Selective Etching of Bifunctional Core-Shell Silica to Hollow Porous Structure and Adsorption for Cd (II) Ions

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Abstract. In this study, two different bifunctional core-shell structures were prepared separately using cyanoethyl-functionalized silica micro/nanospheres (CN-SiO₂) and vinyl-functionalized silica micro/nanospheres (V-SiO₂) as core, ureidopropyl-functionalized silica spheres (UD-SiO₂) as shell, denoted as CN-SiO₂@UD-SiO₂ and V-SiO₂@UD-SiO₂, respectively. The results were showed that the amounts of cetyl trimethyl ammonium bromide (CTAB) had a great influence on the morphologies of bifunctional organic silica core-shell structures. Furthermore, the above core-shell structures have been etched in alkaline conditions to obtain hollow porous structures, and it was found from the etching experiments that the well-defined porous structures had been obtained using V-SiO₂ as core. At the same time, the adsorption experiment was showed that there was a higher adsorption capacity for Cd(II) ions using V-SiO₂@UD-SiO₂ prepared with 0.008g of CATB as absorbent, due to their well-defined porous structures, larger surface areas and porous volume.

1. Introduction

Hollow micro/meso porous structures are highly attractive in both fundamental research and practical applications due to their large surface area, high porous volume and excellent biocompatibility, which have been widely applied in catalysis, controlled release, energy storage and adsorption[1-5]. Especially, organic inorganic hybrid hollow micro/mesoporous architectures merging the properties of inorganic materials and macromolecular building blocks have found an incredible resonance and attracted widespread interest as a fundamental and technological challenge to chemists, physicists and engineers during the past two decades[6-8]. So far, the templating method is probably the most effective and general route to prepare hollow micro/meso porous structures. While the reported synthetic approaches can be classified into three major categories: hard-templating methods, soft-templating methods and self-templating method[9-10]. Among these, the templates in self-templating methods not only act as a supportive frame and are used to create inner hollow structures, but they also directly participate in the formation of the shell, that is, the template material is directly converted into a shell or as a precursor of the shell[11-12].

Herein, we reported a novel strategy to prepare hollow porous organosilica materials via selective etching of bifunctional core-shell organosilica micro/nanospheres based on self-templating method. Firstly, one type of organic silica micro/nanospheres was synthesized via a one-step method. Secondly, another type of organic silane was hydrolyzed and co-condensed on the surface of the prepared organic silica to form bifunctional organic silica core-shell structure. Finally, hollow porous structures might be obtained by selective etching of different bifunctional core-shell organosilica micro/nanosphere in
alkaline condition. In addition, adsorption experiment for Cd(II) ions was also carried out using etched bifunctional organic silica as adsorbents.

2. Experiments

2.1 Materials
γ-Mercaptopropyltrietoxysilane (MPTES, 99%), 2-cyannethyltrietoxysilane (CTES, 99%), vinyltrietoxysilane (VTES, 99%) and [3- {[Tri(ethoxy)silyl]propyl]urea} (UPTES, 99%) were obtained from Sinopharm Chemical Reagent Co. Ammonia solution (NH₃·H₂O, 28%), cetyl trimethyl ammonium bromide (CTAB) were purchased from Damao Chemical Reagent Company in Tanjing.

2.2 Preparation of CN-SiO₂@UD-SiO₂ and V-SiO₂@UD-SiO₂
Monodisperse organic silica core-shell micro/nano spheres were prepared via post-grafting method. While CN-SiO₂ and V-SiO₂ was firstly prepared via a one-step microemulsion, respectively. And then organic silica core-shell structures were further obtained through hydrolysis and condensation of another organic silane on the surface of the assynthesized V-SiO₂. Finally, the above mixtures were cooled to room temperature, the mixture was centrifuged and washed several times with water and ethanol, separately.

