Rational synthesis of carbon-coated hollow Ge nanocrystals with enhanced lithium-storage properties†

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High-capacity anode materials based on alloy-type group IV elements always have large volume expansion during lithiation when they are used in lithium-ion batteries. Designing hollow structures is a well-established strategy to accommodate the volume change because of sufficient internal void space. Here we report a facile template-free route to prepare hollow Ge nanospheres without using any templates through a quasi-microemulsion method. Ge nanocrystals are preferably self-assembled along the interface of liquid vesicles between water and tetrahydrofuran, and well-defined hollow architectures of ∼50 nm in diameter are formed. Both the wall thickness and hollow interiors can be easily tuned. After subsequent carbon coating via pyrolysis of acetylene, the as-formed Ge@C nanocomposite with hollow interiors exhibits a highly reversible capacity of about 920 mA h g⁻¹ at 200 mA g⁻¹ over 50 cycles, and excellent rate capability. The small size and the high structural integrity of hollow Ge@C structures contribute to the superior lithium-storage performances.

Introduction

Micro-/nanostructured materials with hollow interiors are attracting much attention in a wide variety of fields including energy storage and conversion, catalysis, sensing, and biomedicine because of their large surface area, rich active sites, and high permeability.¹⁴ Generally, hollow structures with various complex interiors, such as core–shell, yolk–shell, and multi-shell structures, are fabricated by a template-assisted method.² Silica,³–⁶ polymers,⁹–¹¹ organogelators,¹² or carbon spheres¹³,¹⁴ are usually utilized as the hard template, and hollow structures are generated upon removal of the templates through a complicated or time-consuming process. In addition, soft-template methods are reported for the synthesis of hollow nanostructures,¹⁵–¹⁷ whereby ionic organic surfactants or nonionic polymers are used to direct the crystal growth. However, they often suffer from the complete removal by subsequent washing, thus limiting their practical applications.¹⁸,¹⁹ Therefore, it is highly desirable to develop a simple and template-free route to prepare nanostructured materials with controllable hollow interiors.

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Here we report a facile but efficient “quasi-microemulsion” strategy to rationally fabricate Ge nanospheres with controlled hollow interiors in a mixed solution of water and tetrahydrofuran (THF) at room temperature. Our route is simple and does not require any surfactant or other harsh processing. The wall thickness, inner size of cavities, and crystallinity of hollow Ge nanospheres can be well tailored. After coating a uniform carbon layer on the surface through pyrolysis of acetylene, the carbon-coated hollow Ge nanospheres exhibit superior lithium-storage performances with a highly reversible capacity and excellent rate capability, taking advantage of the small size, high architectural integrity of hollow core/shell nanostructures, and sufficient inner void space.

Experimental section
Preparation of hollow Ge nanospheres
GeO$_2$ (200 mg) was dissolved in an aqueous solution of NH$_3$·H$_2$O (1.5 mL NH$_3$·H$_2$O; 45 mL H$_2$O). After adding THF (4 mL) and NaBH$_4$ (720 mg), the mixture was continuously stirred for 12 h. The final product was collected after centrifugation, washing with de-ionized water several times, and drying at 120 °C in a vacuum oven for 4 h.

Preparation of hollow Ge@C nanospheres
Typically, the product of hollow Ge nanospheres was put on an alumina boat that was placed in the central heating zone of a tube furnace with flowing N$_2$ gas. After heating to 620 °C (heating rate: 5 °C min$^{-1}$), the N$_2$ gas was replaced by a gas flow of C$_2$H$_2$/Ar (v: v = 10%: 90%), and the furnace was kept at 620 °C for 1 h. Then, the mixed gas of C$_2$H$_2$/Ar was replaced by N$_2$, and the furnace was cooled to room temperature. The black-colored product of hollow Ge@C nanospheres was eventually obtained.

Material characterization
The morphology and microstructure of the products were studied by field-emission scanning electron microscopy (FESEM) (FEI, Sirion 200), and transmission electron microscopy (TEM) (Tecnai G2 F30, Holland). The X-ray diffraction (XRD) patterns of the products were collected from an X’Pert PRO diffractometer (PANalytical B.V., Holland) with CuK$_{α1}$ irradiation (λ = 1.5406 Å). Thermogravimetric (TG) analysis was performed with a PerkinElmer Diamond apparatus. The surface composition was analyzed by X-ray photoelectron spectroscopy (XPS) (a VG MultiLab 2000 system with a monochromatic AlK$_{α}$ X-ray source, Thermo VG Scientific).

