Hollow periodic mesoporous organosilica nanospheres by a facile emulsion approach

Xiaobo Ma,^a Junjie Zhang,^b Meng Dang,^b Jin Wang,^b Zenzen Tu,^b Lihui Yuwen,^b Guotao Chen,^c
Xiaodan Su,^{*,b} and Zhaogang Teng^{*,c}

^a School of Optoelectronic Engineering, Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210023, P.R. China.

^b Key Laboratory for Organic Electronics & Information Displays and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210046, P.R. China.

^c Department of Medical Imaging, Jinling Hospital, School of Medicine, Nanjing University, Nanjing 210002, P.R. China

Abstract

Periodic mesoporous organosilicas (PMOs) with homogeneously incorporated organic groups, highly ordered mesopores, and controllable morphology have attracted increasing attention. In this work, one-step emulsion approach for preparation of hollow periodic mesoporous organosilica (HPMO) nanospheres has been established. The method is intrinsically simple and does not require any sacrificial templates, corrosive and toxic etching agents. The obtained HPMO nanospheres have high surface area ($\sim 950 \text{ m}^2 \text{ g}^{-1}$), accessible ordered mesochannels ($\sim 3.4 \text{ nm}$), large pore volume ($\sim 3.96 \text{ cm}^3 \text{ g}^{-1}$), high condensation degree (77%), and diameter ($\sim 560 \text{ nm}$), hollow chamber size

* Corresponding authors

E-mail addresses: zhaogangteng@163.com (Z. Teng), iamxdsu@njupt.edu.cn (X. Su).

(~400 nm), and shell thickness (~80 nm). Furthermore, cytotoxicity show the cell viability is higher than 86% after incubating with the HPMO nanospheres at a concentration of up to 1200 $\mu\text{g mL}^{-1}$ for 24 h. The hemolysis of HPMO nanospheres is lower than 1.1% at concentrations ranging from 10 to 2000 $\mu\text{g mL}^{-1}$. The lower hemolysis and cytotoxicity make the HPMO nanospheres great promise for future biomedical applications.

Keywords

Periodic mesoporous organosilica, Hollow structure, Mesoporous materials, Eemulsion approach, Biocompatibility

1. Introduction

Periodic mesoporous organosilicas (PMOs) have attracted more and more research attention because of their combined advantages of ordered mesoporous structure, organic and inorganic fragments hybridized frameworks, and controllable morphologies. The morphology of the PMOs is very important for their practical applications. Up to now, different morphologies of PMOs, such as spheres,^[1-4] rods,^[5-7] polyhedrons,^[8,9] films,^[10-13] monoliths,^[14] and hollow or yolk-shell structured particles,^[15-20] have been prepared for different applications. Among them, hollow structured PMOs is especially attractive because of their large void space, low density and potential applications in confined catalysts,^[21] drug/gene delivery,^[22-25] and enzyme encapsulation.^[26,28]

Generally, HPMO nanospheres can be prepared by co-assembly of bridged silsesquioxanes with surfactant templates on polymer or inorganic cores and then selective etching the sacrificial hard templates.^[29-31] However, the hard templating methods for the HPMO nanospheres are complex, uneconomic, and time consuming. Recently, we report that HPMO nanospheres can be synthesized

via an interface-transformation method, which is implemented by hydrothermal treatment of mesostructured organosilica particles.^[32,33] However, the method still requires two steps including the pre-preparation of mesostructured organosilicas *via* surfactant-directed sol–gel processes and a following hydrothermal treatment. Water/oil emulsion based soft templating methods are very simple and facile for preparation of hollow nanoparticles because the hollow structures can be directly obtained through one step.^[34-36] Oil phase such as decane, octadecene, decahydronaphthalene, cyclohexane, 1,3,5-trimethylbenzene has been introduced in the previous synthesis methods.^[37,38] However, the successful preparation of hollow particles by soft templating method depends on two crucial factors: (1) formation of large amount of highly stable water or oil droplets in the reaction solution, and (2) deposition of precursors on the water/oil interfaces to form the shells.^[39] Because the water or oil droplets are generally thermodynamically unstable, the emulsion method for the hollow structures needs strict reaction conditions. Therefore, preparation of HPMO nanospheres through one-step emulsion method is still a big challenge.

Herein, we successfully prepare ethane-bridged HPMO nanospheres by a facile emulsion approach. The method involves direct deposition of 1,2-bis(triethoxysilyl)ethane (BTSE) with cetyltrimethylammonium bromide (CTAB) surfactant on the decane emulsion droplets. The process for the synthesis of HPMO nanospheres is very simple, effective, and low cost and the product are completely hollow in structure. The obtained HPMO nanospheres have high surface area ($950 \text{ m}^2 \text{ g}^{-1}$), radially oriented mesochannels (3.4 nm), large pore volume ($3.96 \text{ cm}^3 \text{ g}^{-1}$), and high condensation degree. Moreover, *in vitro* cytotoxicity and hemolysis experiments show that the HPMO nanospheres have excellent biocompatibility, demonstrating their potential for future biomedical applications.

