Facile synthesis of hollow silica spheres with nanoholes

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The synthesis of designed nanostructures is an ultimate target of nanomaterial science. Here, silica spheres with nanoholes have been selectively prepared. Coating the necklace-like structured and magnetic nanoparticles along carbon nanotubes, which is an essential step of the simple synthetic procedure of silica hollow spheres, led to the formation of silica hollow spheres with controllable sized nanoholes in their shell walls. The synthesized hollow spheres with nanoholes would be a good support for loading large molecules, e.g. drugs and proteins.

1. Introduction

Future nanotechnology aims at the fabrication of new nanomaterials possessing distinct structural and functional features. Among them, hollow nanospheres have attracted much research and industrial interest due to their special shape, low density, and large fraction of voids. Hollow nanospheres possess a series of advantages, such as tunable void volume, excellent flow performance, and large surface area. The large internal volume provides a storage space or artificial reaction cells that can serve many functions.2

The controlled synthesis of inorganic materials with well designed structures at the nano-size level is extremely important in materials science. In particular, the preparation of hollow inorganic spheres with a defined structure has received increasing attention, because of their potential applications, such as the encapsulation of various substances, as controlled release systems for drug delivery and the manufacture of advanced materials.3 Interestingly, most of these functions rely only on permeation control through the hollow sphere walls and/or specific interactions at their outer surfaces. Functionalities of inner surfaces of hollow spheres have not been fully explored except for some pioneering examples4 although biological cells effectively use inner surface functions as can be seen in signal transduction and photoenergy conversion. Considered simply, effective use of hollow sphere inner surfaces and inner space could double the available functionality relative to traditional systems. Additionally, the interior space environment is not susceptible to particle agglomeration.

The use of hollow inorganic shells in these applications is very important. A breakthrough is the design of the interior space as a storage space or a reaction cell and the shell structure containing paths through which desired molecules can be loaded or released.5 Hollow silica nanospheres have potential applications in drug delivery, ultrasound imaging, catalysts and adsorptive filters.6 Many researchers have developed many ways to create inorganic hollow structures with sponge-like interiors, mesoporous shell structures, spheres with surface perforations or self-organized porous spherical particles.7 However, a hollow spherical structure, with a defined interior space and a shell provided with through nanometer scale holes, sufficiently large enough to allow the passage of biomacromolecules, is essentially unknown.8 Very recently, silica hollow spheres with nanoholes like diatomaceous earth have been synthesized, although the formation mechanism of the macroholes is still unclear.9 The generation of hollow sphere structures with nanohole channels remains the ultimate challenge to researchers in the field.

The drugs loaded in mesoporous hollow spheres10 can be released through many channels. However, this will decrease the releasing time. If the loaded drugs can be released only through one or two nanochannels, it will prolong the releasing time dramatically. An unexplored breakthrough concept in controlled drug release, fabrication of hollow silica spheres with accessibility to their interiors, which we refer to as nanoholes, can be a good choice. Herein, in this communication we report the fabrication of novel silica hollow spheres with a nanohole (<20 nm diameter) obtained by the calcination of Fe3O4@SiO2–CNT hybrid materials and subsequent acid treatment. Fe3O4@SiO2–CNT was synthesized by the combination of a hydrothermal reaction to form necklace structured Fe3O4–CNT and the subsequent silica coating process. One can

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envision the removal of such encapsulated carbon nanotubes and Fe₃O₄ as a way to control the morphology of the silica nanostructures. The removal of templates is a general technique to transfer the diverse template structure to inorganic products. Through the nanohole, large molecules or proteins can be loaded and released in a controlled manner.

2. Experiment

2.1. Assembling Fe₃O₄ nanospheres along CNTs

The pristine MWCNTs were first dispersed into concentrated nitric acid at 130 °C with constant stirring for 6 h. Then, the black solution was treated with an ultrasonicator for 30 min. Afterwards, the solution was diluted with distilled water and rinsed several times until the pH value reaches neutral. The resulting MWCNTs were separated from the solution by filtration and dried in a vacuum at 60 °C for further use. In our experiment, the generation of Fe₃O₄ beads was carried out by modified reduction reactions between FeCl₃ and ethylene glycol in the hydrothermal system. Typically, 0.40 g FeCl₃ was dissolved in 20 mL ethylene glycol to form an orange solution. Then, 100 mg acid treated MWCNTs were dispersed in the solution by ultrasonication for 3 h. After that, 1.8 g NaAc and 0.5 g polyethylene glycol were added with constant stirring for 30 min. The mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 200 °C for 8 h, and cooled to ambient temperature. The black products were rinsed with ethanol several times and dried at 60 °C for 10 h (Fe₃O₄–CNT).

