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Monodisperse SiO₂ Microspheres with Large Specific Surface Area: Preparation and Particle Size Control

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Abstract:

Monodisperse SiO₂ microspheres have found applications in catalysis, drug delivery, coatings, cosmetics, optical sensing and plastics. The particle size of monodisperse SiO₂ microspheres is closely related to its application. In this paper, monodisperse SiO₂ microspheres with tunable diameter were successfully synthesized using cetyltrimethylammonium bromide (CTAB) as template. The monodisperse SiO₂ microspheres with diameters ranging from 200 nm to 3 μm were obtained by controlling the concentration of CTAB, tetraethyl orthosilicate (TEOS), diethanolamine (DEA) and reaction temperature. The BET surface area could reach 835 $m^2 \ g^{-1}$ and mean pore diameter was 2.3 nm. The formation mechanism of monodisperse SiO₂ microspheres was investigated.

Keywords: Monodisperse; SiO₂ microspheres; template method

1 Introduction

For the past few years, the superior performance of nanomaterials has received extensive attention from scholars. Monodisperse mesoporous SiO₂ microspheres have been widely used in catalysis [1-5], drug loading [6-8], coatings [9-10], optical sensing [11], plastics and other fields by virtue of their large specific surface area, good biocompatibility, stable physical and chemical properties, and easy functionalization of surface hydroxyl groups [12].

As we all known, the particle size of monodisperse SiO₂ microspheres plays a decisive role in their application. For example, nanoscale monodisperse SiO₂ microspheres are widely used in biopharmaceuticals [13], and micron-sized monodisperse SiO₂ microspheres are mostly used in cosmetics, coatings and other fields [14-17]. Sol-gel method is the most widely used method for preparing SiO₂ particles [18]. However, the size of SiO₂ spheres is less then 900 nm and can only be regulated between 10-500 nm. Although seed-mediated growth method can be used to prepare SiO₂ microspheres with a wider range of particle size, this reaction requires strict control of the proportion of various raw materials, as well as the addition rate of tetraethyl orthosilicate, stirring rate, reaction time, and other factors. The preparation of SiO₂ microspheres by a multi-step synthesis method is complicated and time-consuming. It is easy to cause agglomeration or multiple nucleation during the growth of particles. Lei and his team used a modified sol-gel method to synthesize SiO₂ microspheres with particle sizes ranging from 1 μm to 3 μm [19]. Monodisperse SiO₂ was prepared by a two-phase reaction. The monodisperse SiO₂ microspheres with core-shell structure were obtained by controlling the stirring speed, and specific surface area reached 233 $m^2 \ g^{-1}$ [20]. To extend the application of monodisperse SiO₂ microspheres in different fields, it is still a great challenge to prepare monodisperse SiO₂ microspheres with a wide particle size range and large specific surface area.

In this work, using cetyltrimethylammonium bromide (CTAB) as a template and diethanolamine (DEA) as a catalyst, monodisperse SiO₂ microspheres with particle sizes ranging from 200 nm to 3 μm were successfully synthesized and the effects of different reaction conditions to the morphology of the prepared monodisperse SiO₂ microspheres were studied and discussed.

2 Experimental section

2.1 Materials

DEA (99 %) and ethanol (99 %) were purchased from Damao Chemical Reagent Company (Tianjin,China). tetraethyl orthosilicate (TEOS, analytical grade) and CTAB (99 %) were obtained from

Aladdin Reagent Company (Shanghai, China). Deionized water was used in all experiments. All chemicals were used as received without purification.

2.2 Preparation of monodisperse SiO₂ microspheres

In a typical experiment, 0.08 g CTAB was dissolved in 15 mL water under stirring in a beaker. The obtained clear solution was heated to 30 ℃ in water bath. 15.0 mL TEOS (0.1 mol/L) was dropped into the above solution under stirring. And then, 2.0 mL DEA (0.1mol/L) was slowly dropped into the above mixture under stirring. After stirring for 30 minutes, the mixture was kept under static conditions for 24 hours. The resulting monodisperse SiO₂ microspheres (sample 1) were separated by centrifuging and washed with ethanol twice and distilled water once and then dried in an oven at 60 ℃. In order to eliminate the organic residues, the obtained products were thermal treated at 550 ℃ for 2 h in the air.

