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Synthesis of three-dimensionally ordered macroporous silica spheres by evaporation-induced assembling template process



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ABSTRACT

Three-dimensionally ordered macroporous silica microspheres were fabricated by colloidal crystal templating method. The colloidal crystals were assembled through the crystallization of monodisperse charged polystyrene (PS) particles during the evaporation of suspension droplets in the self-assembly process. Viscous silicone oil was used as dispersion medium to confine specific geometry. Followed by infusing silica precursor into colloidal crystals and a final calcination for PS removal, silica skeleton was formed in the interstices and macropores were left at PS's sites. The macroporous silica made by this method was macroscopically spherical with a diameter of few tens of micrometers and the pores were close-packed and well-ordered in three-dimensions. This paper provides a facile technique to fabricate ordered colloidal crystal microballs and macroporous materials.

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1. Introduction

Three-dimensionally ordered macroporous (3DOM) materials exhibit significant properties such as well-defined porosity, unique surface structure and high surface area. These advantages provide 3DOM materials with great potential applications, such as in photonic band-gap materials, chemical and biochemical sensors, catalysts, and chromatographic separation [1–6]. Especially, ordered macroporous silica spheres with a pore size of a few hundred nanometers, displaying excellent temperature and solvent resistance, high mechanical strength, easy pore functionalization, and prompt mass transfer ability, are the most appreciated materials for the chromatographic packing [7,8]. Regularly shaped materials with multiple macro-/mesoporous structure have the advantages of exhibiting shorter diffusion path length, higher filling density, and lower back pressure during usage. Thus macroporous supports can be designed to maintain high chromatography efficiency and excellent trapping ability of large guest molecules [9].

Recently, the techniques of highly ordered colloidal crystal templating for macroporous materials have been studied by a number of researchers [10,11]. However, the macroporous materials are generally in the form of macroscopically irregular shapes such as films or blocks [12,13]. Considering their practical applications and unique properties, it is desirable to synthesize them as well-shaped objects with good uniformity in size and morphology,

such as photonic balls. Herein, we report on the fabrication of three-dimensionally ordered macroporous silica microspheres from colloidal crystals, which are in good sphericity and possess narrow pore size distribution with highly ordered packing. The structures of as-obtained colloidal crystals and macroporous silica spheres have been characterized in detail.

2. Experimental

Fig. 1 is the schematic of the three-step preparation method for 3DOM SiO₂ spheres. First, non-cross-linked monodisperse PS particles synthesized by emulsifier-free emulsion polymerization [14] were assembled into colloidal crystal templates. A suspension system was prepared by suspending PS latex droplets in the viscous silicone oil to confine geometries [15]. The concentration of PS particles was adjusted to 3–5 wt% and the volume ratio of PS latex to oil phase was 1:20. The suspension system was vigorously stirred, and then colloidal crystallization of PS particles gradually occurred in droplets when the water was evaporated at 80 °C. The oil soaked into the structure was washed with petroleum ether and dried in the air. Second, the colloidal crystals were immersed in silica precursor solution for one week. The precursor solution was composed of tetraethylorthosilicate (TEOS) and ethanol (volume ratio was 1:1). The infiltrated spheres were washed with ethanol and then hydrolyzed with moisture from the atmosphere. Finally, the PS particles were removed by calcination at 600 °C for 5 h. The heating rate was fixed at 2 °C/min.

The structure of colloidal crystal templates and macroporous silica spheres was characterized by a scanning electron microscope

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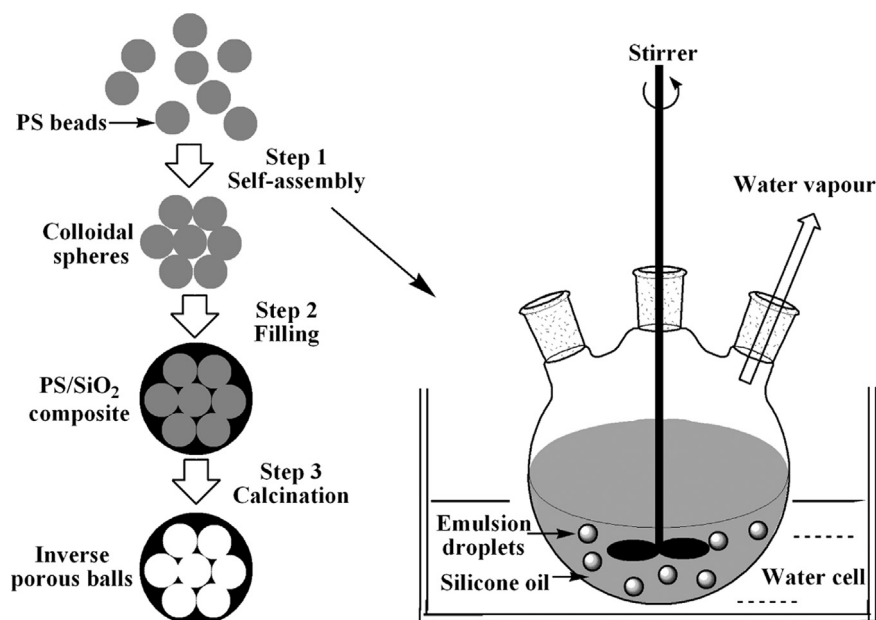


Fig. 1. Schematic of the fabrication method for 3DOM silica spheres.

