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Selective Basic Etching of Bifunctional Core-Shell Composite Particles for Fabrication of Organic Functionalized Hollow Mesoporous Silica Nanospheres

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Hollow mesoporous silica nanospheres with high-density functional groups were successfully prepared based on an effective basic selective etching strategy. In this work, thiol-functionalized hollow mesoporous silica nanospheres were synthesized by the etch of cyano-SiO₂@thiol-SiO₂ and vinyl-SiO₂@thiol-SiO₂ core-shell composite particles. The composite particles were fabricated respectively via two-step sol-gel reaction of different organosilanes. The different alkali resistance between inner core and outer shell of the composite particles is the key to fabricating hollow silica nanospheres in this paper. When the core-shell composite particles were treated with Na₂CO₃ and NaOH, thiol functionalized outer shell showed higher stability than cyano and vinyl functionalized inner core. The inner core, which is less stable in alkaline condition, will be etched off in base, resulting in a hollow structure. Transmission electron microscopy (TEM) results demonstrate that large-scale hollow mesoporous silica nanospheres can be obtained through this method. In addition, it's also found that the morphology of samples may be regularly changed by manipulating the concentration of alkali in etching process. Fourier transform infrared (FT-IR) and energy dispersive spectrometer (EDS) confirm that the thiol groups exist in the obtained organic functionalized hollow mesoporous silica Nanospheres. We expect this facile strategy can be extended to fabricate organic functionalized hollow mesoporous silica nanospheres with more other valuable functional groups.

Key words: Hollow mesoporous structure; Organic functionalized; Selective etching; Bifunctional composite particles

1. Introduction

Organic-inorganic hybrid silica materials have attracted growing interest in nanomaterials area due to their special properties, such as low density, large surface area, good biocompatibility, high chemical and thermal stability.¹⁻⁵ As one of the advanced types in these materials, organic functionalized hollow mesoporous silica nanospheres (OHMSNs) have important features of hollow cavities, high-loading functional groups and permeable mesoporous shells,⁶⁻⁹ which have been extensively applied in drug/gene delivery, catalysis, and biomedicine.

Generally, hard template¹⁰⁻¹⁴ and soft template¹⁵⁻¹⁹ routes are recognized as two common methods to prepare OHMSNs. Solid nano-particles such as polymer beads and metallic oxide particles were used as sacrificial templates in hard-templating methods, while soft-templating methods utilized micelle and vesicles to form porous and hollow structures. Compared with above two conventional pathways, self-templating methods developed by Yin and co-workers have apparent advantages of simpler procedures and controllable process,²⁰⁻²³ and the self-templating methods adopt silica particles as templates and fabricate HSNSs through appropriate etching process. Shi's groups have further developed this method by proposing structural difference-based selective etching strategy,²⁴⁻²⁷ which can be described as three-step process: (1) the synthesis of template particles, (2) the synthesis of composite particles with core-shell structure, (3) etching the composite particles into hollow structures.

However, most of the reports on selective etching strategy for preparing OHMSNs make use of the difference of

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condensation degree between pure silica and organic-inorganic hybrid silica.^{28,29} To our knowledge, few efforts have been paid to fabricate and etch core/shell silica particles with different organic functional groups distributing in both inner core and outer shell. In fact, wide varieties of organosilanes can provide a broader range for selective basic etching strategy. It's believed that selective basic etching based on the difference of alkali resistance of organic functionalized silica can further extend self-templating method.

In this work, we adopt different organosilanes to form inner core and outer shell of composite particles through two simple processes: (1) one-step synthesis of cyano-SiO₂ and vinyl-SiO₂ nanospheres separately via sol-gel reaction of 2-cyanoethyltriethoxysilane(CTES) and vinyltriethoxysilane(VTES) in pure water system,³⁰⁻³² (2) fabrication of cyano-SiO₂@thiol-SiO₂ and vinyl-SiO₂@thiol-SiO₂ composite particles from the reaction between 3-mercaptopropyltrimethoxysilane(MPTMS) and the as-synthesized organic SiO₂ nanospheres in previous step. Thiol functionalized hollow mesoporous silica nanospheres (T-HMSNSs) are successfully synthesized by etching the composite particles in Na₂CO₃ and NaOH solution. This method is simple and effective, and all the processes are conducted in aqueous phase. Hollow mesoporous silica nanospheres with high-density organic groups distributing evenly in outer layer can be obtained directly by utilizing organosilanes as precursors. In addition, it's found that both of the composition of core-shell particles and etching condition influence the morphology of the OHMSNs.