2. Materials and methods

2.1. Reagents and materials

CTAB, concentrated ammonia aqueous solution (25 wt %), concentrated HCl (37 %), and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 1,2-Bis(triethoxysilyl)ethane (BTSE) were bought from Sigma–Aldrich (St. Louis, MO, USA). Decane with a purity of >99% were purchased from Acros Organics (Merck, Germany). Millipore water was used in all experiments.

2.2. Preparation of the HPMO nanospheres

The HPMO nanospheres were prepared *via* an emulsion method in ethanol aqueous solution containing CTAB, n-decane, ammonia, and BTSE. Typically, CTAB (0.193 g) was dissolved in a mixed solution of water (76.4 mL), ethanol (7.6 mL), concentrated ammonia aqueous solution (3.6 mL, 25 wt%), and decane (0.6 mL). Afterward, the mixture was transformed to emulsion solution by 40 KHz ultrasonication for 10 min and heated to 50 °C. The mixed solution of 0.4 mL BTSE and 1.6 mL ethanol was then added under vigorous stirring (1100 rpm). After 12 h, white reaction products were collected by centrifugation and washed with water three times. Finally, CTAB templates were removed from the products by three solvent-extractions in a solution containing ethanol (60 mL) and concentrated HCl (120 μ L, 37 %) at 60 °C for 3 h. After washing with ethanol for three times and dried under a high vacuum, the HPMO nanospheres were obtained.

2.3. Characterization of the HPMO nanospheres

Transmission electron microscopy (TEM) images were obtained by using an HT7700 microscope (Hitachi, Tokyo, Japan) operated at an accelerating voltage 100 kV. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet NEXUS870 spectrometer (USA), using KBr pellets of the solid samples. X-ray power diffraction (XRD) was measured on a Bruker model D8

focus diffractometer with Cu K α radiation (0.154 nm) operated at 40 kV and 40 mA. Nitrogen sorption isotherms were measured using a Micromeritics Tristar 3000 analyzer at $-196\text{ }^{\circ}\text{C}$. The samples were degassed at $150\text{ }^{\circ}\text{C}$ for 10 h before the measurements. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) method by using the adsorption data in a relative pressure range from 0.09 to 0.22. The pore size distribution was obtained by applying proper nonlocal density functional theory (NLDFT) methods from the adsorption branch of isotherms. The total pore volume was evaluated from the adsorbed amount at a relative pressure (p/p_0) of 0.995. ^{29}Si magic-angle spinning (MAS) NMR spectra were recorded at 79.48 MHz on a Bruker AVIII400 spectrometer, using a 7-mm probe, a spinning rate of 6.0 kHz, and a recycle delay of 120 s. Dynamic light scattering (DLS) measurements were conducted on ZetaPALS (Brookhaven, USA). Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu K α radiation (40 kV, 35 mA).

2.4. Cell Viability Assay

Human embryo kidney 293 cells obtained from American Type Culture Collection (ATCC) were seeded into 96-well plate with a density of 1×10^4 cells per well and incubated for 24 h. Afterward, different concentrations of the HPMO nanospheres dispersed in Roswell Park Memorial Institute (RPMI) 1640 medium were added to the cell culture. After 24 h, the culture was replaced with 200 μL of fresh medium containing 20 μL of 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) in culture medium (5.0 mg ml^{-1}). After 4 h, the cell culture was further replaced with 150 μL of dimethyl sulfoxide. Finally, the absorbance of each sample was measured on a microplate reader (BioTek Instruments, Winooski, VT, USA) at 570 nm. The cell viability (%) was calculated as (mean absorbance of treated cells / mean absorbance of control cells) $\times 100$.

2.5. Hemolysis Assay

2 mL of blood sample was added to physiological saline and centrifuged at 2000 rpm for 5 min. After washing with saline three times, the obtained red blood cells (RBCs) were dispersed in 10 mL of saline. 0.2 mL of the diluted RBC suspension was then mixed with 0.8 mL of the HPMO nanospheres in saline and kept in 37 °C for 2 h. The same amount of water or physiological saline was used as the positive or negative control, respectively. Finally, the suspensions were centrifuged at 2000 rpm for 5 min, and the absorbance values of the supernatants were measured at 490 nm. The hemolysis of RBCs (%) was calculated as $((\text{absorbance of sample} - \text{absorbance of negative control}) / (\text{absorbance of positive control} - \text{absorbance of negative control})) \times 100$.