2.3 Characterization

The morphologies of the products were observed by a SEM equipped with an EDS (Hitachi, S-3400N). The nitrogen adsorption and desorption isotherms were measured on a BELSORP-mini II apparatus. The pore size and the pore diameter distributions were derived from the desorption branches of the isotherm with the Barrett-Joyner-Halenda (BJH) model. X-ray diffraction (XRD) patterns were collected using a Rigaku/Max-3A X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at a voltage of 30 kV and a current of 10 mA. ATA-50 thermal analyzer was used to record the TG curve at a heating rate of 10 ℃ min^{-1} from room temperature to 800 ℃ under an air atmosphere.

3 Results and discussion

3.1 Characterizaton of the typical product

SEM was carried out to observe the size and morphology of the synthesized sample 1. Figure 1 shows that the sample is composed of a large number of spheres with smooth surface and uniform particle size. Figure 2 is the energy spectrum of the sample. In order to further analyze the sample composition, XRD pattern of sample 1 is shown in Figure 3. The diffraction peak centered at 22 ° indicates that the obtained sample is amorphous structure SiO₂ [21]. Figure 4 shows the thermogravimetric spectrum of the prepared sample. It can be seen from the thermogravimetric curve of the sample that the first weight loss is between 40 and 200 ℃, mainly due to the desorption process of water molecules adsorbed on the surface of the silica microspheres. The second weight loss is between 200 and 550 ℃, presumably caused by the decomposition of surfactants and some organic substances in the sample, and the two weight loss rates are about 25%. Figure 5 shows a type Ⅰ isotherm implying the existence of mesoporous, which is confirmed by the pore diameter distribution curve. Sample 1 has a specific surface area of 835 m^2 g^{-1} and the mean pore diameter is 2.3 nm. From the above characterization, it can be seen that Sample 1 is a monodisperse silica microsphere with high purity and amorphous structure.
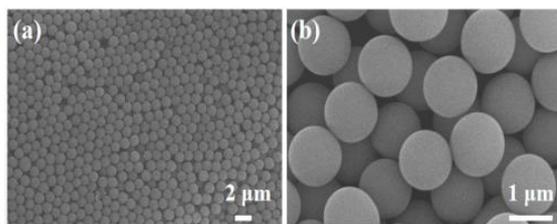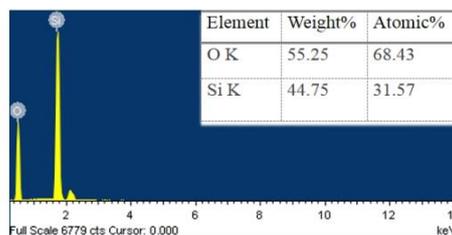