2. Experimental section

2.1 Chemicals and reagents

2-Cyanoethyltriethoxysilane(CTES,95%) was purchased from TCI. 3-Mercaptopropyltrimethoxysilane (MPTMS,97%). Vinyltriethoxysilane (VTES, 99%) were purchased from Aladdin. Aqueous ammonia solution(28 wt%), sodium carbonate, sodium hydroxide 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 cyano-SiO₂@thiol-SiO₂ and vinyl-SiO₂@thiol-SiO₂

1ml CTES was dissolved in 30ml water. Ten minutes later, 1ml ammonia solution (28 wt%) was added into the solution slowly. The mixture was stirred for 5 h at room temperature (25°C), forming a white colloidal suspension. Then, 0.25ml MPTMS was added into mixture solution. After a reaction time of about 10 h, the obtained cyano-SiO₂@thiol-SiO₂ composite particles were isolated by centrifugation. Then the white sample was washed with ethanol three times and dried under 50°C. The synthesis procedure of vinyl-SiO₂@thiol-SiO₂ composite particles was similar to above process, except that the CTES was replaced with VTES.

2.3 Preparation of T-HMSNSs by selective etching cyano-SiO₂@thiol-SiO₂

The obtained cyano-SiO₂@thiol-SiO₂ composite particles were dispersed into 30ml water of Na₂CO₃ aqueous solution(0.06M, 0.12M, and 0.24M), and then stirred at 50°C for 12 h. Finally, the products were collected by filtration and dried at 60°C overnight.

2.4 Preparation of T-HMSNSs by selective etching vinyl-SiO₂@thiol-SiO₂

The obtained vinyl-SiO₂@thiol-SiO₂ composite particles were dispersed into 30ml water of NaOH aqueous solution(0.04M, 0.08M, and 0.16M), and then stirred at 60°C for 12 h. Finally, the products were collected by filtration and dried at 60°C overnight.

2.5 Characterization methods

Transmission electron microscopy (TEM) (JEM-2100F) and energy dispersive spectrometer (EDS) were conducted with a JEM 2100F electron microscope operated at 200 kV. Fourier transform infrared (FTIR) spectra were collected with a Nicolet Nexus 470 IR spectrometer with KBr pellet. Element content analysis was conducted with elemental analyzer (CHNSO)/(Vario EL cube). The nitrogen absorption 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 The formation mechanism of T-HMSNSs

Before preparing organic HMSNSs, the alkali resistance of the silica materials formed from CTES, VTES, and MPTMS (correspond to a, b, c in Fig. 1) by one-step process has been explored via comparison test. At first, we synthesized CN-SiO₂, CH₂=CH-SiO₂, and SH-SiO₂ nanospheres respectively from sol-gel reaction of CTES, VTES and MPTMS. The SEM images of obtained organic functionalized SiO₂ nanospheres were shown in Fig. S1, and then the three types of SiO₂ nanospheres were treated under the same etching condition. As shown in Fig. 1, the morphology of sample formed from MPTMS basically remained, while the other two samples have been destroyed on different levels. The results of comparison test make it possible for making composite particles with different alkali resistance between core and shell.

In this study, the synthesis of T-HMSNSs was schematically shown in scheme 1, which can be divided into three processes. Firstly, organic functionalized SiO₂ nanospheres were prepared via the hydrolysis and condensation of organosilanes such as CTES and VTES, by using ammonia as alkali catalyst. Secondly, the thiol functionalized outer shell was formed by the hydrolysis and condensation of MPTMS on surface of the nanospheres. And then thirdly, rattle-type or hollow organic silica nanospheres were obtained after etching the composite particles under appropriate condition. The TEM images of cyano-SiO₂@thiol-SiO₂ and vinyl-SiO₂@thiol-SiO₂ composite particles were showed in Fig. S2.