2.2. Coating Fe₃O₄ nanobeads with SiO₂ layer

0.30 g of Fe₃O₄–CNT composite was treated with 0.1 M HCl aqueous solution (50 mL) by ultrasonication. After the treatment for 10 min, the Fe₃O₄–CNT was separated and washed with deionized water, and then homogeneously dispersed in the mixture of ethanol (160 mL), deionized water (40 mL) and concentrated ammonia aqueous solution (2.0 mL, 28 wt%), followed by the addition of tetraethyl orthosilicate (TEOS, 1 mL). After stirring at room temperature for 6 h, the Fe₃O₄@SiO₂–CNT was separated and washed with ethanol and dried at 60 °C.

2.3. Removal of Fe₃O₄ and CNT template

For synthesis of hollow silica spheres with nanoholes, the above dry products have been treated with concentrated HCl (36 wt%) to remove Fe₃O₄ cores and then heated at 650 °C for 12 h to burn off the tubes. Finally, hollow silica spheres with nanoholes were obtained.

3. Results and discussion

Shown in Scheme 1 is the formation process of silica hollow spheres with nanoholes. First, carbon nanotubes were oxidized by HNO₃, forming –COOH groups on the surface of CNTs. In the next step, the carboxylic groups on the CNTs could catch and strongly bond with Fe³⁺ ions in FeCl₃ solution through electrostatic attractions. In the following hydrothermal process, some of these ferric ions would be in situ reduced into Fe²⁺ ions by ethylene glycol and then co-precipitated into Fe₃O₄ crystallites, through which the position-selective decoration of CNTs with magnetite was realized. In the third step, silica selectively coated on the Fe₃O₄ nanobeads, forming core/shell structures. In the last step, through acid treatment and calcination processes, carbon nanotubes and Fe₃O₄ were completely removed, only leaving the silica hollow spheres with nanoholes on the silica shell. Through above processes, silica hollow spheres with nanoholes were finally prepared.

The size and morphology of the as-produced samples were investigated by transmission electron microscopy (TEM). In Fig. 1a, spherical Fe₃O₄ nanoparticles, with average diameters of ca. 200 nm and narrow size distribution, were discretely immobilized along CNTs. It is noteworthy that, beside the limited positions decorated with magnetite beads, the CNTs
are completely clean and free from Fe$_3$O$_4$. It is visible that the CNT pass through the middle of the Fe$_3$O$_4$ bead that is constructed with tiny nanocrystallites. When TEOS hydrolyzed in basic ethanol solution, most of the silica species have been selectively deposited onto Fe$_3$O$_4$ nanobeads. After Fe$_3$O$_4$–CNTs coating with silica, the structure and morphology of Fe$_3$O$_4$@SiO$_2$–CNT were also characterized by TEM. As shown in Fig. 1b and c, only Fe$_3$O$_4$ nanospheres are coated by silica homogeneously, silica shell thickness is about 20–30 nm and different thicknesses of silica shell can be obtained through the controlling of TEOS amount. After Fe$_3$O$_4$@SiO$_2$–CNT was treated with concentrated HCl, Fe$_3$O$_4$ was almost completely removed, only silica and carbon components were left. As shown in Fig. 1d, after removal of the Fe$_3$O$_4$ core, CNTs were clearly observed to pass through the hollow silica spheres.

Further observation on scanning electron microscopy (SEM) provided more structural information about three-dimensional morphology of the Fe$_3$O$_4$@SiO$_2$–CNT hybrid materials. Fig. 2a reveals that, at low magnification, the product consisted of a large quantity of spherical nanospheres and carbon nanotubes. From the close observation in Fig. 2b, it can be clearly seen that CNTs threaded these beads and formed necklace-like nanostructures, which are consistent with the results of TEM results (Fig. 1b and c).