Figure 1　SEM images of sample 1
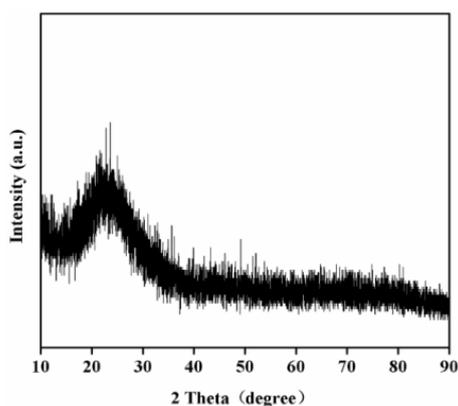

Figure 2　EDX spectrum of sample 1

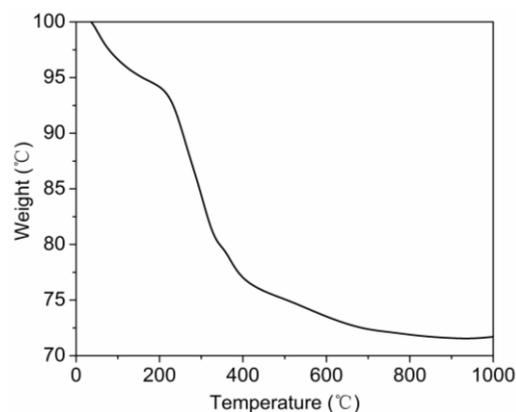**Figure 3**　PXRD patterns of sample 1

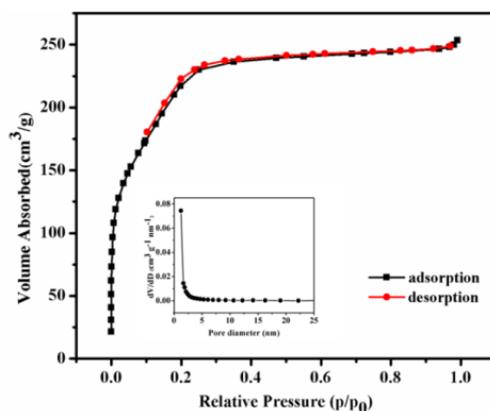**Figure 4**　TG curve of the silica microspheres

Figure 5　Nitrogen adsorption-desorption isotherms of sample 1 and the corresponding BJH pore size distribution curves
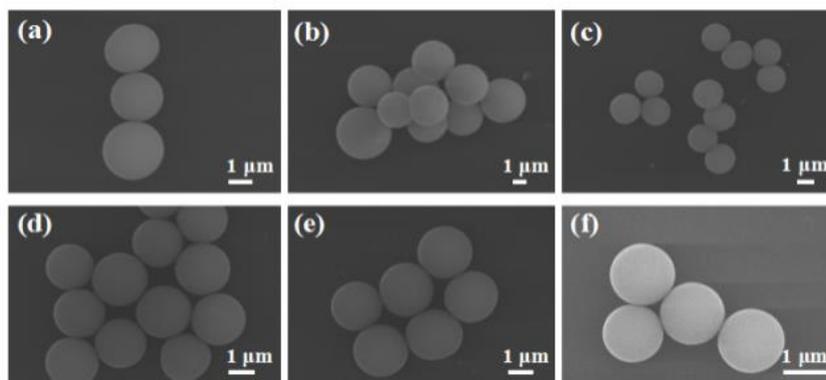

Figure 6　SEM images of SiO$_2$ particles obtained with different amount of CTAB in the solution: (a) 0.01 g, (b) 0.02 g, (c) 0.03 g, (d) 0.05 g, (e) 0.06 g, (f) 0.08 g

3.2 Effect of the CTAB on particle size and morphology

In the absence of CTAB as a template, no precipitation was observed in the solution, because the TEOS cannot undergo hydrolytic polycondensation. When the concentration of CTAB is low, the size of SiO$_2$ microspheres is uneven and the sphericity is not good, because low concentration of CTAB leads to the formation of very large micelles which is called worm-like micelles. When the concentration is greater than the critical micelle concentration, the shape of the micelles is usually spherical [22-23]. In a typical experiment, at the same concentration of TEOS, the particle size of the monodisperse SiO$_2$ microspheres gradually decreases from 2.28 μm to 1.53 μm with the increase of CTAB (Figure 6), the particle size of the monodisperse SiO$_2$ microspheres gradually decreases to the similar size. Finally, the size of the SiO$_2$ microspheres was uniform and spherical. Figure 7 shows the size of the monodisperse SiO$_2$ microspheres, the corresponding particle sizes are 2.28, 2.05, 1.70, 1.80, 1.70, 1.53 μm.
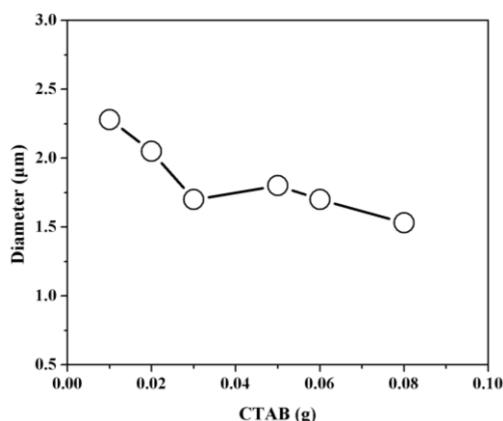