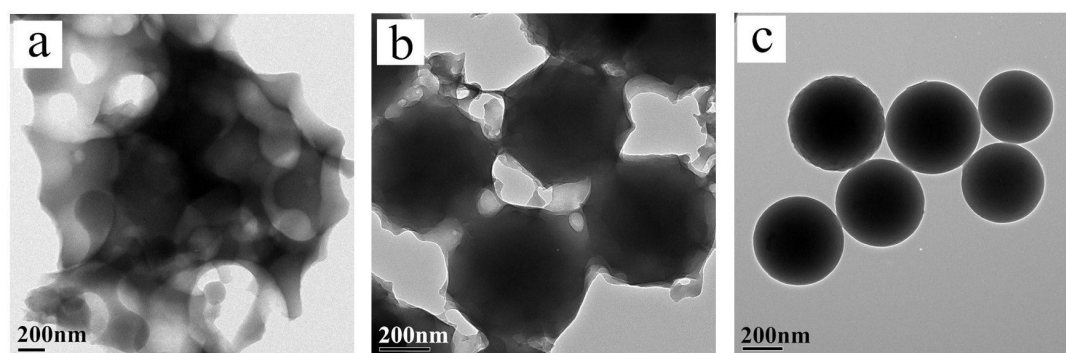
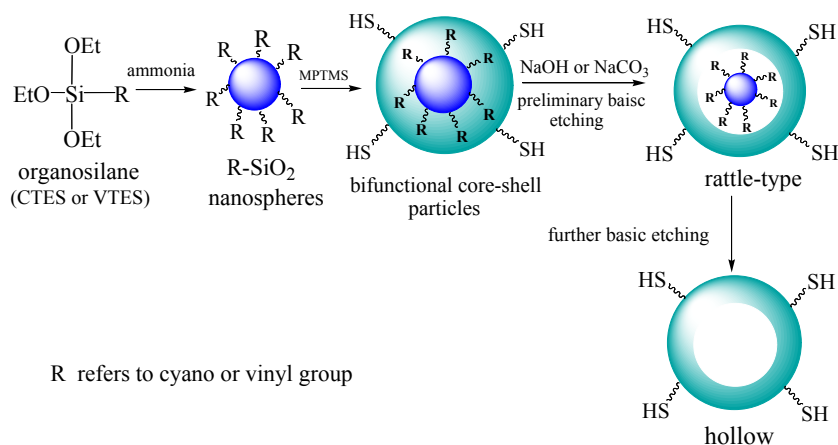


Fig.1 TEM images of organic functionalized SiO₂ nanospheres after treatment with Na₂CO₃ aqueous solution (0.24M) at 50 °C for 1h. The nanospheres were respectively prepared from (a) CTES. (b) VTES. (c) MPTMS.



Scheme 1 Schematic illustration for the preparation of thiol functionalized HSNs based on the selective basic etching strategy.

3.2 T-HMSNs prepared from cyano-SiO₂@thiol-SiO₂

For cyano-SiO₂@thiol-SiO₂ composite particles, we chose Na₂CO₃ as etch agent. After treated the composite particles in Na₂CO₃ solution (0.06M) at 50 °C for 12h, the typical TEM images of cyano-SiO₂@thiol-SiO₂ composite particles with about average of 50nm thick shells and 350nm size core were shown in Fig. 2 a,b. The core of obtained samples was not destroyed seriously under this condition, and the particles still remained perfect spherical structure and high dispersibility. Fig. 2 c,d showed the TEM images of samples obtained by treating cyano-SiO₂@thiol-SiO₂ in 0.12 M Na₂CO₃ solution at 50 °C for 12h. As mentioned before, in the cyano-SiO₂@thiol-SiO₂ particles, alkali resistance of inner core was far weaker than outer shell. Therefore, when further etched, inner core of cyano-SiO₂@thiol-SiO₂ should be destroyed preferentially. From the TEM images showed in Fig. 2 c,d, it could be observed that the core in cyano-SiO₂@thiol-SiO₂ became loose, and more mesopores were generated, so the hollow structure was initially formed. And then, the concentration of Na₂CO₃ solution was increased sequentially to convert cyano-SiO₂@thiol-SiO₂ into complete hollow nanosphere. If other conditions were unchanged, when the concentration of Na₂CO₃ solution rose to 0.24M, T-HMSNs were finally fabricated as shown in Figure 2 e,f. More SEM images and corresponding TEM images were showed in Fig. S3.

