An in Situ Template for the Synthesis of Tunable Hollow Carbon Particles for High-Performance Lithium−Sulfur Batteries

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ABSTRACT: Nanostructured materials with hollow interior voids are gaining great attention due to their fantastic geometries and unique physicochemical properties competent for many applications. However, the development of a fast approach to prepare the hollow structured particles remains challenging. Herein, a new and efficient in situ hard-template method was developed to synthesize hollow carbon nano- and microparticles using the as-prepared SiO2 particles as a hard template directly, without any separation, drying, or redispersion. In this way, the hollow carbon particles with tunable diameters and shell thickness can be synthesized readily, which is simpler and more efficient than the traditional ones. In addition, the universality of this strategy allows us to study the different behaviors of hollow carbon particles in lithium−sulfur batteries when the architectures of hollow particles (i.e., diameter, shell thickness, etc.) were changed. We believe that this in situ method is applicable for synthesizing other core−shell or hollow structured materials (e.g., metal oxide), and also, the high performance of hollow carbon particles in lithium−sulfur batteries and beyond can be further explored.

INTRODUCTION

Hollow carbon nano- and microparticles have widespread applications in the fields of catalysis,1 electrochemistry,2,3 energy (e.g., dye-sensitized solar cells),4 supercapacitors,5 rechargeable batteries,6–8 and biotechnology9,10 due to their hollow structure, physical stability, chemical inertness, high conductivity, and biocompatibility. To date, the most commonly used synthesis approach has been the well-known hard-template method,11 the steps of which usually consist of the synthesis of core particles as a template followed by coating the presynthesized core particles (e.g., silica gel,12 polystyrene,13 or metal (oxide) nanoparticles14,15) with a layer of carbon and finally removing the core to form a hollow structure. Despite considerable research on this process having been carried out over the past few decades, a significant problem remains in that the core particles aggregate after centrifugation and drying before they are reused as templates. One effective approach has been a long ultrasonic treatment in order to redisperse the core particles; however, the individual and uniform distribution of core particles from the dried solid powders in solution appears to be irreversible in most cases, such as in the redispersion of silica gel.16–22 Inevitably, the aggregation of core particles results in a poor distribution of the interior hollow structures of particles. To overcome this problem and simplify the process, we present an in situ hard-template method for the synthesis of hollow carbon particles in which the as-prepared core particles are directly used as templates without any separation.

RESULTS AND DISCUSSION

Synthetic Features. The great features of our presented strategy are being efficient, convenient, and cost-effective in which there is no need for separation during the hard-template method (Figure 1a). In detail, silica gel templates with different particle diameters were prepared first by varying the molar ratio of (3-mercaptopropyl)trimethoxysilane (MPTMS, 0.1−10 g) and water (Figure 1b). Sucrose was then added as a carbon source (0.5−15.4 g), and water was then added into the primary silica gel solution while stirring. Next, the mixture underwent hydrothermal treatment in an autoclave while stirring for several hours. The core−shell structured SiO2@C-rich particles were formed after the hydrothermal reaction (C-
rich indicates that the shell materials are rich in carbonaceous materials\(^{23}\) (Figure 1c). After this step, hollow carbon particles were obtained followed by the carbonization of SiO\(_2\)-rich to SiO\(_2\)-C and then HF etching of the SiO\(_2\) core.

**Architectural Features.** The hollow carbon particles (i.e., HCP) with different diameters were obtained as shown in Figure 2. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that well-dispersed hollow carbon particles with an average diameter of 162 nm were prepared using 0.5 g of MPTMS and 2.0 g of sucrose (Figure 2a,b,a1) (i.e., HCP-162-22). Note that the abbreviation of the HCP-diameter-shell thickness means the hollow carbon particles with a certain diameter and shell thickness. By increasing the amount of carbon precursor in the form of sucrose from 2.0 to 3.3 g, the average shell thickness could be finely controlled from 22 to about 34 nm (Figure 2b1,c,c1). This result confirms that the shell thickness can be readily tuned by varying the concentration of carbon precursors. Alternatively, by increasing the amounts of MPTMS and sucrose to 10 and 15.4 g simultaneously, large, hollow carbon particles with an average diameter of 415 nm were synthesized. Their shell thickness was about 82 nm, and their spherical interior void was 251 nm in diameter (i.e., HCP-415-82). Increasing the amount of MPTMS increased the size of the silica particles, and increasing the amount of sucrose increased the thickness of the particle shells. Note that the hollow carbon particles prepared using this strategy have

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**Figure 1.** Typical SEM images and particle size distributions of (a,b) SiO\(_2\) template and (c,d) SiO\(_2\)@C (the carbon shell is after calcination). The inset picture of panel (c) is the local TEM image of SiO\(_2\)@C.

**Figure 2.** Characterizations of the typical HCP. (a) SEM and (b) TEM images of HCP-162-22 (the acronym of HCP-162-22 represents hollow carbon particles with an average diameter of 162 nm and shell thickness of 22 nm, the followed example is the same for comparison). (a1) Particle size and (b1,c1) the shell thickness distributions of HCP-162-22 and HCP-174-34. TEM images of (c) HCP-174-34 and (d) HCP-415-82. (d1) Particle size and the shell thickness histogram of the HCP-415-85.
high surface areas. For example, high surface areas of 1631 and 1495 cm$^2$ g$^{-1}$ with a broad pore size distribution were confirmed for the samples HCP-162-22 and HCP-415-82 (Figure 3).