(SEM: Carl Zeiss, Ultra 55). The Brunauer–Emmett–Teller (BET) specific surface area and pore volume by N₂ adsorption/desorption at 77 K were performed by an automated surface area and pore size analyzer (Quantachrome instruments, Quadrasorb SI).

3. Results and discussions

The first step of the process to obtain 3DOM silica balls is the self-assembly of PS particles into a well-ordered colloidal crystal that will be used as template. The experiments were conducted with the charged monodisperse PS latexes in the size range of 400–500 nm as shown in Fig. 2a. A good uniformity of PS microspheres can be found. The inset of size distribution indicates that PS latex spheres have an average diameter of 423 nm and the monodispersity is about 2.5%, which is crucial for the self-arrangement into ordered colloidal crystals.

The colloidal balls of latex particles were obtained by the evaporation-induced assembling process in a suspension system in which silicone oil was used as continuous phase and PS latex droplets suspending in the oil as disperse phase. A sufficiently high oil/water volume ratio and constant stirring rate were essential for the stable suspension system, as the droplet aggregation or destruction caused by low phase ratio and stirring disturbance should be omitted. With the combined effect of shearing force, surface tension and electrostatic repulsion force, the suspension droplets were in dynamic equilibrium and shaped into microballs. The ball size decreased monotonically with time during the evaporation of water. As the PS concentration exceeded a certain transition value, the colloidal crystallization occurred and PS latex spheres were automatically arranged into a closely packing structure. Fig. 2 shows the SEM images of crystal balls obtained under these conditions. Colloidal crystal balls with good sphericity can be observed. The surface of the crystal ball is in a hexagonally close-packed arrangement, even though some linear defects or vacancies exist throughout the crystal ball. These defects can be attributed to several reasons, such as size deviation of PS spheres, or plane dislocations. There are three possible stacking structures of closely packed plane: hexagonal close packing (hcp), face-centered cubic (fcc) and a mixture of hcp and fcc. The internal stacking of PS particles (Fig. 2d) displays that each PS particle is

surrounded by six neighbors in one plane and by three other neighbors from upper and lower planes, forming an ABC type as fcc structure. The experimental results are well agreeable with theoretical calculations that fcc structure is more stable than hcp structure [16].

It is concluded that the droplet-assisted method can provide a convenient and controllable way for well-shaped colloidal crystals with high ordering, which is also regarded as the most productive method to obtain colloidal crystals [1]. The size of the crystal balls can be controlled by changing the experimental conditions, such as the solid content of suspension droplet, stirring speed and the ratio of oil phase to aqueous latex. The percentage of crystal balls with diameter of 100–150 μm accounted for over 60% under certain conditions.

The as-prepared PS latex crystal balls were immersed in silica precursor solution, which was diffused into the interspaces between PS latex particles by capillary force. After fully infiltration for several days, the crystal balls were filtrated out and exposed to the air. With moisture from the air, the silica precursor was hydrolyzed, and the organic–inorganic composites were obtained. It deserves to pay special attention that the excess silica precursor remaining on the surface of crystal balls should be washed. Otherwise, the residual precursor solution will gel into a thick film on the macroporous balls. In this study, we treated the latex/silica composite balls with isopropanol. Finally, the PS latex templates inside the silica were removed by calcination at 600 °C for 5 h, leaving ordered void space at their sites as shown in Fig. 3. From the low-magnification SEM image of macroporous silica (Fig. 3a), the macroporous silica maintains well spherical shapes. Fig. 3b shows that the voids' size is in the range from 320 to 360 nm in diameter, which is 15–24% smaller than the PS latex particles. Samples undertake shrinkage during calcinations. The wall thickness of the voids is about 48 nm. As noted from SEM images, the macroporous silica spheres are the conversely duplicated production of crystal balls, which consist of uniform close-packed spherical pores and hexagonal silica ring skeleton, and channels connecting pores of different planes indicate that the sample is an open-pore structure. There is a clear evidence that the pores are interconnected in three dimensions and the ordering extends to the whole volume of the silica balls (Fig. 3c). The macropores traverse the whole balls, which may realize rapid

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