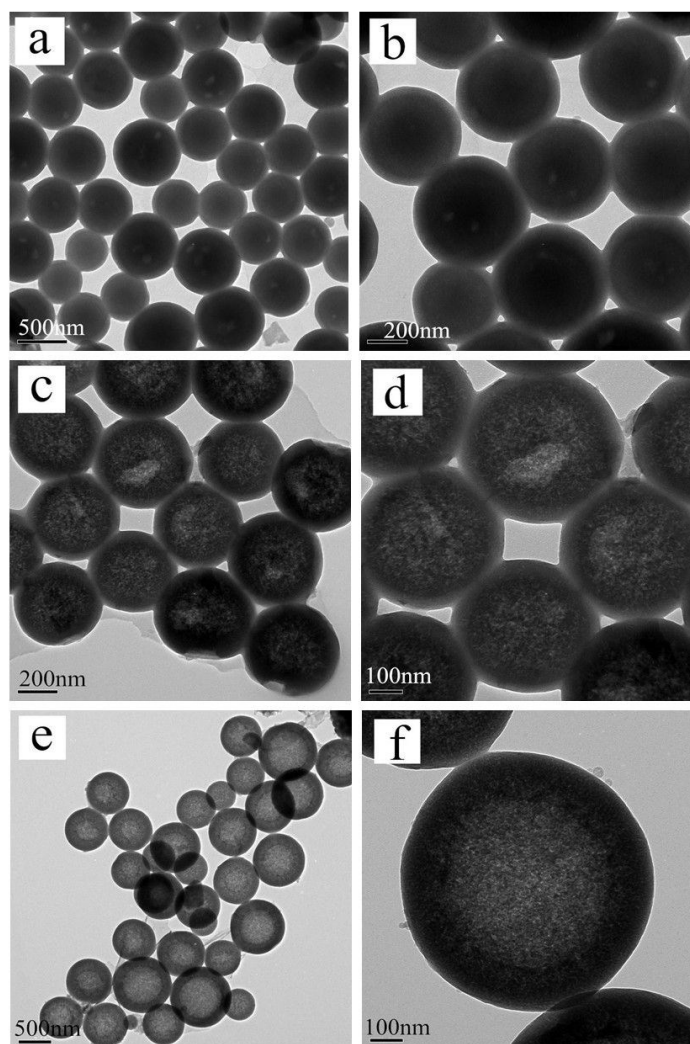


Fig.2 TEM images show the effect of Na_2CO_3 concentration on the conversion of cyano- SiO_2 @thiol- SiO_2 to T-HMSNSs. The Na_2CO_3 concentrations used were (a,b) 0.06 M, (c,d) 0.12 M, (e,f) 0.24 M. All the other reaction conditions were the same: 50 °C for 12 h.

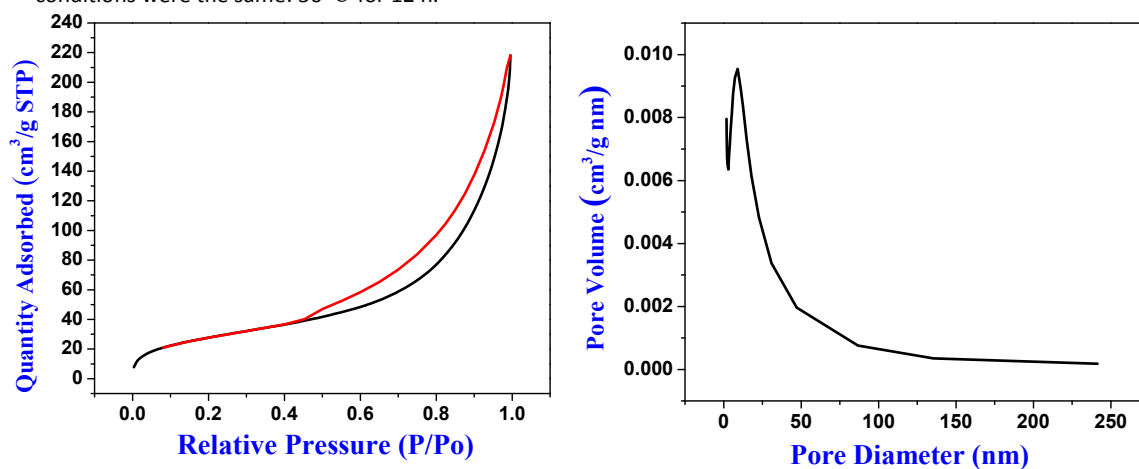


Fig.3 Brunauer–Emmett–Teller (BET) N_2 adsorption–desorption curve (left) and pore distribution (right) of T-HMSNSs prepared from cyano- SiO_2 @thiol- SiO_2 .