Moreover, a series of particles of different sizes (130–415 nm) and shell thicknesses (8–82 nm) could be synthesized by changing the amounts of MPTMS and sucrose (Figure 4). This experiment demonstrates the feasibility of this method. Using this strategy, the SiO$_2$ core particles were used directly without any separation, washing, drying, or redispersion, which is very different from other methods.$^{16-22}$ In addition, the SiO$_2$ core can be removed completely, as confirmed by the energy-dispersive X-ray spectroscopy (EDX) (Figure 4c). These results confirm that an in situ hard template can be used to prepare hollow carbon particles over a wide range of sizes and shell thicknesses. More importantly, this concept can be easily extended to other kinds of systems with different core particles, such as polystyrene,$^{23}$ carbon colloids,$^{24}$ and metal (oxide) nanoparticles.$^{26}$ This approach facilitates the preparation of core–shell structured and hollow metal (oxide) particles at reduced energy and cost as it is simpler and more effective than traditional hard-template methods.

**Sulfur Impregnation.** To date, research has focused on the use of varied carbon materials in lithium–sulfur batteries because nanostructured carbon materials such as layered graphene (oxide),$^{27}$ carbon nanotubes,$^{28}$ and porous carbon$^{29}$ play a critical role in embedding sulfur, enhancing the conductivity of electrodes, and suppressing diffusion of the polysulfide intermediates in order to maintain good cyclic performance. Previous results have confirmed the role of carbon as the host for sulfur.$^9-11$ Recently, some efforts have focused on using hollow carbon particles as substrates due to their intriguing hollow structures.$^{10-32}$ However, the electrochemical properties have always been studied under a relative low current density (e.g., 0.1, 0.25 C, wherein 1 C = 1675 mA g$^{-1}$) due to the intrinsic fast capacity degradation of Li–S battery systems, especially at high current densities. Herein, we investigated the performances of three kinds of hollow carbon particles in lithium–sulfur applications at a high current density (e.g., 1 C) and found that one type showed good performance. We also discuss the effects of particle size and shell thickness on electrochemical properties.

First, sulfur was impregnated into hollow carbon particles using the vapor method. After impregnation, the S@HCP composite still maintained its spherical structure and showed relatively individual distribution (Figure 5a,b). The elemental distribution analysis of a typical S@HCP-415-82 particle confirms the presence of a large amount of sulfur concentrated in the hollow interior (Figure 5c). However, due to the differences in particle size and shell thickness, the hollow carbon particles showed different abilities to encapsulate sulfur and increase shell thickness. As shown in Figure 5d, HCP-415-82 particles demonstrated the highest sulfur content (58.5 wt %) compared with HCP-162-22 (48.2 wt %) and HCP-174-34 (55.0 wt %). Particle size and shell thickness clearly determine the sulfur-encapsulation ability, even when particles have similar hollow structures. Moreover, the variation in the evaporation curves of sulfur from the S@HCP composite demonstrates the difference in strength between the carbon host and sulfur (Figure 5d). The HCP-162-22 particles show the strongest interaction with sulfur. The temperature at which complete evaporation occurred was about 430 °C, which is
The electrochemical performance of S@HCP-415-82 was further demonstrated by the voltage versus capacity profiles (Figure 6b), which is well consistent with the CV curves. We find that the cell can cycle well at a high rate of 1 C with an initial capacity of 900 mA h g\(^{-1}\). Besides, the average capacity can achieve 792 mA h g\(^{-1}\) in the initial 100 cycles where the capacity retention is 76.3%. By contrast, average capacities of 570 and 447 mA h g\(^{-1}\) were obtained for the S@HCP-174-34 and S@HCP-162-22, respectively. The capacities of the Li–S cell using the S@HCP-174-34 and S@HCP-162-22 electrodes decrease from 773 to 384 mA h g\(^{-1}\) and from 703 to 250 mA h g\(^{-1}\) with capacity retentions of 49.5 and 35.4%, respectively, after the same cycling period (Figure 6c). Thus, the S@HCP-415-82 composite exhibits the best performance. In addition, high capacities of 1391, 1160, 985, 845, 658, and 338 mA h g\(^{-1}\) can be delivered for the S@HCP-415-82 at rates of 0.1, 0.25, 0.5, 1, 2.5, and 5 C, respectively (Figure 6d). Although these results show the effect of particle size and shell thickness on electrochemical performance, rational correlation and reason for the difference need to be further investigated due to the complexities of the reduction and oxidation processes in lithium–sulfur batteries.45–47 Our preliminary results show that a medium particle size could be probably good for the fast transportation of electrons and lithium ions during the reactions (Figure 6e), while a small particle size (i.e., small hollow voids) and a thin shell thickness might decrease the transportation rate of electrons and lithium ions. In addition, a too small particle size might bring more contact boundaries within the electrode and then cause an increased electric resistance, thereby leading to a low sulfur utilization and a low capacity (Figure 6f). Besides, the thin shell is not good for suppressing the lithium polysulfide shuttling effect because the polysulfide is easy to diffuse outside from the hollow particles. As a result, the S@HCP-415-82 demonstrates a good rate capability and long cycle life over 200 cycles even at a high rate of 2.5 C, under which a high average capacity of 578 mA h g\(^{-1}\) can be delivered (Figure 7).