2.3 Selectiv etching of bifunctional core-shell silica to hollow porous structure
For the preparation of hollow porous micro/nanostructures, the as-synthesized products were collected and then extracted by refluxing in certain amount of ethanol containing concentrated aqueous HCl solution for 20 h to completely remove the surfactant. The final surfactant-free products were collected after filtration, water washed and air dried at 50 °C. The final solid product was dispersed in 20 mL of Na₂CO₃ 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, and air-dried at 50 °C to obtain the final etched products, denoted as hollow porous UD-SiO₂ and SH-SiO₂, respectively.

2.4 Adsorption of organic functionalized porous silica for Cd (II) Ions
Adsorption of Cd (II) ions from aqueous solutions was investigated in batch experiments. To measure the maximum adsorption capacity, all of the above organic functionalized hollow porous silica prepared as sorbents, respectively. Various concentrations of Cd (II) solutions (10, 50, 100, 150 mg/L) at pH 7 were applied for the experiments keeping the concentration of sorbents constant at 15 mg/100 mL. The concentrations of the metal ions in the aqueous phases were measured by using a FAAS. Adsorption capacity (mg/g) was calculated as the difference in Cd (II) ions concentration of the pre- and post-adsorption solutions divided by the weight of dry sorbents. The adsorption capacity of Cd (II) ions can be obtained from equilibrium binding data according to Eq. As follow [13-14].

\[
Q = \frac{(c_i - c_f)V}{1000W}
\]

where Q represents the adsorption capacity (mg/g); Ci and Cf are the initial and final concentrations of Cd(II) (mg/L), respectively. V is the volume of the solution (mL); W is the mass used of organic-functionalized hollow porous silica sorbents (mg).

3. Results and Discussion

3.1 Strategy of selective etching of bifunctional core-shell silica to hollow porous structure
The synthetic strategy of hollow porous organic silica micro/nano spheres formed by selective etching of bifunctional core-shell silica is schematically illustrated in Scheme 1. In a typical process, firstly, organic silica micro/nanospheres were prepared by the one-step sol–gel method in microemulsion system. Secondly, UPTES was chosen to further hydrolyze and condense on the surface of CN-SiO₂.
and V-SiO₂ to form CN-SiO₂@UD-SiO₂ and V-SiO₂@UD-SiO₂ core–shell structures, respectively. Finally, all of these core–shell structures were further etched in alkaline condition.

![Scheme 1](image)

### Scheme 1  Schematic illustration for the selective etching of bifunctional core-shell silica to hollow porous structure

#### 3.2 Synthesis of organic silica core-shell structures

In this study, organic functionalized silica core-shell micro/nano spheres were obtained via post-grafting method. Table 1 showed the experimental results prepared by different organosilanes in the presence of CTAB under the same conditions.

| CN-SiO₂ (g) | V-SiO₂ (g) | H₂O (mL) | CTAB (g) | NH₃·H₂O (mL) | UPTES (mL) | \( \bar{x} \) (nm) | CN-SiO₂ | CN-SiO₂@UD-SiO₂ | V-SiO₂ | V-SiO₂@UD-SiO₂ |
|------------|------------|----------|----------|--------------|-------------|----------------|--------|----------------|--------|----------------|
| 0.05       | 0          | 50       | 0        | 0.5          | 0.5         | 2100           | -      | -              | -      | -              |
| 0.05       | 0          | 50       | 0.0085   | 0.5         | 0.5         | 2100           | agglomeration | -    | -              | -      | -              |
| 0.05       | 0          | 50       | 0.0172   | 0.5         | 0.5         | 2100           | 208             | -    | -              | -      | -              |
| 0          | 0.05       | 50       | 0        | 0.5         | 0.5         | -              | -                | 690  | 785            |
| 0          | 0.05       | 50       | 0.008    | 0.5         | 0.5         | -              | -                | 690  | 785            |
| 0          | 0.05       | 50       | 0.0168   | 0.5         | 0.5         | -              | -                | 690  | 835            |

| a | The average spheres size (\( \bar{x} \) (nm)) of organic silica core-shell micro/nanospheres measured by SEM are defined as follows: \( \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \), where \( x_i \) is the spheres size obtained by measuring \( n \) spheres (at least one hundred) for each samples using SEM. |

