A facile and general fabrication method for organic silica hollow spheres and their excellent adsorption properties for heavy metal ions†

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This paper presents a facile and general method for fabrication of organic silica hollow spheres by co-hydrolysis and condensation reactions of TEOS and other silane coupling agents under the catalysis of ammonia. Silane coupling agents were first pre-hydrolyzed to form micelles. When TEOS was added, a sol–gel reaction takes place between TEOS and the Si–OH and methoxy groups, at the surfaces of the micelles to form porous silica shells, producing organic silica hollow spheres. Taking vinyl silica hollow spheres as an example, the as-obtained hollow spheres exhibited considerably high adsorption properties for Pb²⁺ and other heavy metal ions.

Introduction

Silica-based hollow spheres have attracted much attention since the discovery of hollow structures because they have large capacity, low density, thermal stability, low toxicity, and are prepared under mild synthetic conditions and have easily controllable morphology.1–5 And more importantly, they have tremendous applications in biomedical materials, catalysis, composite materials, environmental technologies and electronic devices.6–11

Many interesting approaches have been developed for the fabrication of silica hollow spheres, especially template-based methods are the most widely used, including both hard and soft templates on polymer colloids,14–18 emulsion droplets,19,20 inorganic nanoparticles,21,22 vesicles23 or micelles,24–27 etc. Nevertheless, removal of these hard templates by etching or calcination is not only time-consuming but can also cause collapse or deformation of the shell, while soft templates usually cannot be used to obtain monodisperse size and spherical morphology because soft templates are usually thermodynamically unstable and easily influenced by factors such as the solvent polarity, the pH value, and the ionic strength of the solution.28,29 Therefore, the development of much more efficient and lower cost methods for fabrication of silica hollow spheres is still highly desired. Koo et al. successfully synthesized monodispersed phenyl-functionalized hollow silica particles with 300–800 nm size by hydrolyzing phenyltrimethoxysilane (PTMS) in acidic medium and then condensing it under basic conditions without using templates.30 Yan et al. clarified that the formation of the above mentioned phenyl-functionalized hollow silica particles occurred through the dissolution of polar solvents.31 Wang et al. fabricated hollow silica particles with a hole on their surface with tetraethoxysilane (TEOS) as the precursor and ammonia as the catalyst without any solvent treatment.32 Recently, Hayashi et al. used 3-thiocyanatopropyltriethoxysilane as the precursor and ammonia as the catalyst to prepare photoresponsive hollow spheres.33 These hollow spheres were photoresponsive and burst under light irradiation, releasing the encapsulated drugs or dyes. Very recently, Zhao et al. developed a simple method for the preparation of organic–inorganic silica hybrid hollow spheres with a golf ball-like wrinkled surface based on the self-assembly of methyltrimethoxysilane and TEOS in an alkaline aqueous solution.34 The micro-sized special particles with hollow structures were obtained due to the possible Ostwald ripening mechanism. After that, they even prepared 0.8–4 μm amino-functionalized organosilica hollow microspheres with an open hole on the shell through the hydrolysis and condensation reactions of 3-aminopropyltriethoxysilane and TEOS without an additional template.35 Nevertheless, there is still dearth of enough evidence and data to understand the formation mechanism of these hollow structures.

In this study, we have successfully fabricated vinyl functionalized silica hollow spheres via the hydrolysis and condensation reactions of vinyl trimethoxysilane (VTMS) and TEOS based on a new formation mechanism. This method can further be extended to the preparation of other organic silica hollow spheres. The as-obtained vinyl silica hollow spheres exhibit...
considerably superior adsorption properties for heavy metal ions such as Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$.

**Experimental procedure**

**Materials**

Vinyl trimethoxysilane (VTMS, CH$_2$CHSi(OCH$_3$)$_3$, ≥97%) was obtained from Aladdin Reagent Chemical Reagent Corp. Lead nitrate (Pb(NO$_3$)$_2$, >99%), zinc nitrate (Zn(NO$_3$)$_2$, >99%), cadmium chloride (CdCl$_2$, >99%), copper chloride (CuCl$_2$, >99%), tetraethoxysilane (TEOS, Si(OCH$_2$CH$_3$)$_4$, 99%) and ammonia (25 wt% NH$_3$ in water) were obtained from Sinopharm Chemical Reagent Corp. Deionized water was used throughout the experiment.