Electrochemical measurements
The electrode was prepared by mixing the active material (80 wt%) with carbon black (super-P, 10 wt%) and the binder polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was spread uniformly on a copper foil current collector and then dried at 80 °C in a vacuum for 12 h. The mass loading of the active material was about 1.2 mg cm$^{-2}$. The coin-type cells (CR2032) consisting of a working electrode of the active material and a counter electrode of a lithium foil were assembled in an argon-filled glovebox. The electrolyte involves LiPF$_6$ (1 M) in a mixed solvent of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume). The electrochemical studies of the coin cells were carried out by using a multichannel battery testing system (LAND, CT2001A). Galvanostatic charge/discharge profiles were obtained at different rates of 0.1–5.0 A g$^{-1}$ within a potential window ranging from 0.01 to 3.00 V. The specific discharge/charge capacities of the Ge@C electrode were calculated according to the total mass of the Ge@C. Cyclic voltammetry (CV) curves (0.01–3.00 V, 0.1 mV s$^{-1}$) were recorded using an electrochemical workstation (CHI, 660E) at room temperature. Electrochemical impedance spectroscopy (EIS) was performed using an Autolab PGSTAT100 electrochemical workstation.

Results and discussion
Scheme 1 illustrates the typical formation process of the porous hollow Ge@C nanospheres based on a quasi-microemulsion route. Initially, water and THF are in a mutually soluble state. It would be broken after GeO$_2$ and NH$_3$·H$_2$O are added. Then, a quasi-microemulsion of liquid vesicles could be generated, and their surfaces provide a large number of sites for crystal nucleation of Ge. GeO$_3$$^{2-}$ anions are reduced by NaBH$_4$ to form Ge nuclei at the surface of the vesicles. To reduce the surface energy, the Ge nuclei tend to congregate on the surface of those liquid vesicles, and hollow Ge nanospheres are obtained.

Fig. 1 shows the field-emission scanning transmission electron microscopy (FE-STEM) images of the product. It is observed that the Ge nanospheres of 50–150 nm in diameter are interconnected and have rough surfaces (Fig. 1a). TEM was used to examine the morphology and microstructure of the
products. As displayed in Fig. 1b, the dark/light contrast is clearly observed. The lighter contrast suggests the existence of hollow interiors within the Ge nanospheres. Detailed TEM observations at a higher magnification indicate that the walls of the Ge nanospheres are porous and the thickness of the walls is about 10–15 nm (Fig. 1c). The outer layer of these hollow nanospheres comprises Ge nanocrystals of 2–5 nm in size. The crystallinity of the products was explored by XRD. As shown in Fig. 1d, the XRD peaks could be readily indexed to the cubic phase of Ge (JCPDS no. 04-0545). The corresponding selected-area electron diffraction (SAED) pattern (inset of Fig. 1c) reveals the diffraction rings of the typical cubic phase of Ge, which is also consistent with the XRD result.

The dependence of quasi-microemulsion on the microstructure of the Ge nanostructures has been explored in detail. In the absence of THF, solid Ge particles of 200 nm were obtained (Fig. S1†). Interestingly, Ge nanospheres with hollow interiors were generated in the presence of 0.5 mL of THF in the reaction solution (Fig. 2a and b). By increasing the THF amount to 1 mL, a uniform hollow structure with a wall thickness of about 30 nm could be formed (Fig. 2c and d). Evidently, the wall thickness of the hollow Ge nanospheres evolves with the THF amount (Fig. 2a–h). The wall thickness decreases from 30 nm (THF: 1 mL) to 25 nm (THF: 2 mL), and even 15 nm (THF: 4 mL). Correspondingly, the interior cavities are relatively enlarged, and the surface evolves into the porous nature. However, XRD results indicate that the crystallinity of the Ge products was slightly weakened upon increasing the THF amount (Fig. S2†). These results suggest that the micro-environment of quasi-microemulsion plays a crucial role in the dynamic ripening process for nanocrystal nucleation and growth.

