Facile Synthesis of Highly Graphitized Carbon via Reaction of CaC₂ with Sulfur and Its Application for Lithium/Sodium-Ion Batteries

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ABSTRACT: In the present work, we report, for the first time, a novel one-step approach to prepare highly graphitized carbon (HGC) material by selectively etching calcium from calcium carbide (CaC₂) using a sulfur-based thermo-chemical etching technique. Comprehensive analysis using X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and N₂ adsorption−desorption isotherms reveals a highly graphitized mesoporous structure for the CaC₂-derived carbon with a specific surface area of 159.5 m² g⁻¹. Microscopic analysis displays micron-scale mesoporous frameworks (4−20 μm) with a distinct layered structure along with agglomerates of highly graphitized nanosheets (about 10 nm in thickness and 1−10 μm lateral size). The as-prepared HGC is investigated for the role of an anode material for lithium- and sodium-ion batteries. We found that HGC exhibits good lithium storage performance in the 0.01−1.5 V range (reversible capacity of 272.4 mA h g⁻¹ at 50 mA g⁻¹ after 100 cycles and 214.2 mA h g⁻¹ at 500 mA g⁻¹ after 500 cycles), whereas, when sodium is considered, we observed a drop in the overall electrochemical performance owing to the high graphitization degree. More importantly, the present study provides a perspective approach to fabricate HGC via a simple, cost-effective, and efficient synthetic route using CaC₂ and sulfur as reactants.

INTRODUCTION

Designing and preparing new carbon materials has long been of interest in the field of materials science and engineering. Various carbon materials with unique structures and morphology have been found to be useful for a variety of applications owing to their outstanding chemical and physical properties.1−3 Extracting metals or metalloids from carbides using halogens, supercritical water, selective oxidation, or vacuum decomposition has been demonstrated to be effective for synthesizing a large family of carbon materials ranging from amorphous carbon to graphite, carbon nanotubes, and graphene, and thus-obtained carbon is termed as carbide-derived carbon (CDC).2,4 The CDC structures have found numerous applications especially in lithium-ion batteries (LIBs), supercapacitors (SCs), gas storage, catalysis, biomedical engineering, tribology, and as membranes.2 Particularly, porous CDC obtained by chlorination has been widely studied for SC application because of the high specific surface area and tunable pore size with a narrow size distribution.5−10 For example, Kou et al. prepared Mo₂C-derived chlorine-doped ordered mesoporous carbon with few-layered graphene walls and investigated its performance as electrode material for SCs and LIBs.5 The Cl-doped porous CDC showed promising potential for electrochemical energy storage (EES) with a high charge capacity of 733 mA h g⁻¹ at the current rate of 0.5 A g⁻¹ after 100 cycles and a high specific capacitance of 250 F g⁻¹ at 0.5 A g⁻¹ in 1 M H₂SO₄ solution. However, most of the available reports on CDC exploit their potential in SCs owing to the high specific surface area, whereas few studies are related to the use of CDC in LIBs.5−10
Among various metal carbides, calcium carbide (CaC$_2$) is a commercially available alkaline earth metal carbide with low cost and serves as an ideal alkynyl source for synthesizing carbon materials. Besides chlorine treatment of CaC$_2$ to produce CDC$_2$\textsuperscript{11} various other methods have been proposed including thermo-reaction of CaC$_2$ using reactants like halogenated hydrocarbon, oxalic acid, AlCl$_3$, carbon nano-onions\textsuperscript{18} and carbon nanosheets\textsuperscript{21} have also been studied for LIBs and sodium-ion batteries (SIBs).