**Synthesis of organic silica hollow spheres**

In a typical experiment, VTMS (0.2 g) and H$_2$O (50 g) were charged into a 100 mL three neck round flask equipped with a mechanical stirrer, a thermometer with a temperature controller and a Graham condenser and then stirred at 40 °C at 500 rpm for 1 h to hydrolyze VTMS. Then TEOS (1 g) and ammonia (20 μL) were added and stirred at the same temperature for another 3 h to directly produce vinyl silica hollow spheres. The as-obtained vinyl silica hollow spheres were centrifuged and then washed twice with absolute ethanol. When VTMS was replaced by MPS or PTMS, organic silica hollow spheres with different sizes were also synthesized. The detailed experimental conditions and results are summarized in Table 1.

**Characterization**

Scanning electron microscopy (SEM) images were obtained using a Philips XL 30 field emission microscope at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were taken on a Hitachi H-800 transmission electron microscope at 75 kV. Fourier transform infrared spectrometer (FTIR) spectrum was obtained with a Nicolet Nexus 470 FTIR microscope at 75 kV. Fourier transform infrared spectrometer images were taken on a Hitachi H-800 transmission electron microscope equipped with a field emission microscope at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was performed on a Hitachi H-800 TEM with a 400 kV accelerating voltage. Energy dispersive X-ray spectroscopy (EDX) analysis and elemental mapping were performed with a Hitachi 7620 electron probe X-ray microanalyzer.

**Results and discussion**

**Morphology and structure of organic silica hollow spheres**

Fig. 1a and b present typical TEM and SEM images of the products derived from the sol–gel reaction of VTMS and TEOS. The obvious contrast between the dark shell and the grey core (TGA) was carried out with a TAQ 5000 at a heating rate of 10 °C min$^{-1}$ in nitrogen (40 mL min$^{-1}$ of gas flow). Nitrogen adsorption and desorption experiments were performed at 77 K on a NOVA 4000 gas adsorption analyzer (Quantachrome Corp.). The surface area was determined using the Brunauer–Emmett–Teller (BET) method. Pore volumes were divided into micropores (pore size <2 nm) and mesopores (pore size: 2–50 nm).

**Measurement of adsorption capacity**

0.025 g adsorbent was introduced into a conical flask with 20 mL metal ion solution at different initial concentrations (Pb$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ or Cu$^{2+}$: 10, 20, 40, 60, 80, 100, 150, 200, 300, 400 and 500 mg L$^{-1}$). This flask was then placed in a thermostatic shaker and agitated at 25 °C for 12 h at a shaking rate of 140 rpm. The sample was taken out periodically for measurement of the metal ion concentration in the aqueous phase by inductively coupled plasma optical emission spectrometry (ICP-OES). The equilibrium adsorption capacity of the adsorbent was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where $q_e$ is the equilibrium adsorption capacity of the adsorbent in mg g$^{-1}$, $C_0$ is the initial concentration of the metal ions in mg L$^{-1}$, $C_e$ is the equilibrium concentration of metal ions in mg L$^{-1}$ at the time of equilibrium, $V$ is the volume of metal ion solution, and $W$ is the weight of the adsorbent in g. For each metal ion, three parallel experiments were conducted and their mean value was reported.

