

Hollow organosilica nanospheres prepared through surface hydrophobic layer protected selective etching



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ARTICLE INFO

Article history:

Received 25 November 2014

Received in revised form 22 February 2015

Accepted 25 February 2015

Available online 5 March 2015

Keywords:

Hollow organosilica nanospheres

Selective etching

Hydrophobic layer protection

One-step method

ABSTRACT

In this study, a facile and effective surface hydrophobic layer protected selective etching strategy has been adopted to fabricate organic functionalized hollow silica nanospheres (OHSNSs). Our experiments demonstrated that the morphology and structure of OHSNSs were greatly affected by the types of organosilanes and concentrations of cetyltrimethylammonium bromide (CTAB) as pore-making agent. At low concentration of CTAB (1.9 mg/mL^{-1}), it was found that the protective effect of the hydrophobic layer of 3-thiocyanatopropyltriethoxysilane (TCPTES) was so strong that can be endured long time etching (8 h), leading to the formation of hollow core and organic porous shell structure. And yet, the protective effect of the hydrophobic layer of vinyltriethoxysilane (VTES) was too weak to withstand alkali etching, resulting in preferentially etched of the outer vinyl protection shell. Whereas, at a higher concentration of CTAB (2.5 mg/mL^{-1}), for TCPTES, the irregular and capsules-like spheres were obtained. In contrast, for VTES, porous core/solid shell structures with shell thickness of 16 nm were generated. In addition, no particles were observed when the CTAB concentration was above 2.5 mg/mL^{-1} .

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1. Introduction

The design and synthesis of hollow nanostructure have been of great interest in the past decades [1–5]. Among which hollow silica nanospheres (HSNSs) have attracted tremendous interest due to their fascinating properties, such as excellent mechanical and thermal stability, favorable biocompatibility, large surface area and pore volume, low toxicity and permeable porous shell [2,5–10]. In general, the most widely and most common synthetic method for HSNSs are the templating method including hard-template and soft-template [1,11–18]. The hard-template is normally considered time-consuming and costly. Especially need to be careful to prevent shell collapse during the template removal process. On the other hand, the morphology and porous structure of the as-obtained hollow samples are usually not easy to be controlled because of the deformability of the soft such as micelle and vesicles. Therefore, facile and appropriate approaches to high-quality HSNSs are desirable.

Recently, new synthetic strategies have been reported to prepare HSNSs. For example, Yin and co-workers proposed

surface-protected etching strategy to fabricate HSNSs through appropriate etching agents, such as NaOH, NaBH_4 , NaBO_2 and even hot water [19–22]. Shi's groups have developed a novel method based on the selective etching strategy to prepare HSNSs [23–25]. Zheng's group exploited a cationic surfactant assisted selective etching strategy to prepare high-quality HSNSs [26]. However, above-mentioned methods commonly adopted post-modification process may lead to pore blockage, resulting in decreased surface area and pore volume. Until very recently, Shi's group reported a in situ hydrophobic layer protected selective etching method to prepare organic functionalized HSNSs, in which hybrid silica outer shell was derived from the condensation between TEOS and organic silane [27].

In this paper, organic functionalized HSNSs were prepared by a surface hydrophobic layer protected selective etching strategy using CTAB as pore-making agent. In the obtained HSNSs, the hybrid silica outer shell was formed directly from organic silane via one-step method. Besides, for HSNSs prepared from organic silane with long chain at low CTAB concentration, the hybrid silica outer shell was still remained intact after etching by alkaline etching agent, and yet pure silica core was preferential etched. On the contrary, for HSNSs prepared from organic silane with short chain at the same CTAB concentration, the hybrid silica outer shell was preferential etched, and yet pure silica inner core was etched partly.

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2. Experimental

2.1. Chemicals and reagents

Tetraethyl orthosilicate (TEOS), 3-thiocyanatopropyltriethoxysilane (TCPTES), vinyltriethoxysilane (VTES) were purchased from Aladdin. Cetyltrimethylammonium bromide (CTAB), aqueous ammonia solution (25–28%), ethanol, hydrochloric acid and sodium carbonate were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the reagents materials were used without further purification. Deionized water was used in all experiments.

2.2. Synthesis of solid SiO_2 spheres (denoted as sSiO_2)

sSiO_2 were synthesized by a modified Stöber method. In a typical synthesis, 3 mL TEOS were rapidly dropwise added into the mixture of 40 mL of ethanol, 2 mL of H_2O , and 2 mL of ammonia aqueous solution. And then the mixture was stirred at room temperature for 4 h, forming a white silica colloidal suspension. The silica particles were centrifugally separated from the suspension and washed with ethanol and deionized water.

