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Synchronous synthesis/modification of multifunctional hollow silica nanospheres through selective etching and application in catalysis

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HIGHLIGHTS

- We have developed a novel etching strategy to synthesize multifunctional hollow materials.
- We have prepared two novel multifunctional silica materials.
- The etching and modification processes can be carried out simultaneously.
- The Au nanoparticles can be immobilized in the multifunctional hollow SiO_2 spheres.

GRAPHICAL ABSTRACT

Synchronous synthesis/modification of multifunctional mesoporous hollow SiO_2 microspheres (SH-CN-NH_2-HMSNs and SH-COOH-HMSNs) by utilizing APTES or H_2SO_4 as etching agent.

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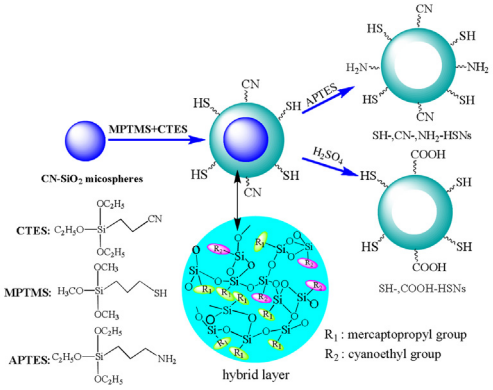

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ABSTRACT

An effective selective etching strategy has been developed to simultaneously synthesize and modify multifunctional hollow SiO_2 nanospheres (HSNs). The key point of this strategy lies in the utilization of (3-aminopropyl)triethoxysilane (APTES) or H_2SO_4 to etch core-shell composite particles, which contribute to the grafting or transformation of organic functional groups in multifunctional HSNs during the etching process. In our study, cyano-SiO_2@cyano-thiol-SiO_2 (CN-SiO_2@SH-CN-SiO_2) composite particles were firstly synthesized by two-step sol-gel reaction of 2-cyanoethyltriethoxysliane (CTES) and 3-mercaptopropyltrimethoxysilane (MPTMS), and then the obtained composite particles could be transformed to be different type of multifunctional HSNs (SH-CN-NH_2-HSNs and SH-COOH-HSNs) after respectively etched by APTES or H_2SO_4. The selective etching strategy greatly simplifies the procedures of preparing multifunctional HSNs. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have demonstrated the hollow structure, and it's found that the morphology of SH-CN-NH_2-HSNs can be regularly changed by manipulating the amount of APTES. Fourier transform infrared (FT-IR) and elemental analyzer have also confirmed

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that the corresponding organic groups certainly exist in the obtained multifunctional HSNs. In addition, when the as-prepared multifunctional hollow SiO_2 spheres were loaded with Au nanoparticles, the composite nanoreactor presented high activity for the catalytic reduction of *p*-nitrophenol.

1. Introduction

The design and fabrication of organic functionalized hollow silica nanospheres (OHSNs) have attracted growing interests in the past decades. As a novel functional material, OHSNs have properties of high-loading organic groups, hollow structure, low density and large surface area, etc [1–5]. So far, many OHSNs with various loading groups, such as –CN, –SH, –CH=CH_2 groups, have been synthesized [6–8], which exhibit high application potential in nanoreactors, biomedicine, drug/gene delivery. However, most of the reported OHSNs just have a single kind of organic group, which limit their application ranges. It's believed that multi-organic functional hollow silica nanospheres with varied organic groups can feature novel special properties, and their application range can also be further extended to a broader variety of fields.

In general, for the process of fabricating hollow structure, the conventional strategies contain Kirkendall effect, hard/soft templating methods, etc. [9–16]. Compared with these methods, new emerging self-templating method based on surface-protected etching or selective etching strategy has advantages of controlling morphology and simpler procedures. Yin and co-workers [17–19] have developed a surface-protecting etching strategy by using PVP as the protective agent. Shi's groups [20–22] have developed a structural difference-based strategy to fabricate HSNs. Recently, a cationic surfactant assisted selective etching strategy developed by Zheng [23] has also been proved to be simple and effective. However, it's difficult to prepare organic functionalized HSNs by these methods. To our knowledge, alkaline (Na_2CO_3, NaOH or ammonia) and hydrofluoric acid (HF) are recognized as the most common etching agents in the self-templating method, which merely apply to the fabrication of hollow structure. Therefore, it is still a challenge to explore novel etching agents which can contribute to the grafting and transformation of organic functional groups in OHSNs during the selective etching process. If the synthesis and modification of organic functionalized OHSNs can be performed synchronously, the preparation process will be greatly simplified.