Figure 1 and figure 2 presented separately the SEM of CN-SiO₂@UD-SiO₂ and V-SiO₂@UD-SiO₂ prepared with different amounts of CTAB. It was obvious from figure 1 that the morphology of organic silica core-shell structures was poorer with increasing of CTAB amounts using CN-SiO₂ as core. Especially, when the amount of CTAB was increased to 0.00185g, the organic silica core-shell was changed from spherical particles to blocky-shaped particles, due to the faster rate of hydrolysis and condensation of organic silane. And interestingly, the particle size was sharply decreased as the amount of CTAB was increased 0.0172g, owing to the hydrolysis of CN-SiO₂ as core.

On the contrast, the encapsulated organic silica core-shell structures using V-SiO₂ as core was better than that using CN-SiO₂ as core. It was showed from figure 2 that the core-shell structures were still keeping spherical morphology when the amount of CTAB was increased.
Figure 1. SEM images of (a) CN-SiO₂, (b) CN-SiO₂@UD-SiO₂ prepared without CATB, (c) CN-SiO₂@UD-SiO₂ prepared with 0.0085g of CATB and CN-SiO₂@UD-SiO₂ prepared with 0.0172g of CATB.

Figure 2. SEM images of (a)V-SiO₂, (b) V-SiO₂@UD-SiO₂ prepared without CATB, (c) V-SiO₂@UD-SiO₂ prepared with 0.008g of CATB and V-SiO₂@UD-SiO₂ prepared with 0.0168g of CATB.

3.3 Formation of hollow porous silica
Figure 3 and figure 4 showed separately the TEM images of the etched CN-SiO₂@UD-SiO₂ and V-SiO₂@UD-SiO₂. Figure 3 gave the corresponding TEM images of the etched CN-SiO₂@UD-SiO₂ obtained without CTAB, it was clearly found that there was some cavitas after etched. For another thing, figure 4 presented the corresponding TEM images of the etched V-SiO₂@UD-SiO₂ obtained
with 0.008g of CATB and 0.0168g of CATB, respectively. It was obvious that the well-defined hollow porous was synthesized using 0.008g of CATB.

Figure 3. TEM images of the etched CN-SiO$_2$@UD-SiO$_2$ prepared without CATB

Figure 4. TEM images of the etched (a) V-SiO$_2$@UD-SiO$_2$ prepared with 0.008g of CATB, (b,c) V-SiO$_2$@UD-SiO$_2$ prepared with 0.0168g of CATB

3.4 Adsorption for Cd (II) Ions
Herein, the obtained hollow porous organic silica were used to adsorb Cd (II) Ions from aqueous solution. The sample 1 refers the etched CN-SiO$_2$@UD-SiO$_2$ prepared without CATB, sample 2 is V-SiO$_2$@UD-SiO$_2$ prepared with 0.008g of CATB and sample 3 is on behalf of V-SiO$_2$@UD-SiO$_2$ prepared with 0.0168g of CATB. It was proved from the adsorption experiment that there was a larger adsorption capacition for Cd(II) ions using V-SiO$_2$@UD-SiO$_2$ prepared with 0.008g of CATB as absorbent, due to their well-defined porous structures, larger surface areas and porous volume.

4. Conclusion
In summary, hollow porous organic silica micro/nano spheres have been prepared by selective etching of bifunctional core-shell silica. The research showed that the amounts of CTAB had very important effect on the formation of bifunctional core-shell silica. At the same time, it was proved from the experiment of adsorption for Cd (II) Ions that the well structure of bifunctional core-shell silica would be in favour of the adsorption for metal ions. This was owing to the well-defined hollow porous structures formed by facile selective etching of bifunctional core-shell silica.
Figure 5. Adsorption capacity of hollow porous silica for Cd (II) at pH = 6.8, time = 30 min

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