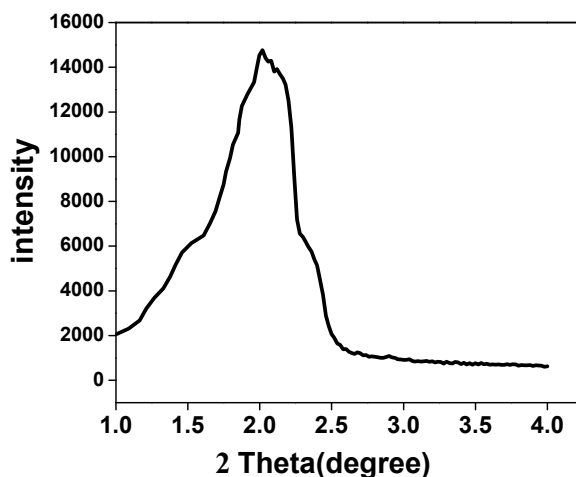


Fig.4 XRD data of T-HMSNS

To further explore the microstructure of obtained T-HMSNSs, N_2 adsorption-desorption measurements were carried out on the products corresponding to the Fig. 2 g,h. The N_2 adsorption-desorption isotherms and pore size distributions were showed in Fig. 3, and specific surface area and pore volumes were $101.524 \text{ m}^2/\text{g}$ and $0.32 \text{ cm}^3/\text{g}$, respectively. These T-HMSNSs had relatively narrow pore size distributions in the range of 2-50 nm and an average diameter of 12 nm. The results of N_2 adsorption-desorption measurements fully illustrated that the typical hollow mesoporous structure of the sample was fabricated. In this work, we only used organosilanes as precursors to prepared T-HMSNSs, and the high-density functional groups of T-HMSNSs may reduce their BET surface area in comparison with previous reports^{33,34} of hollow silica materials with larger BET surface area. The mesoporous structure of T-HMSNSs was further supported by X-ray diffraction (XRD) as shown in Fig. 4, and Fig. S5 showed the pore surface area. To our best knowledge, $s\text{SiO}_2$ solid nanospheres do not diffract at low angles, while the obtained T-HMSNSs exhibited a definite diffraction peak from 1.5° to 2.5° , which is a important of sign of mesoporous structure.³⁵

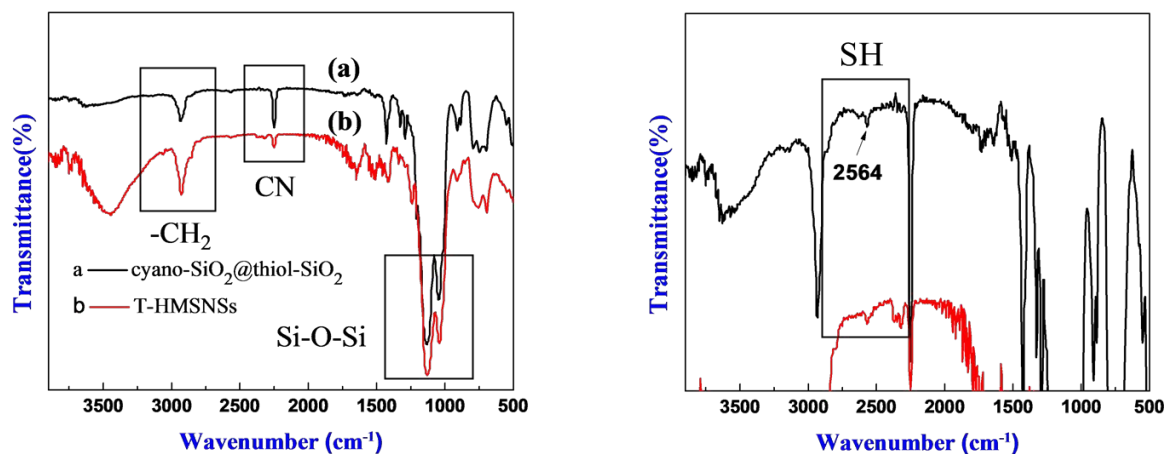


Fig.5 FTIR spectra of (a) cyano- SiO_2 @thiol- SiO_2 composite particles and (b) T-HMSNSs