Figure 7　Effect of the amount of CTAB in the solution on the particle diameter
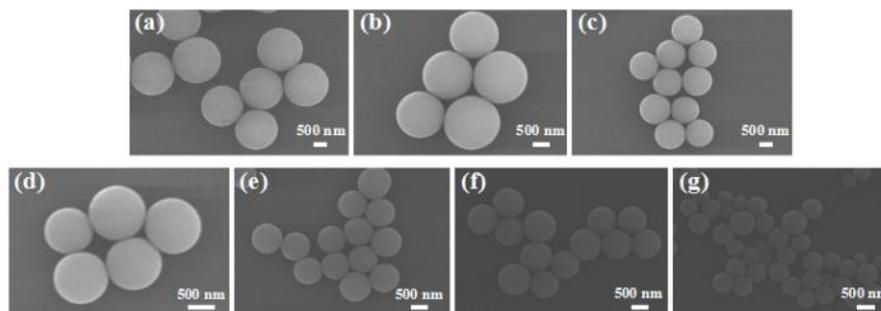
3.3 Effect of DEA on particle size

Figure 8   SEM images of SiO$_2$ particles obtained with different amount of DEA in the solution: (a) 1 mL, (b) 2 mL, (c) 3 mL, (d) 4 mL, (e) 5 mL, (f) 7 mL, (g) 9 mL

It can be seen from the Figure 8 that the particle size of the monodisperse SiO$_2$ microspheres gradually decreases from 1.70 μm to 0.55 μm with the increase of DEA. This is thought to be caused by the increasing of the hydrolysis rate of TEOS with the increase of DEA concentration, and thus resulting in the formation of SiO$_2$ core particles are formed in the early stage. At the same time, the DEA has the dual nature of ammonia and alcohol and it partially ionizes in water, which effectively controls the alkaline environment of the system. The hydroxyl group in the molecule of DEA can also be complexed with the silicon hydroxyl group to terminate the self-condensation of the TEOS [24]. Figure 9 shows the size of monodisperse SiO$_2$ microspheres, the corresponding particle size is 1.70, 1.53, 1.16, 1.03, 0.82, 0.76, 0.55 μm, respectively.
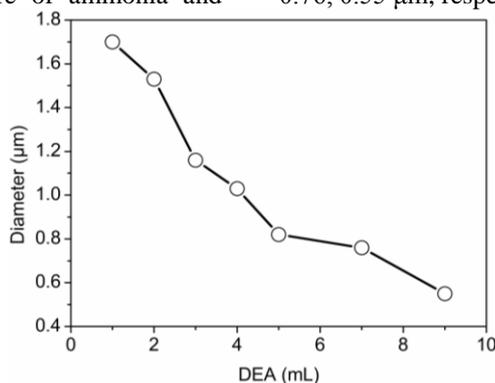

Figure 9   Effect of the DEA on the particle diameter

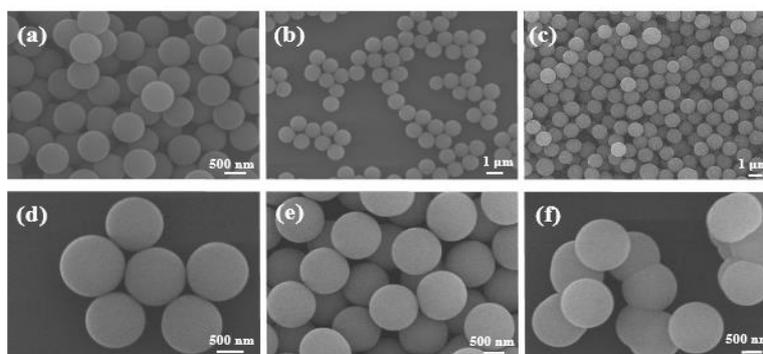## 3.4 Effect of the TEOS on the particle size

Figure 10   SEM images of SiO$_2$ particles obtained with different amount of TEOS in the solution: (a) 0.01 mol/L, (b) 0.05 mol/L, (c) 0.1 mol/L, (d) 0.15 mol/L, (e) 0.2 mol/L, (f) 0.3 mol/L