**Table 1**

<table>
<thead>
<tr>
<th>Runs</th>
<th>Silanes</th>
<th>Silane : TEOS (weight ratio)</th>
<th>Ammonia (μL)</th>
<th>Hydrolysis conditions (h/°C)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VTMS</td>
<td>1 : 5</td>
<td>20</td>
<td>1/40</td>
<td>Hollow sphere</td>
</tr>
<tr>
<td>2</td>
<td>VTMS</td>
<td>1 : 1</td>
<td>20</td>
<td>1/40</td>
<td>Bowl-like particle</td>
</tr>
<tr>
<td>3</td>
<td>VTMS</td>
<td>3 : 2</td>
<td>20</td>
<td>1/40</td>
<td>Bowl-like particle</td>
</tr>
<tr>
<td>4</td>
<td>VTMS</td>
<td>1.2 : 0</td>
<td>20</td>
<td>1/40</td>
<td>Spherical solid particle</td>
</tr>
<tr>
<td>5</td>
<td>VTMS</td>
<td>1 : 5</td>
<td>20</td>
<td>1/20</td>
<td>Bowl-like particle</td>
</tr>
<tr>
<td>6</td>
<td>VTMS</td>
<td>1 : 5</td>
<td>20</td>
<td>1/30</td>
<td>Hollow sphere with central indentation</td>
</tr>
<tr>
<td>7</td>
<td>VTMS</td>
<td>1 : 5</td>
<td>10</td>
<td>1/40</td>
<td>Hollow sphere</td>
</tr>
<tr>
<td>8</td>
<td>VTMS</td>
<td>1 : 5</td>
<td>20</td>
<td>1/50</td>
<td>Hollow sphere</td>
</tr>
<tr>
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<td>30</td>
<td>1/40</td>
<td>Hollow sphere</td>
</tr>
<tr>
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<td>1 : 3</td>
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<td>1/60</td>
<td>Hollow sphere with central indentation</td>
</tr>
<tr>
<td>11</td>
<td>PTMS</td>
<td>1 : 1</td>
<td>30</td>
<td>3/80</td>
<td>Hollow sphere with central indentation</td>
</tr>
</tbody>
</table>
The weight ratio of VTMS to TEOS was used, monodisperse morphology of the products is displayed in Fig. 2. When the spheres are composed of silica and vinyl-groups. And a strong and broad absorption band at 3420 cm\(^{-1}\) for the characteristic peaks of the silica hollow sphere, other bands at 3062 cm\(^{-1}\) and 2961 cm\(^{-1}\) for the vibration absorptions of \(\text{CH}\) and \(\text{CH}_2\) groups, and 1407 cm\(^{-1}\) for the banding deformation of Si–CH–\(\text{CH}_2\), can be observed for the vinyl silica hollow spheres. And a strong and broad absorption band at 3420 cm\(^{-1}\) is also observed due to the vibration absorption of Si–OH groups.

Fig. 1d further illustrates the TGA curves of the as-obtained vinyl silica hollow sphere and the silica hollow spheres after calcination at 500 °C for the sake of comparison are demonstrated in Fig. 1c. The strong absorption band at 1139 cm\(^{-1}\) is attributed to the stretching vibration of Si–O–Si groups. The peak at 764 cm\(^{-1}\) corresponds to the stretching vibration of Si–O groups. Except for the characteristic peaks of the silica hollow sphere, other bands at 3062 cm\(^{-1}\) and 2961 cm\(^{-1}\) for the vibration absorptions of \(\text{CH}\) and \(\text{CH}_2\) groups, 1602 cm\(^{-1}\) for the vibration of C=C groups and 1407 cm\(^{-1}\) for the banding deformation of Si–CH–\(\text{CH}_2\), can be observed for the vinyl silica hollow spheres. And a strong and broad absorption band at 3420 cm\(^{-1}\) is also observed due to the vibration absorption of Si–OH groups.

Effect of the weight ratio of VTMS to TEOS

The effect of the weight ratio of VTMS to TEOS on the morphology of the products is displayed in Fig. 2. When the weight ratio of 1:5 for VTMS to TEOS was used, monodisperse hollow spheres with an average diameter of 390 nm and a shell thickness of 50 nm were obtained (Fig. 2a). When this ratio was increased to 1:1, bowl-like particles with 880 nm length \(\times\) 660 nm width were produced (Fig. 2b). Further increasing this ratio to 3:2, the length and width were increased to 1.3 \(\mu\)m and 1 \(\mu\)m, respectively for most of the bowl-like particles (Fig. 2c), and a very small amount of particles showed 1 \(\mu\)m length and 250 nm width. When pure VTMS was used, spherical solid particles with a mean size of 1.3 \(\mu\)m were obtained (Fig. 2d). This could be explained as follows: when the VTMS concentration was low, the micelles formed by the hydrolyzed VTMS did not supply sufficient space for TEOS droplets. The micelles were generally small. Most of the TEOS droplets were dispersed in water and hydrolyzed and condensed with the Si–OH groups at the oil–water interfaces of micelles to form a porous silica shell, producing vinyl hollow silica spheres. Increasing the VTMS amount would improve the ability of the micelles to dissolve oil droplets. The migration of TEOS towards micelles in turn increased the sizes of micelles. As TEOS was consumed at the oil–water interfaces of micelles to form silica shells, more and more TEOS molecules migrated from inside the micelles and the oil droplets dispersed in water. Because the micelle sizes were increased, the hollow spheres increased in diameter. These increasing hollow structures caved in to produce bowl-like particles, which can be confirmed by using an optical microscope (Fig. S1†). When only VTMS (even with a very small amount of TEOS) was used as the precursor, it was hydrolyzed and condensed to form solid particles because no strong hydrolysis and condensation reactions occurred at the oil–water interfaces of micelles.
Fig. 3 demonstrates the typical nitrogen adsorption/desorption isotherms and mesopore size distribution of the vinyl silica particles with various morphologies. The nitrogen adsorption/desorption isotherms (Fig. 3a) of both hollow spheres and bowl-like particles show typical type-IV curves, revealing the characteristics of mesoporous materials with mean pore sizes of 4.25 and 6.55 nm (Fig. 3b), respectively. No evident adsorption is observed in the isotherm of the solid particles, indicating the absence of any pores. The hollow spheres show a much larger surface area (259.9 m² g⁻¹), pore volume (0.355 cm³ g⁻¹) and micropore surface area (75.3 m² g⁻¹) than the bowl-like particles (55.1 m² g⁻¹, 0.205 cm³ g⁻¹ and 5.60 m² g⁻¹, respectively) (Table S1†). But the former has a much smaller mean micropore size (0.54 nm) than the latter (0.66 nm), as shown in Fig. S2.†