Fig. 5 exhibited the FTIR spectra of (a) cyano- SiO_2 @thiol- SiO_2 composite particles and (b) T-HMSNSs, and the bands at 2250 cm^{-1} were related to stretching vibration of CN³⁶ groups. MPTMS displayed characteristic $-\text{CH}_2$ stretching bands at 2945 cm^{-1} .³⁷ The strong Si-O-Si stretching vibrations band at 1097 cm^{-1} in $s\text{-SiO}_2$ was split into two peaks (1028 and 1145 cm^{-1}) and the bands at 2952 cm^{-1} were attributed to the symmetrical and asymmetrical stretching peak of $-\text{CH}_2$,³⁰ suggesting that organic groups have been introduced into silica nanospheres. In addition, the right picture is partial enlarged drawing of the left, in which weak absorption peak of SH at 2564 cm^{-1} can be observed.³⁸

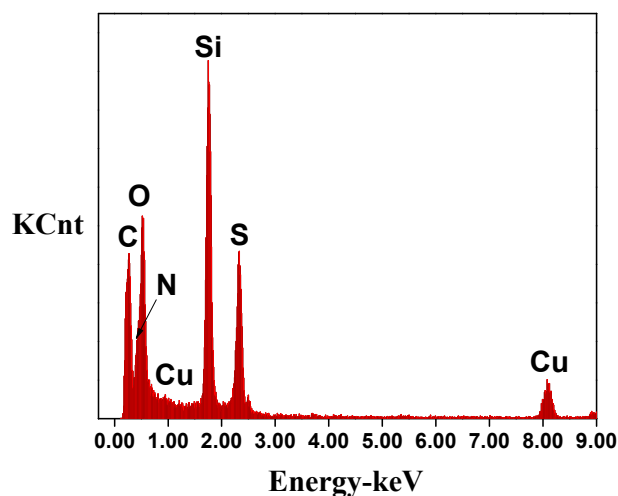


Fig.6 Intergrated EDS of T-HMSNSs

Table 1 Element contents analysis of cyano-SiO₂@thiol-SiO₂ particles and T-HMSNSs samples

Sample	N(%)	C(%)	H(%)	S(%)
cyano-SiO ₂ @thiol-SiO ₂	9.68	32.25	4.238	6.337
T-HMSNS	3.21	29.28	4.584	14.902

The results showed in Fig. 5 revealed that the obtained T-HMSNSs samples contained Si, S, H, N, C, Cu and O (the Cu signals were attributed to the TEM grid of copper used for the EDS experiments). Among these elements, Si, S, C and H confirmed the presence of thiol-SiO₂ synthesized from MPTMS, while N showed the remain of cyano-SiO₂ which was not etched completely. Table 1 presented element contents analysis results of cyano-SiO₂@thiol-SiO₂ before and after etching. The lower level of N was observed after etching, while the content of S increased. The results further supported that cyano functionalized inner cores formed from CTES were etched preferentially.

3.3 T-HMSNSs prepared from vinyl-SiO₂@thiol-SiO₂ composite particles

In order to explore the impact of different combinations of organosilanes, vinyl-SiO₂@thiol-SiO₂ composite particles were also etched under different conditions. As exhibited in Fig. 6, cyano-SiO₂ showed weaker stability than vinyl-SiO₂, therefore stronger etching agent NaOH was chosen to etch vinyl-SiO₂@thiol-SiO₂ composite particles. Fig. 6 showed the representative TEM images of the samples prepared by etching at same temperature and time but at different concentrations of NaOH: (a,b) 0.04M, (c,d) 0.08M and (e,f) 0.16M. When the concentration of NaOH was 0.04M, typical rattle-type nanospheres were obtained (Figure 6 a,b), indicating that vinyl functionalized inner cores were destroyed initially. While the NaOH concentration was increased to 0.08M, a novel void@SiO₂@void@SiO₂ structure was fabricated (Fig. 6 c,d), and it was also found that particles began to blend and a layer of thin film was formed. This was because that the frame structure of composite particles became destabilized and collapsed partly under such strong alkaline condition. Large-scale hollow nanospheres with shell thickness of 20 nm were obtained when NaOH concentration was increased to 0.16M as shown in Fig. 6 e,f. It could be observed that inner cores disappeared completely and the outer shell became thinner, suggesting that thiol-SiO₂ was also destroyed to a certain extent. More SEM images and corresponding TEM images were showed in Fig. S4.