Furthermore, we propose a growth mechanism for the formation of Ge nanospheres with hollow interiors based on the above results (Fig. 3). Despite the fact that water and THF can form an infinitely miscible solution without other substances, it is believed that the precursor solution in this work is far from homogeneous. After GeO₂ and NH₃·H₂O are added, water and THF are in the half-miscible status owing to a salting-out effect. As a result, a kind of micro-environment based on “quasi-microemulsion” is generated, which is similar to the oil-in-water. Since GeO₂ dissolves only in alkaline aqueous solution, the reduction reaction of GeO₂ into Ge occurs in water, instead of THF. The reduction reaction together with subsequent nucleation, crystallization, and crystal growth processes of Ge nanocrystals is carried out in the presence of water molecules. Meanwhile, the interface of liquid vesicles between water and THF based on the quasi-microemulsion should have the lowest surface energy, in contrast to the aqueous bulk. Therefore, Ge nanocrystals are preferentially oriented and self-assembled on the surface of the liquid vesicles in quasi-microemulsion, whereby the THF vesicles may serve as a soft framework (Fig. 3). The unique nature of the quasi-microemulsion micro-environment is further evidenced.
by the formation of solid Ge particles in the absence of THF (Fig. S1†). The nucleation of Ge nanocrystals on the surface of the liquid vesicles would deplete the substance of Ge. As a consequence, the Ge precursor becomes scarcer in the inner aqueous region, leading to an unsatisfying environment for the further crystal growth of Ge nanocrystals. The wall thickness of hollow Ge nanospheres would become thinner. If the opportunity for the contact of Ge nanocrystals is further decreased to a degree where the amount of Ge substances is not enough for filling the gaps between the newly-formed Ge nanocrystals, hollow architectures with porosity can be generated.

Fig. 4a and b show the scanning TEM (STEM) and bright-field TEM images of hollow Ge nanospheres with carbon coating. It is clear that the hollow architecture is well maintained. Fig. 4c displays the high-resolution TEM (HRTEM) image for a part of an individual carbon-coated Ge nanosphere. After an acetylene-pyrolysis process for 2 h, a uniform carbon layer is formed on the surface of the hollow Ge nanospheres. The thickness of the carbon layer is around 4 nm. Fig. 4d shows the XRD pattern of the as-prepared hollow Ge@C NPs. The XRD pattern can be indexed to a cubic phase of Ge (JCPDS card no. 04-0545), which agrees well with the XPS results (Fig. S3†). The fringes in the HRTEM images are separated by ∼3.33 Å, which agrees well with the (111) lattice spacing of cubic Ge. Fig. 4e–h shows the bright-field TEM image and corresponding elemental mappings of a single hollow Ge@C nanosphere, indicating that a uniform carbon layer has been successfully coated on the surface of hollow Ge nanospheres. The carbon content of the hollow Ge@C nanosphere was determined to be about 15.5 wt% by TG analysis (Fig. S4†). The electrochemical impedance spectra of the hollow Ge and hollow Ge@C electrodes were investigated (Fig. S5†). The depressed semicircle of the Nyquist plots at high frequency is attributed to the charge-transfer reaction at the electrolyte/electrode interface, while the linear Warburg part at low frequency depicts the diffusion of ions in the bulk electrode. Evidently, the Ge@C electrode exhibits a much lower resistance than that of the Ge electrode.

The electrochemical lithium-storage properties of the as-formed hollow Ge@C nanospheres have been further explored. Fig. 5a shows the CV results of the initial three cycles at a scan rate of 0.1 mV s⁻¹ between 0.01 and 3 V (vs. Li⁺/Li). During the first lithiation step, the peaks from ∼1.1 to 0.4 V are assigned to the formation of Ge and the solid electrolyte interface (SEI) layer.²¹ Two reduction peaks between 0.25 and 0.1 V arise from lithium alloying with Ge. From the second cathodic scan, the alloying reactions occur at about 0.35 and 0.1 V.²²,²³ In the reversed anodic scans, the broad peaks at 0.45 V are attributed...
to the de-lithiation from the carbon layer and the Li–Ge alloy, respectively. Also, a broad bump between 1.0 and 1.5 V during the oxidation scan may be related to the reoxidation of germanium to germanium oxide.54