RESULTS AND DISCUSSION

The carbon formation achieved by selectively etching calcium from CaC$_2$ using sulfur can be expressed as: CaC$_2$ + S = CaS + 2C. The Gibbs-free energy of the reaction at 550 °C is $\Delta G^\circ_{\text{m}} = -374.5$ kJ mol$^{-1}$, suggesting the occurring of a spontaneous reaction. Furthermore, the enthalpy evaluation returns a strong negative value of $\Delta H^\circ_{\text{m}} = -433.2$ kJ mol$^{-1}$, implying that the reaction of CaC$_2$ with sulfur is thermodynamically advantageous. Indeed, owing to this negative enthalpy value, the reaction will tend to release heat which will facilitate the proper completion of the reaction itself. At the end of the reaction the final carbon product can be easily retrieved by removing the CaS byproduct through washing with dilute hydrochloric acid and deionized water. The X-ray diffraction (XRD) pattern of the resulting product is shown in Figure 1a. The sharp diffraction peak around 2$\theta$ = 26.4° is attributable to the (002) reflection of hexagonal graphite (JCPDS no. 41-1487), confirming the formation of carbon with high graphitization degree. Calculated by the Bragg’s law, the interplanar spacing of (002) reflection is 0.337 nm, similar to graphite. The weak reflections at 42.3, 44.4, and 54.5° result from the (100), (101), and (004) planes of hexagonal graphite, respectively, whereas the two remaining diffraction peaks around 35° and 60° are ascribed to contaminating SiC (JCPDS no. 49-1428). We speculate that the presence of Si can be associated to impurity elements present in the HGC product. These impurities could not be removed by acid washing owing to their chemical bonding with HGC, as also confirmed by the energy-dispersive X-ray spectrometry (EDX) result shown in Figure S2. We believe that SiC was probably formed during the synthesis process of carbon from CaC$_2$ at 550 °C. Similar XRD results have also been found for carbon materials derived from CaC$_2$ and polyhalogenated hydrocarbons by interfacial mechanochemical reactions.\textsuperscript{15}

The structure of the as-prepared carbon was identified by Raman spectroscopy (Figure 1b). The peak at about 1380 cm$^{-1}$ (D-band) is associated with the defects and disordered structures of carbonaceous solids, whereas the peak around 1600 cm$^{-1}$ (G-band) is ascribed to the stretching modes of the C–C bond of typical graphite.\textsuperscript{14–16} The intensity of the G-band ($I_G$) is much higher than that of the D-band ($I_D$) with an $I_G/I_D$ value of 3.2, suggesting that the as-prepared carbon is of high graphitization degree,\textsuperscript{14,21} consistent with the XRD result.

Figure 1. (a) XRD pattern, (b) Raman spectrum, (c) high-resolution XPS spectrum of C 1s, and (d) N$_2$ adsorption–desorption isotherms of the resulting product obtained by the reaction of CaC$_2$ and sulfur at 550 °C for 5 h. The inset in (d) is the pore-size distribution.
The structure of the HGC was further investigated by X-ray photoelectron spectroscopy (XPS) (Figure 1c). The high-resolution XPS spectrum of C 1s could be deconvoluted into four peaks centered at 284.8, 285.5, 286.5, and 288.9 eV, attributed to sp²-C, sp³-C, C=S, and C=O, respectively. The predominant sp²-C peak is indicative of the high graphitization degree of the carbon product. The presence of the C=S peak demonstrates slight S-doping in the carbon. The bonding information between carbon and sulfur is further revealed in the high-resolution S 2p spectrum (Figure S1, Supporting Information), where the two peaks centered at 164.2 (S 2p₃/2) and 165.4 eV (S 2p₁/2) with an intensity ratio of 2:1 and binding energy difference of 1.2 eV correspond to spin-orbital splitting of thiophene-like sulfur incorporated into graphite. The sulfur doping is preferential in polarizing electron pairs, improving the graphitization degree of carbon and introducing redox reactions owing to the large size and high chemical activity. As evidenced both theoretically and experimentally, heteroatom doping could improve the electrical properties and chemical activity of carbon, thus is favorable for energy storage capability.

In addition, the specific surface area of HGC was evaluated by N₂ adsorption–desorption isotherms (Figure 1d). The product exhibits typical IVa isotherms with an H3 type hysteresis loop at a relative pressure of 0.4–1.0, indicative of the presence of meso- and macropores in the carbon framework. The specific surface area and pore volume are 159.5 m² g⁻¹ and 0.34 cm³ g⁻¹, respectively. From the pore-size distribution curve (the inset in Figure 1d), the mesopores are primarily 21 and 39 nm in size and the macropores are larger than 50 nm. These pores, formed during the removal of CaS from the reaction product, are conducive to improving the electrolyte permeability, increasing the electrode/electrolyte contact interface and facilitating Li⁺ ion transportation.