When the calcination process was applied to Fe$_3$O$_4$@SiO$_2$–CNT, CNTs were completely burnt off in air at 650 °C for 24 h. Therefore, this step resulted in the formation of silica shells with nanoholes the size of previously burnt carbon nanotubes. To prove this, TEM was applied to characterize the sample. As presented in Fig. 2c and d, silica spheres with nanoholes were clearly observed. In this sample, nanoholes were found in the silica shell, which directly pass through to the inner space. Furthermore, the size of nanoholes formed in the silica shell is strictly dependent on the size of carbon nanotubes. So the size of the nanohole in the silica shell could be selectively tuned by the diameter of carbon nanotube introduced. This provides opportunities for the controllable synthesis of silica hollow spheres with different sizes of nanoholes for different applications. Furthermore, the shell thickness can also be controlled through adding different amounts of TEOS. Fig. 2e and f show SEM images of the hollow silica spheres with nanoholes. The hollow spherical structure of the silica sphere was preserved even after HCl treatment and calcination processes, and the characteristic through-holes were formed in the silica shell structures. The typical hollow silica spheres with nanohole structure have a silica shell with a thickness of 20–30 nm and through-holes with a diameter smaller than 20 nm. The particle size of typical hollow silica spheres is ca. 200 nm. The through-holes of hollow sphere shell structures were individually patterned at random even in the same sample. The morphological variety of the through-hole structure was observed in relation to the number, size, and shape of through-holes. The through-hole pattern is very relative to the structural nature of Fe$_3$O$_4$ on the carbon nanotubes. Hollow silica spheres with nanoholes are mechanically fragile so that fragmentation or collapse of particles, as seen in Fig. 2f, easily occurred.

Fig. 3a–d show the TEM images of two nanothed hollow silica spheres, the through-holes are clear to see on the hollow spheres. When the sample holder is gradually tilted the hole became more visible. The fraction of supporting carbon film is also observed through the hollow spheres (Fig. 3a–d).

After decoration of the pretreated CNTs with magnetite, a powder X-ray diffraction pattern (XRD) of the sample (as shown in Fig. 4) was recorded. Analysis indicates that the product is a mixture of two phases: cubic Fe$_3$O$_4$ and CNTs. All diffraction peaks of cubic Fe$_3$O$_4$ can be readily indexed according to JCPDS file no. 75-0033, and the diffraction peak at 26° can be indexed to the (002) reflection of the CNTs. No obvious peaks from other phases are observed. The main peaks of Fe$_3$O$_4$ in the XRD pattern are broadened, indicating the crystalline portion of the Fe$_3$O$_4$ particle is very small. After SiO$_2$ coating on the Fe$_3$O$_4$, a new abroad diffraction peak at 23° appeared, combined with TEM images, which means that SiO$_2$ has been successfully coated on the Fe$_3$O$_4$ nanoparticles. However, through calcination and HCl acid treatments, the diffraction peaks which belong to CNT and Fe$_3$O$_4$ disappeared.

![Fig. 2](image-url) (a, b) SEM images of Fe$_3$O$_4$@SiO$_2$–CNTs nanostructures; (c, d) TEM images of hollow silica spheres with nanoholes; (e, f) SEM images of hollow silica spheres with nanoholes.
with only a broad peak around 23° left. This proved the formation of the silica structure.

The nitrogen adsorption–desorption isotherm of silica hollow spheres with nanoholes and its corresponding pore size distribution curve are shown in Fig. 5. The isotherm can be classified as type IV isotherms characteristic of materials. The corresponding pore size distribution data calculated from the desorption branch of the nitrogen isotherm by the BJH (Barrett–Joyner–Halenda) method shows a narrow pore size distribution peaked at 9.6 nm, which are close to the size of carbon nanotubes. However, the calcination process led to a slight decrease of the nanohole diameter in the shell. The specific surface area and pore volume reach 62 m² g⁻¹ and 0.379 cm³ g⁻¹ calculated from the linear part of the BET (Brunauer–Emmett–Teller) plot.

In summary, silica hollow spheres with nanoholes were synthesized through a templating method. Based on the formation of a necklace structure from carbon nanotubes and Fe₃O₄ nanobeads, after coating Fe₃O₄ spheres along the carbon nanotubes with silica, the necklace structure operate as a sacrificial template for the formation of silica spheres with nanoholes. Furthermore, the size of the nanohole in the silica shell can be controlled by the diameter of carbon nanotubes and also the silica shell thickness can also be tuned at will. The through-holes and interior space offered by the novel hollow spheres with nanohole structures have the potential to be developed for applications such as controlled release systems. Silica hollow spheres with nanoholes would be a great container for the big sized proteins or macromolecules in the applications of delivery system.

Acknowledgements

The work was supported by the Foundation for Polish Science within Focus with contract F4/2010. We also thank Adrian Sandu and Keriya Mam, SEM application, specialist at FEI Company.

References