Effect of temperature

Fig. 4 shows the influence of temperature on the morphology of the as-obtained particles. When the temperature was 20 °C, bowl-like hollow spheres with a mean diameter of 500 nm and a 30 nm thick shell were obtained (Fig. 4a). When the temperature was increased to 30 °C, the mean size of the bowl-like hollow spheres with the same shell thickness decreased to 460 nm, and the dents became weak (Fig. 4b). At 40 °C, monodisperse hollow spheres with a mean diameter of 390 nm and a shell thickness of 50 nm were observed (Fig. 4c). However, with further increasing the reaction temperature to 50 °C, inhomogenous hollow spheres with decreased sizes were obtained (Fig. 4d). This is because higher temperatures cause faster hydrolysis and condensation reactions of VTMS and TEOS.

Effect of NH₃H₂O content

As the amount of NH₃H₂O increased, the average size of the hollow spheres decreased, as shown in Fig. 5. At 10 µL ammonia, the mean diameter of vinyl silica hollow spheres was 450 nm with a shell thickness of 32 nm (Fig. 5a and b). When 20 µL ammonia was used, the average size of hollow spheres decreased to 390 nm with a shell thickness of 50 nm (Fig. 5c and d). Further increasing the ammonia concentration would produce smaller vinyl silica hollow spheres (260 nm in the mean diameter) and a thicker shell (54 nm). And some tiny solid nanoparticles were observed on the surfaces of the vinyl silica hollow spheres (Fig. 5e and f). This should be attributed to the faster sol–gel reactions of VTMS and TEOS at higher amounts of ammonia.

Syntheses of other organic silica hollow spheres

When VTMS was substituted by MPS, methacryloxy propyl silica hollow spheres with a mean diameter of 1.1 µm and a shell thickness of 76 nm were also obtained (Fig. 6a). Each hollow sphere displayed an obvious dent in its center and an accented surface (Fig. 6b). When PTMS was used to replace VTMS, phenyl silica hollow spheres with smooth surfaces and light dents in their centers were obtained (Fig. 6c and d). The mean
diameter was 1.5 μm and the shell thickness was about 150 nm. This means that the present method can be easily extended to fabrication of other organic silica hollow spheres.