Fig. 5b shows the lithiation/delithiation potential profile of the electrode made of the as-formed hollow Ge@C nanospheres at a current density of 200 mA g⁻¹. The initial specific discharge and charge capacities are 1553 and 1041 mA h g⁻¹ (based on the total mass of the Ge@C nanocomposite), respectively, with a relatively high initial Coulombic efficiency of 76%. The capacity loss in the first cycle may be mainly from the irreversible formation of the SEI film on the surface of the Ge@C nanocomposite. The hollow Ge@C nanocomposite delivers a highly reversible capacity of about 920 mA h g⁻¹ at 200 mA g⁻¹ (Fig. 5c) upon 50 discharge/charge cycles. Interestingly, the specific capacity of the composite is 843 mA h g⁻¹ after 200 discharge/charge cycles at 500 mA g⁻¹, with a Coulombic efficiency of ~99% (Fig. S6†). Furthermore, the morphology evolution of the active materials upon Li-cycling was investigated by TEM. It is observed that the hollow structure of Ge@C could be well maintained after 200 discharge/charge cycles at 500 mA g⁻¹ (Fig. S7†).

Fig. 5d shows the rate performance of the hybrid Ge/C electrode. High reversible capacities of 1192, 1117, 996, 890, 782 and 685 mA h g⁻¹ at 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0 A g⁻¹ are achieved. The electrode can also deliver a reversible capacity of 568.5 mA h g⁻¹ even at a high current density of 5 A g⁻¹. After 70 charge/discharge cycles, the current density was switched from 5 to 0.1 A g⁻¹, and the capacity could be recovered to 1152.5 mA h g⁻¹, demonstrating the outstanding high-rate capability of the hybrid Ge@C electrode. For comparison, the cycling performance of solid Ge particles, hollow Ge nanospheres, and hollow Ge@C nanospheres has been further explored (Fig. S8†). Evidently, the electrode of the hollow Ge/C nanocomposite shows a much superior stability and a higher capacity. The excellent electrochemical performance of the Ge@C nanohybrid is mainly attributed to the well-defined nanoarchitecture: hollow Ge encapsulated with a carbon layer. Such an unusual core–shell Ge@C nanostructure with hollow interiors possesses abundant electrochemically active sites and shortened transport pathways for electrons and Li ions. In particular, the space from hollow interiors is effective for buffering the huge volume expansion during Li-cycling processes, which helps to maintain the integrity of the electrode and enable the high performances with high capacity, and superior rate capability, and excellent cyclability. To demonstrate the feasibility of the hollow Ge@C electrode as an alternative material for new-generation lithium-ion batteries, CR2032 coin-type full cells were assembled by using the Ge@C nanocomposite as the anode and commercialized LiCoO₂ as the cathode. The cyclability was studied at a current density of 100 mA g⁻¹ within a cut-off voltage range of 2.6–3.8 V (Fig. S9†). Our preliminary results show that the initial charge/discharge capacities are 1330 and 1087 mA h g⁻¹, respectively, with an initial Coulombic efficiency of about 81%. Upon 20 charge/discharge cycles, the reversible capacity of about 950 mA h g⁻¹ is retained, indicating a good cycling stability. Of course, the conditions for the full cells need to be further optimized in the future.

Conclusions

In conclusion, hollow Ge nanospheres based on a quasi-microemulsion strategy have been controllably synthesized through a simple, template-free, and mild route. Both the wall thickness and the size of inner cavities could be easily tailored.

The micro-environment based on quasi-microemulsion plays a crucial role in the formation of hollow Ge spheres made of self-assembled Ge nanocrystals. After surface modification with a uniform carbon layer, the core–shell-structured Ge@C nanocomposite with tailored hollow interiors exhibits superior reversible capacity and rate capability, when used as an anode material for LIBs. Our work provides the possibility of constructing unique hollow structures that are generally designed for alloy-type anodes (e.g., Si, Ge, and Sn) for high-energy LIBs. Furthermore, the template-free quasi-microemulsion strategy based on the micro-heterogeneity in a polarity-similar mixed solvent can be extended to design and engineer other functional nanomaterials with hollow interiors for various advanced applications in catalysis, sensing, etc.

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