3. Results and discussion

The preparation procedure of the HPMO nanospheres by the emulsion method is shown in Figure 1. First, an ethanol aqueous solution containing CTAB surfactant, ammonia, and small amount of decane was ultrasonicated to create an oil-in-water (O/W) emulsion (Step 1). Dynamic light scattering (DLS) measurements show the hydrodynamic diameter of the oil droplets is 346 nm (Figure S1). Then, organosilica precursor BTSE was added to the emulsion solution under stirring. The added BTSE was gradually hydrolyzed to form negatively charged oligomers. The oligomers could co-assemble with the CTA^+ through electrostatic interaction and cross-link each other on the oil droplets, resulting in mesostructured organosilica shells (Step 2). After extraction of CTAB surfactants from the shells by acidic ethanol, HPMO nanospheres are obtained (Step 3).

Figure 1. Schematic illustration of the synthesis procedures of the HPMO nanospheres by the emulsion approach.

The transmission electron microscopy (TEM) images clearly show that the ethane-bridged HPMO nanoparticles synthesized *via* the emulsion approach have a large hollow chamber encapsulated in a gray shell (Figure 2A, C). The diameter, hollow chamber size, and shell thicknesses of the HPMO nanospheres are measured to be about 560, 400, and 80 nm, respectively. Noteworthy, the HPMO nanospheres have excellent dispersibility and no aggregation of the nanospheres is observed, which is important for biomedical applications. Besides, we found that all the HPMO nanospheres synthesized by the emulsion approach are hollow in structure, suggesting the method is very effective. DLS measurements demonstrate the hydrodynamic diameter of the HPMO nanospheres is 580 nm (Figure 2B), which is well consistent with the TEM results. High-magnification TEM image further demonstrates that the HPMO nanospheres possess a large hollow cavity and a porous shell (Figure 2C). Importantly, it is observed that the HPMO nanospheres have radially oriented mesochannels with openings at surface (Figure 2D), meaning that the mesochannels of the hollow spheres are readily accessible. The radially oriented mesochannels favor the adsorption and release of guest molecules, such as anticancer drugs. Furthermore, we found that the diameter, hollow chamber size, and shell thickness of HPMO nanospheres can be

facilely controlled by adjusting the addition volume of BTSE. The diameter, hollow chamber size, and shell thickness of the HPMO nanospheres synthesized with 0.1 mL BTSE are 163, 56, and 66 nm, respectively (Figure S2). As the BTSE increased to 2 mL, the particle size, the hollow chamber size, and the shell thickness are increased to 493, 336 and 70 nm, respectively. It is deduced that the added hydrophobic BEST precursor would first penetrate into the emulsion droplets and result in formation of larger droplets. After condensation of the organosilcia precursor BTSE on the surface of the droplets, HPMO with larger hollow void spaces are obtained. Simultaneously, the increase of the BTSE would induce the increase of the shell thickness. Furthermore, with the increase of the BTSE, the ratio of BTSE in the oil droplets would change, which may affect the final sizes of the hollow spaces. Furthermore, the products were collected with reaction times of 5, 10 and 30 min. TEM images show that the all the products are hollow in structure (Figure S3), suggesting the growth of the organosilica is fast. Also, with the extension of reaction time, the study observed that the HPMO nanopheres possesses large size, which is most likely attributed that the emulsion droplets grow bigger with time.

Figure 2. (A) TEM image and (B) DLS size distribution of the HPMO nanospheres prepared by the emulsion approach. (C) High magnification TEM image of single HPMO nanosphere. (D) High magnification TEM image showing the oriented mesochannels of the HPMO nanosphere.

The composition of the prepared ethane-bridged HPMO nanospheres was characterized by FT-IR spectra and ^{29}Si magic-angle spinning (MAS) NMR. The FT-IR spectrum of the HPMO nanospheres displays absorbance peaks of the stretch vibrations of the C–H bond around 2900 and 2980 cm^{-1} and bending vibration of the C–H bond in the $-\text{CH}_2-\text{CH}_2-$ moieties at 1414 cm^{-1} (Figure 3A), indicating that the ethane units are incorporated frameworks of the HPMO nanospheres.^[40,41] The ^{29}Si MAS NMR spectrum of the HPMO nanospheres shows three obvious signals at -47 , -58 , and -66 ppm (Figure 3B), corresponding to T^1 ($\text{C}-\text{Si}(\text{OSi})_1(\text{OX})_2$, $\text{X}=\text{H}$ or Et), T^2 ($\text{C}-\text{Si}(\text{OSi})_2(\text{OX})$), and T^3 ($\text{C}-\text{Si}(\text{OSi})_3$) species (Figure 3B).^[42,43] The presence of these T sites in the spectrum further confirms the silsesquioxane framework. Quantitative analysis based on relative peak areas