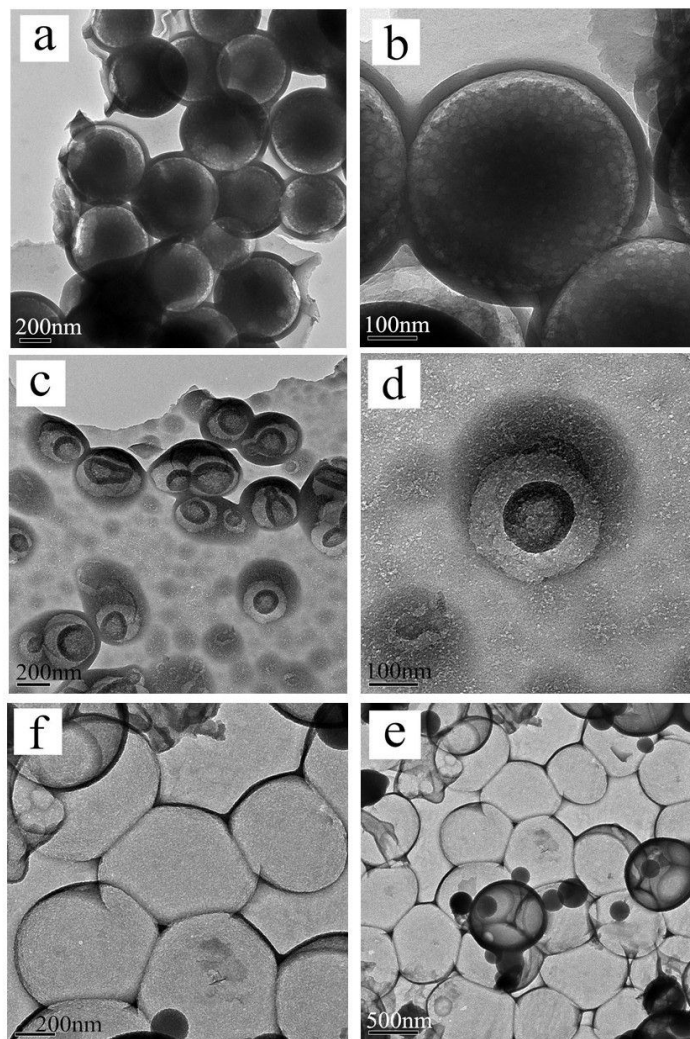


Fig.7 TEM images show the effect of NaOH concentration on the conversion of cyano-SiO₂@thiol-SiO₂ to T-HMSNSs. The NaOH concentrations used were (a,b) 0.04 M, (c,d) 0.08 M, (e,f) 0.16 M. All the other reaction conditions were the same: 50 °C for 12 h.

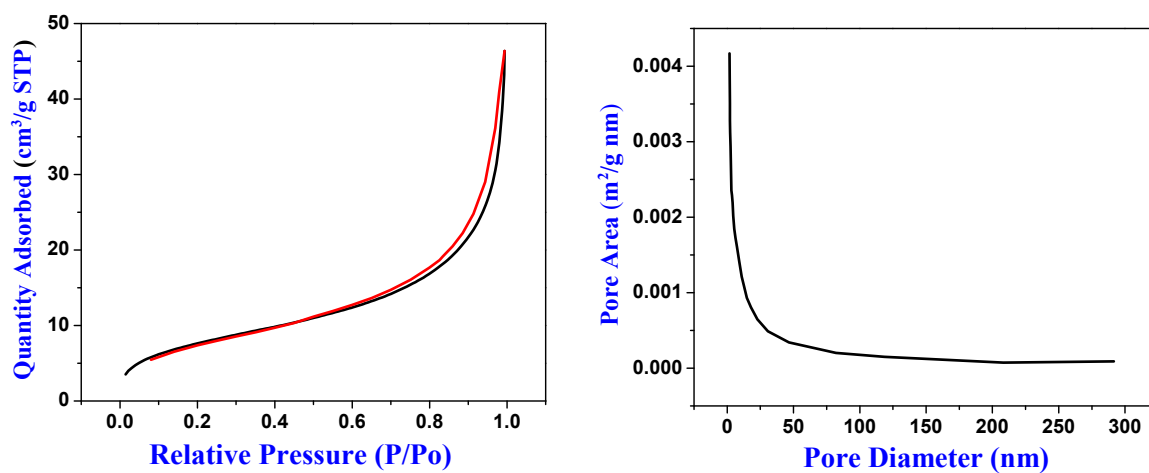


Fig.8 Brunauer–Emmett–Teller (BET) N₂ adsorption–desorption curve (left) and pore distribution (right) of T-HMSNSs prepared from vinyl-SiO₂@thiol-SiO₂.