**Formation mechanism of vinyl silica hollow spheres**

Based on the above experimental results, a mechanism by which the organic silica hollow spheres were formed is proposed in Scheme 1. The VTMS droplets were dispersed in the aqueous phase under stirring due to their hydrophobic properties, which quickly produced hydrolysis and condensation reactions due to the presence of methoxy groups. At low VTMS amounts, more VTMS molecules were hydrolyzed rather than condensed. These hydrolyzed VTMS molecules easily formed the micelles, as indicated by the TEM image shown in Scheme 1. After addition of TEOS and NH₄H₂O, most of the TEOS was dispersed as droplets in water, only a very small amount of TEOS was dissolved into the micelles. Under the catalysis of ammonia, the hydrolysis and condensation reactions of TEOS and TEOS with the Si–OH groups at the oil–water interfaces of micelles should be very fast to form silica shells. The dissolved TEOS inside the micelles and the TEOS droplets dispersed in the aqueous phase continuously migrated towards these reactions as monomer reservoirs until exhausted, producing vinyl silica hollow spheres. As more VTMS was used, much larger micelles were formed due to more TEOS coming in, when TEOS and ammonia were added, the sol–gel reactions at the oil–water interfaces of micelles also formed silica shells to produce larger hollow structures. However, these large hollow structures are easy to collapse. Any parameters to decrease the sizes of particles, e.g., increasing reaction temperatures or catalysis amounts, are propitious to form spherical organic silica hollow structures. MPS and PTMS have longer hydrophobic chains, and thus could form larger micelles. When TEOS and ammonia were added, larger hollow structures were obtained which showed dents under TEM and SEM observations.

**Adsorption properties of vinyl silica hollow spheres**

Fig. 7a presents the adsorption kinetic behavior of vinyl silica hollow spheres for Pb²⁺ ions by addition of 0.025 g hollow spheres into 20 mL 100 mg L⁻¹ Pb²⁺ solution at 25 °C and pH 5. It can be seen that the Pb²⁺ adsorption was very rapid within the initial 5 min, and then slowed down in the following time, and finally reached the equilibrium after 50 min. This adsorption should be attributed to the electrostatic interactions between Pb²⁺ ions and the negatively charged Si–OH groups on the surfaces of the hollow spheres. As shown in Fig. S3,† at pH 2, the zeta potential of the hollow sphere is 10.54 mV due to the existence of H⁺. However, the hollow spheres exhibit a negative surface charge from pH 4 to 10. The isoelectric point is about 3.8, which demonstrates that there is plenty of –OH on the surfaces. The adsorption experiment was determined at pH 5. Furthermore, the removal of Pb²⁺ ions depends on the pH of the solution, wherein an acidic environment generally favors their removal.⁹ When pH > 7, Pb²⁺ ions precipitated in solution. So the pH was chosen from 2 to 7. The highest removal efficiency of Pb²⁺ was obtained at pH 5 as shown in Fig. S4,† To reduce the influence of different equilibrium times required for Pb²⁺ with different concentrations, the adsorption experiments were conducted for 12 h to ensure complete adsorption equilibrium and to get a value of qₑ. Fig. 7b illustrates the typical adsorption isotherms of the vinyl silica hollow spheres as a function of different metal ion (Pb²⁺, Zn²⁺, Cd²⁺, and Cu²⁺) concentrations. A Langmuir adsorption model, which assumes a surface with homogeneous binding sites, is used to present the relationship between the amount of adsorption at equilibrium (qₑ, mg g⁻¹) and the equilibrium solute concentration (Cₑ, mg L⁻¹).

\[
q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)
\]
where \( q_m \) (mg g\(^{-1}\)) is the maximum uptake capacity corresponding to complete monolayer coverage and \( b \) (L g\(^{-1}\)) is the Langmuir constant that represents the affinity between solute and adsorbent. The values of \( q_m \) are found to be 75.6, 71.5, 65.8, and 54.7 mg g\(^{-1}\) for Pb\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), and Cu\(^{2+}\) ions, respectively. The excellent adsorption properties of the as-obtained hollow silica spheres for heavy metal ions should be ascribed to both the abundant \(-\text{OH}\) groups and the high surface area.

**Conclusion**

Organic silica hollow spheres have been successfully synthesized via a template-free method. In this approach, hydrolyzed silane coupling agents (VTMS, PTMS or MPS) formed micelles in the aqueous phase. After addition of TEOS and ammonia, the hydrolysis and condensation reactions between TEOS and the silanes at the surfaces of the micelles produced silica shells and a final hollow structure. However, when the organic silica hollow spheres were too large, they would form concavities in their centers or bowl-like structures as observed by SEM or TEM. The as-obtained vinyl silica hollow spheres exhibit excellent adsorption performances for heavy metal ions through electrostatic interactions because they have a lot of negatively charged Si–OH groups and high specific surface areas. And because these organic silica hollow spheres contain some functional groups such as vinyl, methacryloxy and phenyl, they can be further functionalized to find more potential applications.

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**References**