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Hollow periodic mesoporous organosilica nanospheres by a facile emulsion approach

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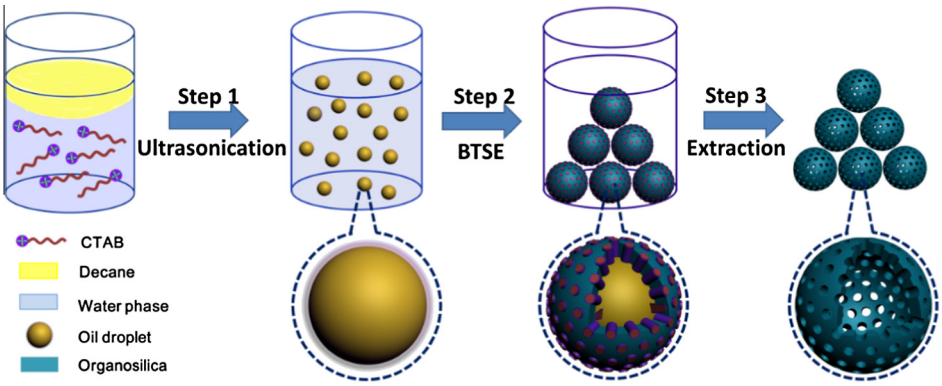
GRAPHICAL ABSTRACT

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 lower hemolysis and cytotoxicity make the HPMO nanospheres great promise for future biomedical applications.



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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 (~950 $m^2 g^{-1}$), accessible ordered mesochannels (~3.4 nm), large pore volume (~3.96 $cm^3 g^{-1}$), high condensation degree (77%), and diameter (~560 nm), hollow chamber size (~400 nm), and shell thickness (~80 nm). Furthermore, cytotoxicity show the cell viability is higher than 86% after incubating with

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Mesoporous materials
Emulsion approach
Biocompatibility

the HPMO nanospheres at a concentration of up to 1200 μg mL^{-1} for 24 h. The hemolysis of HPMO nanospheres is lower than 1.1% at concentrations ranging from 10 to 2000 μg mL^{-1}. The lower hemolysis and cytotoxicity make the HPMO nanospheres great promise for future biomedical applications.

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 introduce 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 m^2 g^{-1}), radially oriented mesochannels (3.4 nm), large pore volume (3.96 cm^3 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 μL, 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 Kα radiation (0.154 nm) operated at 40 kV and 40 mA. Nitrogen sorption isotherms were measured using a Micromeritics Tristar 3000 analyzer at −196 °C. The samples were degassed at 150 °C for 10 h before the measurements. The specific surface area was calculated with the Brunaue-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 Kα 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