reveals the relative percentages of T^1 , T^2 , and T^3 are 16%, 36%, and 48%, respectively. The overall condensation degree of the HPMO nanospheres is calculated up to 77% (Figure 3C). One scattering peaks at $\sim 0.115 \text{ nm}^{-1}$ is observed in the SAXS pattern of the HPMO nanospheres (Figure S4), indicating the hierarchical uniform mesostructured of the HPMO nanospheres. The XRD pattern of the HPMO nanospheres shows one peak and one weak peak (Figure 3D), associated with the 100 and 110 reflections of hexagonal symmetry with the space group $p6mm$.^[32] This is in good agreement with that of the typical mesoporous silica materials MCM-41,^[44] suggesting an ordered hexagonal mesostructured.

Figure 3. (A) FT-IR spectrum, (B) ^{29}Si MAS NMR spectrum and (C) corresponding fitting curves, and (D) XRD pattern of the ethane-bridged HPMO nanospheres prepared by the emulsion approach.

Nitrogen sorption isotherms of the HPMO nanospheres show a type IV curve according to the IUPAC nomenclature with well-defined steps, at relative pressures (P/P_0) of 0.4-0.55 and 0.95-1.0

(Figure 4A), corresponding to capillary condensation and desorption in mesopores in the shell and interstitial or hollow spaces, respectively. The surface area and pore volume are calculated to be as high as $950 \text{ m}^2 \text{ g}^{-1}$ and $3.96 \text{ cm}^3 \text{ g}^{-1}$, respectively. The large pore volume is related to the mesopores in the shell and some other pores, perhaps interstitial pores or the hollow void spaces. The pore size distribution calculated based on the nonlocal density functional theory (NLDFT) reveals that the HPMO nanospheres have uniform mesopores of about 3.4 nm (Figure 4B). The yield of the HPMO nanospheres with the size of 560 nm is 56%.

Figure 4. (A) Nitrogen sorption isotherms and (B) NLDFT pore size distribution curve of the HPMO nanospheres prepared by the emulsion approach.

The unique hollow cavity, silsesquioxane framework, and ordered radial mesochannels of the HPMO nanospheres make the materials ideal candidates for applications in biomedical fields. Therefore, the hemocompatibility was assessed because silanol groups often caused the hemolysis of RBCs. As shown in Figure 5A, the hemolysis percentage is lower than 1.1% at HPMO concentrations of 10 to $2000 \mu\text{g mL}^{-1}$, which is significantly lower than that of pure silica nanoparticles.^[16,28] The lower hemolysis of the HPMO nanospheres is attributed to the incorporation of the ethane groups and decrease of the cell contactable silanol groups, which is benefit for their *in*

vivo biomedical applications involving intravenous administration and transport. The biocompatibility of the HPMO nanospheres were further assessed with human embryo kidney 293 cells. It is observed that the cell viability is retained 100% when they are incubated with the HPMO nanospheres at a concentration of 10–50 $\mu\text{g mL}^{-1}$ for 24 h (Figure 5B). Also, the cell viability is still higher than 86% with the HPMO nanospheres at a high concentration of 1200 $\mu\text{g mL}^{-1}$, indicating an excellent biocompatibility of the materials.

Figure 5. (A) Percentage of hemolysis of RBCs incubated with the HPMO nanospheres at concentrations of 10 to 1200 $\mu\text{g mL}^{-1}$. (B) *In-vitro* viability of human embryo kidney 293 cells incubated with different concentrations of HPMO nanospheres.

4. Conclusions

In summary, we have demonstrated a facile emulsion approach strategy to fabricate monodisperse HPMO nanospheres with radially oriented channels. To the best of our knowledge, this is the first report about synthesis of HPMO by soft-templating method. The one-step method for preparation of the HPMO nanospheres is very simple, effective and does not require any sacrificial templates or corrosive etching agents. The obtained HPMO nanospheres have high surface area (950 $\text{m}^2 \text{g}^{-1}$), radially oriented mesochannels (3.4 nm), large pore volume (3.96 $\text{cm}^3 \text{g}^{-1}$), and high condensation degree. Moreover, *in vitro* cytotoxicity and hemolysis experiments show that the

HPMO nanospheres have excellent biocompatibility. It is expected that the emulsion approach opens up a new route for preparation of various HPMOs by utilizing different organosilica precursors for different applications such as drug delivery, catalysis, and so on.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis>.

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