It can be seen from the Figure 10 that the particle size of the monodisperse SiO$_2$ microspheres increases gradually from 0.75 μm to 1.34 μm with the increase of the concentration of TEOS. However, too high concentration of TEOS destabilizes the reaction system, leading to the adhesion of SiO$_2$ microspheres [25-26]. The conclusion is that with the

increase of TEOS, the particle size of SiO_2 microspheres increases and the output is improved. Figure 11 shows the size of monodisperse SiO_2 microspheres, the corresponding particle size is 0.75, 1.07, 1.13, 1.16, 1.18, 1.34 μm.
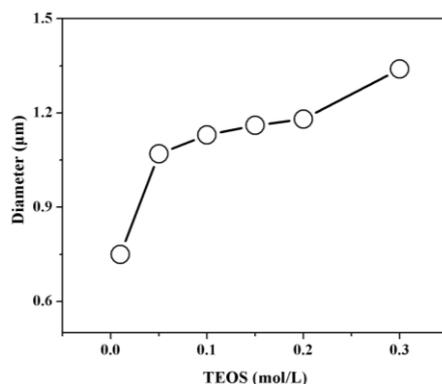

Figure 11　Effect of the TEOS on the particle diameter

3.5 Effect of temperature on the particle size

Experiments were carried out at different temperatures to investigate the effect of temperature on the formation of SiO_2 spheres. It was found that the reaction at low temperature was slow under the condition of equal DEA. With the increase of temperature, precipitation time is shortened, and precipitation occurs immediately at 60 ℃. It can be seen from the Figure 12 that the particle size of the monodisperse SiO_2 microspheres decreases with the increase of temperature. At the same concentration of TEOS, due to the slow hydrolysis rate of TEOS at low temperature, the formation of small particles of silicic acid nuclei is less, and the main reaction is polycondensation, which leads to the growth of SiO_2 microspheres. When the temperature is high, the hydrolysis rate of TEOS is accelerated. In the early stage, a large amount of TEOS is consumed to form a large number of small nucleating particles. In the later stage, smaller microspheres are formed [27]. As shown in Figure 13, the corresponding particle size is 1.53, 1.25, 1.13, 0.91, 0.87, 0.25 μm.
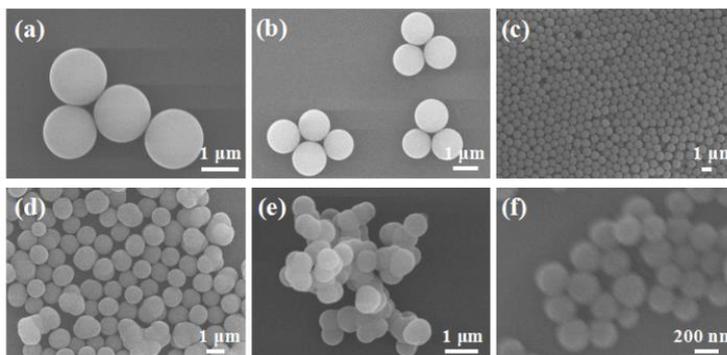

Figure 12　SEM images of SiO_2 particles obtained at different temperatures: (a) 5 ℃, (b) 20 ℃, (c) 30 ℃, (d) 40 ℃, (e) 50 ℃, (f) 60 ℃
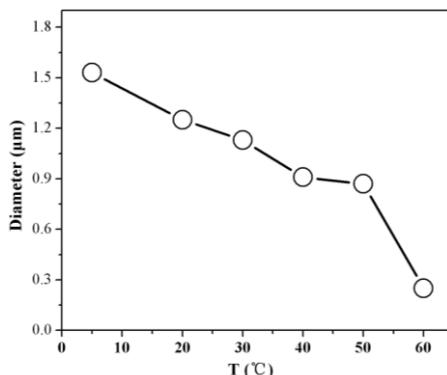

Figure 13　Effect of temperature on the particle diameter

4 Conclusions

Monodisperse SiO_2 microspheres with diameter from 200 nm to 3 μm are synthesized successfully by a template method, and BET surface area could reach 835 m^2 g^{-1}, mean pore diameter was 2.3 nm. The particle size range of the preparation of monodisperse SiO_2 microspheres was expanded, with the increase of CTAB concentration, the role of template causes SiO_2 microspheres to change from non-spherical to spherical and particle size of SiO_2 microspheres gradually decreased and remained unchanged. The sphericity and dispersion of SiO_2 microspheres gradually increased. With increase of DEA or temperature, the hydrolysis rate of TEOS is increased，more silicic acid nucleus particles are formed in the early stage, leading to the formation of smaller SiO_2 microspheres. The modest increase of TEOS concentration contributes to SiO_2 microspheres growth.

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