Field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were employed to examine the morphology and microstructure of the HGC. From the FE-SEM image (Figure 2a), the product consists mainly of three-dimensional (3D) fluffy carbon of about 4–20 μm in size with an uneven surface, which is in fact composed of thin carbon sheets with a lateral size of about 1–10 μm (Figure 2b). From the high-magnification SEM image in the inset of Figure 2a, the carbon framework displays a layered structure with plentiful mesopores. According to the EDX spectrum of HGC (Figure S2b), the carbon content accounts for about 86.26 wt % (91.76% in atomic percent) and the S-doping content is about 5.80 wt % (2.31% in atomic percent). The other elements of O (7.05 wt %), Si (0.12 wt %), and Ca (0.77 wt %) stem from the strong adsorption of CO₂ and H₂O on the porous HGC and the impurities in CaC₂. The element mappings for C and S (Figure S2a) indicate the uniform distribution of sulfur throughout the product, further confirming the S-doping in the HGC. The TEM image of the carbon sheets and the corresponding selected area electron diffraction (SAED) pattern are shown in Figure 2c, whereas the distinct diffraction rings in the inset confirm the high graphitization of carbon. From the high-resolution TEM (HRTEM) image of a single carbon sheet (Figure 2d), the planar spacing is about 0.34 nm, matching well with graphite. Moreover, some disordered carbon could also be observed on the surface of the graphitized nanosheet. As a consequence, the HGC including 3D frameworks and two-dimensional (2D) nanosheets reveals long-range ordered rearrangement of carbon atoms occurring during the selective thermo-chemical etching of CaC₂ by sulfur.

Starting from the aforementioned electro-optical characterizations, we argue that the obtained HGC characterized by high graphitization degree, mesoporous structure, high surface area, and slight S-doping might indeed be endowed with good electrochemical lithium storage performance as the LIB anode. The assembled LIBs were charged and discharged galvanostatically in the narrow voltage range of 0.01–1.5 V (vs Li⁺/Li) instead of the widely used 0.01–2.5 V or even 3 V as we were aiming for realistic applications. For the first discharge profile (Figure S3), three plateaus at about 1.7, 0.75, and 0.1 V can be observed, which are due to the reaction of chemically bonded sulfur with Li⁺ to form Li₂S, the decomposition of LiS to form Li₂S₂, and insertion of Li⁺ into graphitic layers, respectively. Upon the subsequent charge process, a plateau at around 0.1 V and a sloped curve above 0.3 V are observed, delivering a charge (reversible) capacity of 296.9 mA h g⁻¹ at the current density of 1.0, indicative of reversible Li⁺ insertion/extraction with long-range ordered rearrangement of carbon atoms occurring during the selective thermo-chemical etching of CaC₂ by sulfur.

The wide peak at 0.7 V disappears after the initial scan, indicating the irreversible formation of the SEI layer during the first cycle. The absence of a high-voltage plateau at about 2.3–2.4 V, related to the multistep lithiation process of elemental sulfur S₈ in the initial discharge process, together with the
absence of the corresponding reduction peak in the CV graph, further confirm that there is no residual S$_8$ but chemically bonded sulfur in the carbon product. This result was indeed in agreement with previous works reported in the literature.$^{23,31,32}$ It should be noticed that because of the choice of adopting a narrow voltage range with an upper cut-off voltage of 1.5 V, the reaction during the first cycle between chemically bonded sulfur with Li$^+$ determines a strongly irreversible reaction, which in turn partially contributes to the cell capacity loss. After the first cycle the capacity becomes stable, showing also a highly reversible process, as evidenced by the overlapped CV curves shown in Figure S4 and charge/discharge profiles shown in Figure 3a. Even though the reversible capacity of HGC as anode for LIBs is considerably lower than those of previously reported carbon-based materials,$^{5,18,21,33}$ because of the narrow voltage range adopted in this work, the HGC exhibits good cycling stability (Figure 3b). The initial Coulombic efficiency (CE) is relatively low, 33.5%, in comparison to standard graphite anodes, which can be attributed to the relatively large surface area of mesoporous HGC as well as to the existence of disorders in the structures.$^{21}$ The CE of the second cycle increases dramatically to 87% and further to more than 95% after five cycles. After 100 cycles at the current density of 50 mA g$^{-1}$ the reversible capacity of HGC is 273.5 mA h g$^{-1}$ with a CE close to 99.5%.

