, and electrochemical properties (PDF)

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Notes
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