In this study, we developed a novel selective etching strategy to realize the synchronous synthesis/modification of multifunctional HSNs, which was performed via a two-step process: (1) fabrication of cyano-SiO_2@cyano-,thiol-SiO_2 core-shell composite particles (2) selective etching of the obtained composite particles by (3-aminopropyl)triethoxysilane (APTES) or H_2SO_4. In the first step, poly(thiocyanatosilesquioxane) micospheres were prepared by using 2-cyanoethyltriethoxysliane (CTES) as precursor, and then CN-SiO_2@SH-CN-SiO_2 core-shell composite particles could be obtained by adding 3-mercaptopropyltrimethoxysilane (MPTMS) into the above mixture solution. It's supposed that the external and internal structures of the prepared core-shell particles are inhomogeneous, and the inner cores are relatively unstable. When the APTES was adopted as etching agent, the amino groups could be grafted on the surface of the nanospheres during the process of etching, and then thiol-cyano-amino-trifunctional hollow SiO_2 spheres (SH-CN-NH_2-HSNs) were obtained. When the CN-SiO_2@SH-CN-SiO_2 core-shell composite particles were etched by H_2SO_4, the –CN groups loaded in outer shell could be transformed to be –COOH groups, while the CN-SiO_2 inner cores were dissolved by H_2SO_4. In the end, CN-SiO_2@SH-CN-SiO_2 core-shell composite particles were successfully converted to thiol-carboxylate-bifunctional hollow SiO_2 spheres (SH-COOH-HSNs). Additionally, the catalytic application of SH-CN-NH_2-HSNs loaded with Au nanoparticles for reduction of *p*-nitrophenol was also researched.

2. Experimental section

2.1. Chemicals and reagents

2-Cyanoethyltriethoxysilane (CTES, 95%) was purchased from TCI. 3-Mercaptopropyltrimethoxysilane (MPTMS, 97%) and 3-Aminopropyltriethoxysilane (APTES) were purchased from Aladdin. Aqueous ammonia solution (28 wt%), sulfuric acid (98%), $HAuCl_4{\cdot}3H_2O$ (99.9%), sodium borohydride, 4-nitrophenol (99%) and other reagents were obtained from Sinopharm Chemical Reagent Company Ltd (China). All materials were of analytical grade and were used without further purification. Deionized water was used in all experiments.

2.2. Preparation of CN-SiO_2@SH-CN-SiO_2

1 ml CTES was dissolved in 30 ml water. Ten minutes later, 1 ml ammonia solution (28 wt%) was added into the solution slowly. The mixture was stirred for 4 h at 25 °C, forming a white colloidal suspension. Then, 0.25 ml MPTMS was added into the mixture solution. After a reaction time of about 3 h, the mixture solution was transferred into a sealed Teflon-lined autoclave and heated at 85 °C for 12 h. The obtained CN-SiO_2@SH-CN-SiO_2 composite particles were isolated by centrifugation. Finally, the white sample was washed with ethanol three times and dried at 60 °C.

2.3. Preparation of SH-CN-NH_2-HSNs

A total of 70 mg obtained CN-SiO_2@SH-CN-SiO_2 composite particles were dispersed into 20 ml isopropanol. After stirring at 60 °C for 10 min, a certain amount of APTES were added, and then the mixture was heated at 80 °C for 1 h. Finally, the products were collected by filtration, washed with water and dried at 60 °C overnight.

2.4. Preparation of SH-COOH-HSNs

A total of 100 mg obtained CN-SiO_2@SH-CN-SiO_2 composite particles were dispersed into 50 ml 30.0% H_2SO_4 with stiring and refluxing for 12 h. Finally, the products were collected by filtration, washed with water and dried at 60 °C overnight.

2.5. Loading of Au metal NPs in SH-CN-NH_2-HSNs

60 mg of as-prepared SH-CN-NH_2-HSNs were dispersed in 40 ml of deionized water by sonication for 10 min, and then 10 ml of chloroauric acid (10 mM) was added under stirring at 25 °C. After stirring for 12 h, 5 ml freshly prepared $NaBH_4$ (0.05 M) was added into the mixture under stirring at 25 °C for another 12 h. Finally, the products were collected by filtration, washed with water and dried at 60 °C overnight.