In order to investigate the possibility of applying HGC to high-power LIBs, its rate performance was evaluated at elevated current densities up to 1600 mA g$^{-1}$. As shown in Figure 3c, the HGC displays an excellent rate capability with reversible capacities of 276.6, 262.3, 236.6, 188, 158.5, and 137.8 mA h g$^{-1}$ at 50, 100, 200, 400, 800, and 1600 mA g$^{-1}$, respectively. Importantly, when the current density was changed back to the initial 50 mA g$^{-1}$, the corresponding capacity was recovered almost entirely by settling to a value equal to 272.4 mA h g$^{-1}$, very similar to the initial 276.6 mA h g$^{-1}$. This reversible capacity capability demonstrates that the HGC electrode is characterized by a robust electrochemical structure resulting in a good stability even after a high rate of cycling. Furthermore, a 500-cycle-long cycle analysis of HGC at the high current density of 500 mA g$^{-1}$ was also conducted, as depicted in Figure 3d. The HGC showed good cycling
stability for over 500 cycles with a reversible capacity of 214.2 mA h g\textsuperscript{-1}. The average CE after the first cycle was about 99.6%.

Besides the possibility of employing HGC within LIBs, their effectiveness was also tentatively investigated within sodium-storage systems as the emerging SIB technology is known to carry the prominent advantage of cost-effectiveness although at the expense of electrochemical performance.\textsuperscript{34} The galvanostatic charge/discharge profiles are illustrated in Figure S5. Here, a long discharge plateau at about 0.5 V (vs Na\textsuperscript{+}/Na\textsuperscript{-}) is observed in the first cycle owing to the decomposition of electrolyte on the surface of the carbon material resulting in SEI film formation. The initial reversible capacity is found to be 86.5 mA h g\textsuperscript{-1} at 50 mA g\textsuperscript{-1}, much lower than that for LIBs. During the subsequent cycles (Figure 4a), the HGC shows sloped charge/discharge voltage profiles without visible plateaus with the reversible capacity becoming fairly stable. Interestingly, a difference that can be found when comparing the charge/discharge voltage profiles for LIBs and SIBs is that the voltage plateaus below 0.2 V for LIBs are absent for SIBs, which could explain the lower sodium storage capacity. The relatively low capacity for sodium storage reflects that HGC is possibly not suitable for SIBs because of the absence of stable Na–C binary compounds and to the relatively large Na\textsuperscript{+} ion dimension that makes Na\textsuperscript{+} ions difficult to be intercalated into graphite.\textsuperscript{34} Nevertheless, owing to the existence of numerous pores and defects inside HGC, a stable reversible capacity around 81 mA h g\textsuperscript{-1} with CE close to 98% during cycling at 50 mA g\textsuperscript{-1} could be delivered (Figure 4b).

\section{CONCLUSIONS}

In summary, a facile and economical route to prepare HGC from low-cost CaC\textsubscript{2} at moderate temperature was developed. The CaC\textsubscript{2}-derived carbon is characterized by a high graphitization degree and it mainly consists of 3D mesoporous frameworks and 2D nanosheets. The synthesized HGC, once employed as anode material for rechargeable LIBs, exhibits good lithium storage performance with reversible capacity of 272.4 mA h g\textsuperscript{-1} at 50 mA g\textsuperscript{-1} after 100 cycles and 214.2 mA h g\textsuperscript{-1} at the high current density of 500 mA g\textsuperscript{-1} after 500 cycles as well as a good rate capability. Furthermore, the sodium-storage behavior of HGC was also investigated, resulting in a limited electrochemical performance because of the high graphitization degree. Finally, we expect that the introduced approach to prepare carbon materials from CaC\textsubscript{2} could be especially exploited by the carbon industry with also the consequence of possibly broadening the research and development on other kinds of carbides.