2.3. Synthesis of HSNSs from TCPTES and VTES, respectively

In a typical synthesis procedure, 50 mg of the above as-synthesized sSiO_2 was firstly homogeneously dispersed in 10 mL deionized water by ultrasonication for 20 min. And then the suspension was added into a mixture solution consisting of 78 mg of CTAB, 15 mL of ethanol, 15 mL of H_2O , and 0.3 mL of ammonia aqueous solution. And stirred at room temperature for 30 min. 0.15 mL of TCPTES was added. The resultant mixture was stirred for additional 6 h, the solid product was recovered by filtration and air-dried at room temperature overnight. Obtaining the solid core/hybrid shell structure, $\text{sSiO}_2@CTAB/h\text{-SiO}_2$. Herein, hybrid shell structure referred to thiocyanato functionalized silica, so the resulting product can be denoted as $\text{sSiO}_2@CTAB/TC\text{-SiO}_2$. For the preparation of HSNSs, $\text{sSiO}_2@CTAB/TC\text{-SiO}_2$ nanoparticles were redispersed in 20 mL of Na_2CO_3 aqueous solution (20 mg), and then stirred at 50°C for 8 h. The obtained products were collected by filtration and washed with ethanol and water for several times. Finally, in order to remove the CTAB, the as-prepared products were extracted by refluxing in certain amount of ethanol containing concentrated

aqueous HCl solution for 24 h. The extracted sample was designated as TC-HSNSs.

For the preparation of HSNSs from VTES, the experimental conditions and procedures were the same as those of the corresponding TC-HSNSs from TCPTES, except that VTES was used as the silane procedure. As described above, obtaining the solid core/hybrid shell structure as well, denoted $\text{sSiO}_2@CTAB/V\text{-SiO}_2$. The extracted sample was designated as V-HSNSs.

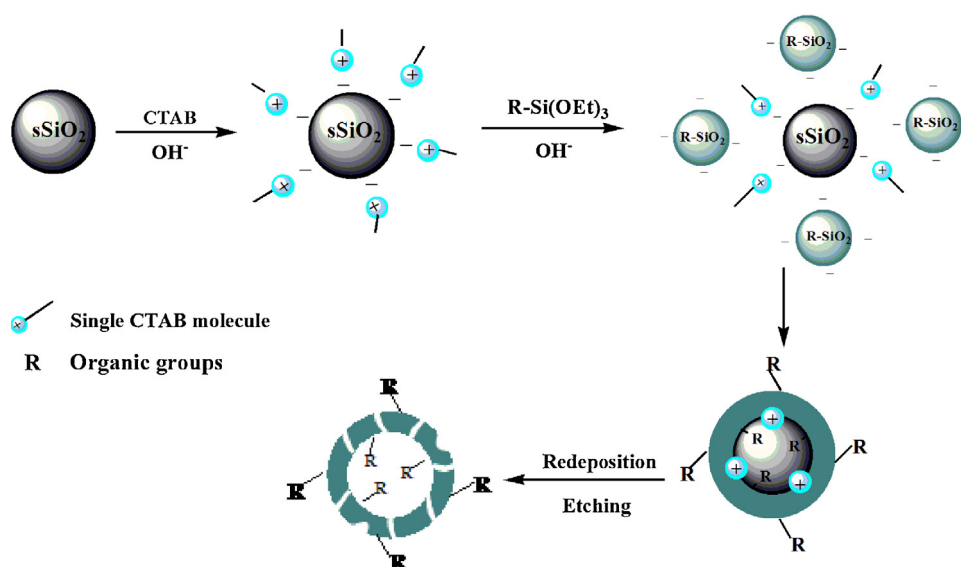
2.4. Characterization methods

Transmission electron microscopy (TEM) (JEM-2100F STEM/EDS) was conducted with a JEM 2100 F electron microscope operated at 200 kV. Fourier transform infrared (FTIR) spectra were collected with a Nicolet Nexus 470 IR spectrometer with KBr pellet. Thermogravimetric analysis (TGA) was carried out on TG 209 instrument to determine the thermal stability of the samples, and the heating rate was $25^\circ\text{C}/\text{min}$ from 25 to 1000°C under room atmospheric pressure. The nitrogen sorption experiment was performed at 77 K on Micromeritics ASAP 2020 system. The pore size distribution was calculated using desorption isotherm branch by the BJH method. Pore volume and specific surface area were calculated by using BJH and BET methods, respectively.

3. Results and discussion

3.1. Synthesis of HSNSs

In present study, the synthesis of HSNSs was schematically illustrated in Scheme 1. Several processes were involved in the conversion of sSiO_2 into the hollow mesoporous structure. Firstly, solid silica particles were prepared via the hydrolysis and condensation of TEOS under alkaline conditions by a modified Stöber method. Secondly, adsorption of cetyltrimethylammonium cations (CTA^+) on the surface of sSiO_2 . Herein, the sSiO_2 spheres showed negative charged under the present alkaline conditions, thereby benefiting the adsorption of CTA^+ on their surface, forming solid $\text{sSiO}_2@CTAB$ structure. And then a hybrid silica shell was further formed on the surface of each aforementioned solid $\text{sSiO}_2@CTAB$ by the hydrolysis and condensation of organosilane, such as TCPTES and VTES, forming solid core/hybrid shell structure, $\text{sSiO}_2@CTAB/h\text{-SiO}_2$. According to the results of Shi's group, which reported a better



Scheme 1. Schematic illustration for the preparation of organic functionalized HSNSs based on the selective etching strategy.

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