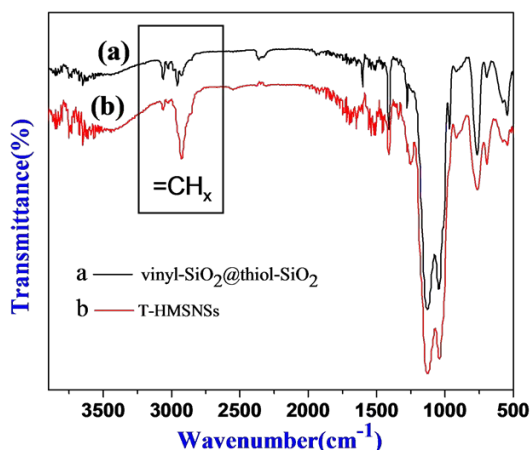


Fig.9 FTIR spectra of (a) vinyl-SiO₂@thiol-SiO₂ composite particles and (b) T-HMSNSs

For T-HMSNSs prepared from vinyl-SiO₂@thiol-SiO₂, the BET surface area and pore volume were only 27.9376 m²/g and 0.0668 cm³/g, and the pore size distribution centered at 1 nm (Fig. 7), which were lower than those of T-HMSNSs prepared from cyano-SiO₂@thiol-SiO₂. In addition, the pore surface area was also smaller (Fig. S5). As seen from Fig. 1, the difference of alkali resistance between thiol-SiO₂ and vinyl-SiO₂ was not great. Thus when cores of vinyl-SiO₂@thiol-SiO₂ were etched, the outer shells were also partly eroded, and the nanospheres reunited seriously, which was responsible for the small surface area and pore volume. Fig. 8 exhibited the FTIR spectra of (a) vinyl-SiO₂@thiol-SiO₂ composite particles and (b) T-HMSNSs, and the stretching vibrations of =CH_x¹⁷ were observed, suggesting that there was still a few vinyl-SiO₂ remained after etching.

4. Conclusion

In summary, an effective selective basic etching strategy has been developed for the synthesis of T-HMSNSs under facile condition. In this strategy, the synthesis of core-shell silica composite particles with tailored resistance to base is key for the formation of the hollow silica spheres. For cyano-SiO₂@thiol-SiO₂ and vinyl-SiO₂@thiol-SiO₂ core-shell particles, thiol functionalized outer layer showed higher stability than cyano and vinyl functionalized inner core. Hollow mesoporous nanospheres with high-density organic functional groups can be obtained by etching the core-shell particles under alkaline condition. The morphology of products was regularly changed via manipulating the concentration of alkali in the etching process. By comparing the etching results of the two types of core-shell particles, it can be concluded that the great difference of alkali resistance between core and shell of composite particles is conducive to the fabrication of hollow structure in etching process. This facile strategy can also be extended to prepare more nanomaterials with different structures and functional groups which contribute to various applications in drug/gene, delivery catalysis, and biomedicine.

Acknowledgements

This work is financially supported by the Nature Science Foundation of Hubei Province (No.2014CFB862), the State Key Laboratory of Natural and Biomimetic Drugs(No.K20140214) and the Fundamental Research Funds for the Central Universities(WUT:2015IB002). We also would like to thank Ting ting Luo and Xiao qing Liu for their HRTEM analysis in the Materials Research and Test Center of WUT.

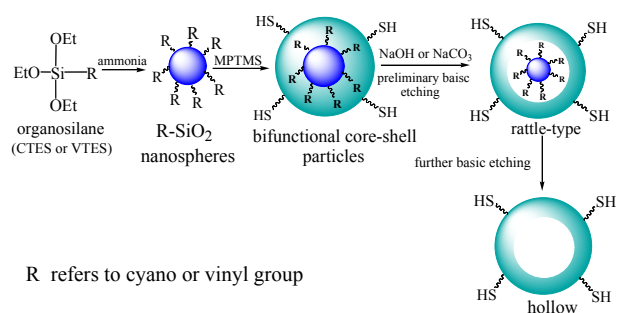
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Graphical Abstract



Bifunctional particles were synthesized by two-step sol-gel reaction of organosilanes, and hollow/rattle-type structures could be fabricated via the basic etching process .