**CONCLUSIONS**

In summary, a simple and efficient in situ hard-template method was developed to synthesize hollow carbon nano- and microparticles using SiO\(_2\) particles as a template directly, without any separation, drying, or redispersion. This strategy not only bypasses tedious steps such as centrifugation, oven drying of core particles, and particle redispersion but also reduces the cost and energy consumption compared to traditional methods. Undoubtedly, this concept could be further extended to other kinds of systems in which polystyrene, carbon, and metal (oxide) particles are used as templates to synthesize core–shell structured and hollow particles. Additionally, the prepared hollow carbon particles have good performance in the lithium–sulfur battery application, particularly at the high rate conditions. We found that particle size and shell thickness largely determine electrochemical performance, which will be helpful for further investigations of hollow carbon particles in lithium–sulfur batteries and beyond.
EXPERIMENTAL SECTION

Materials Preparations. The hollow carbon particles were synthetized, and sulfur impregnation was carried out as follows. First, 0.4−10 g of (3-mercaptopropyl)trimethyloxysilane (MPTMS) (Sigma Aldrich) was added dropwise into 100 mL of distilled water with vigorous stirring until the solution became transparent. Next, 0.05 mL of NH₄OH was added to the solution (pH = 11), and the reaction was allowed to progress for 12 h at room temperature. After completion of the reaction, a silica colloidal solution with monodispersed SiO₂ particles was formed. Subsequently, 1.0−15.4 g of carbon precursor was dissolved into 200 mL of distilled water and mixed with the SiO₂ colloidal solution, which was then transferred into a stainless steel autoclave. Hydrothermal treatment was carried out at 180 °C for 5 h. The resulting slurry was filtered and washed with distilled water and ethanol.

Figure 6. (a) Cyclic voltammetry curves at 0.1 mV s⁻¹ scanning rate, (b) galvanostatic charge−discharge profiles, and (c) cycling performance of S@HCP-415-82 at a rate of 1 C from the 1st to 100th cycles. (d) Typical charge−discharge curves in the rate test. Comparative reaction behaviors of the sulfur in the (e) large (e.g., S@HCP-415-82) and (f) small (e.g., S@HCP-162-22) hollow carbon particles.

Figure 7. (a) Rate capabilities, (b) galvanostatic charge−discharge profiles, and (c) cycling performance of S@HCP-415-82 at a rate of 2.5 C from the 1st to 200th cycles.
The obtained powder was vacuum-dried at 100 °C for 24 h and annealed at 1000 °C for 2 h under an argon atmosphere. The resulting black powder was immersed in an aqueous HF solution for 24 h to etch away the SiO2 template followed by filtration and washing. After this step, hollow carbon particles (HCP) were obtained. For the sulfur impregnation, 0.3 g of hollow carbon particles and 1.0 g of elemental sulfur were placed on the separated ends of a Y-type glass, and then the Y-type tube was sealed under vacuum. The Y-type glass tube was then heated to 600 °C over 4 h (heating rate, 2 °C min⁻¹) and then cooled to room temperature.

**Materials Characterizations.** The architectural structures of particles were characterized by scanning electron microscopy (SEM), which was performed on a field-emission Hitachi S-4800 instrument operating at an accelerating voltage of 10 kV. The core–shell and hollow characteristics of particles were confirmed by transmission electron microscopy (TEM), which was performed using an FEI Tecnai G2 S-Twin instrument with a field-emission gun operating at 200 kV. Thermogravimetric (TG) analysis was performed from room temperature to 500 °C with a heating rate of 10 °C min⁻¹ under the N2 flow using an STA 449 Jupiter (NETZSCH) thermogravimetry analyzer. The N2 adsorption/desorption measurements were conducted with a Micromeritics ASAP 2010 instrument at various temperatures using the Barrett–Joyner–Halenda (BJH) method.

**Electrochemical Measurement.** The sulfur-based electrode was prepared as follows. The active materials S@HCP and polyvinylidene fluoride (PVDF) binder were mixed in N-methyl-2-pyrrolidone (NMP) to form a uniform slurry, which was then cast on the Al foil and then roll-pressed after vacuum filtration and washing. After this step, hollow carbon particles and 1.0 g of elemental sulfur were impregnated into the slurry. For the sulfur impregnation, 0.3 g of HCP were obtained. For the sulfur impregnation, 0.3 g of hollow carbon particles and 1.0 g of elemental sulfur were placed on the separated ends of a Y-type glass, and then the Y-type tube was sealed under vacuum. The Y-type glass tube was then heated to 600 °C over 4 h (heating rate, 2 °C min⁻¹) and then cooled to room temperature.

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