\section{EXPERIMENTAL SECTION}

\textbf{Preparation of CaC\textsubscript{2}-Derived Carbon.} In a typical procedure, the raw materials of 3.2 g of chemically pure sublimated sulfur (S\textsubscript{8}) and 6.4 g of industrial CaC\textsubscript{2} powder (corresponding to a molar ratio of 1:1) were mixed and put into a stainless-steel autoclave of 30 mL capacity. As a reactor, the tightly sealed autoclave was heated in an electric oven to 550 °C and maintained for 5 h. When the autoclave was naturally cooled to ambient temperature, the solid product in the autoclave was collected and washed consecutively with dilute hydrochloric acid and deionized water until all soluble materials were removed. After drying at 100 °C for 12 h in an oven, black powder was ultimately obtained.

\textbf{Material Characterization.} An XRD pattern was obtained on a Rigaku Dmax-rC diffractometer with Ni-filtered Cu Kα radiation (\(\lambda = 0.1541 \text{ nm}\)) at a scanning rate of 4° min\textsuperscript{-1}. The morphology of the resulting carbon product was examined using a Hitachi SU-70 field-emission scanning electron microscope with an energy-dispersive X-ray spectrometer and a JEOL JEM-2100 high-resolution transmission electron microscope. A Raman spectrum was collected on a LabRAM HR800 with excitation from an argon ion laser (632.81 nm). XPS analysis was carried out on a KARTOS XSAM800 X-ray photoelectron spectrometer, using Al Kα (hv = 1486.6 eV) radiation as the excitation source (\(V = 12 \text{ kV}, I = 10 \text{ mA}\)). The core-level energies were corrected with the C 1s binding energy of 284.8 eV. Nitrogen adsorption–desorption isotherms were acquired at −196 °C in a Quanadrasorb SI sorption analyzer with the samples being degassed at 300 °C for 3 h under a vacuum in the degas port. The specific surface area was calculated with the Brunauer–Emmett–Teller model, and the pore-size distribution was calculated in accordance with the Barrett–Joyner–Halenda method.

\textbf{Electrochemical Measurements.} Electrochemical properties of the CaC\textsubscript{2}-derived carbon materials were investigated using CR2025-type coin cells that were assembled in an argon-filled glovebox. The working electrodes were prepared by coating the slurry of the as-prepared carbon (80 wt %), carbon black (10 wt %), and polyvinylidene fluoride (10 wt %) dissolved in n-methyl pyrrolidinone onto a Cu foil substrate and dried in a vacuum oven at 120 °C for 12 h. The mass loading of the active material was around 1.2 mg cm\textsuperscript{-2} on each electrode. A lithium metal foil (sodium metal used for SIBs) was used as a counter electrode while a glass filter (Whatman) was used as a separator. The employed electrolyte was a solution of 1 M LiPF\textsubscript{6} in ethylene carbonate and dimethyl carbonate (1:1 by volume) (for SIBs, 1 M NaClO\textsubscript{4} in ethylene carbonate and propylene carbonate −1:1 by volume). The cells were galvanostatically discharged and charged at varied current densities in the voltage range from 0.01 to 1.5 V (vs Li\textsuperscript{+}/Li\textsuperscript{-}) or Na\textsuperscript{+}/Na\textsuperscript{-}) using a Biologic BCS-805 multichannel battery test instrument at room temperature. CVs were also measured on the same instrument at a scan rate of 0.1 mV s\textsuperscript{-1} in the same voltage range.

\section{ASSOCIATED CONTENT}

\section{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00448.

High-resolution S 2p XPS spectrum, FE-SEM image together with the corresponding element mappings and EDX spectrum, initial charge/discharge profiles, and CV curves (PDF)

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