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Template Polymerization-solvent Extraction: A New Method for Fabrication of Hollow Polysiloxane Particles

Hui Gang WANG, Ping CHEN, Xiao Ming ZHENG*

Department of Chemistry, Zhejiang University, Hangzhou 310028

Abstract: Hollow polysiloxane particles with diameters between 1.40 and 1.60 micrometres were fabricated by consecutive cocondensation of methyltrimethoxysilane and diphenyldimethoxysilane monomers onto polydiphenylsiloxane, subsequently removing the templated polydiphenylsiloxane by exposure to solvents. TEM and AFM measurement reveal that there are obvious hollow sphere structures for the polysiloxane microsphere particles. The hollow spheres are envisioned to have applications in areas ranging from dye-industry, catalysis, pharmaceutics to materials science.

Keywords: Hollow polysiloxane particles, emulsion polymerization, template.

In recent years, there has been intense interest surrounding the fabrication of micro-and nanoparticles that comprises either organic or inorganic shells with hollow sphere shape[1-3]. So far the majority of approaches reported for the preparation of hollow particles are based on template strategy. But it has led to difficulties in complete coverage of the template core or to overcoverage[4], agglomeration, and the formation of micronetworks[5] when it was applied to the adsorption of noncharged species. An alternate approach for the preparation of hollow spheres applying emulsion polymerization technique should also be included[6,7]. Usually rather aggressive reaction conditions, like a prolonged alkali and acid treatment at high temperature[6], or high pressure are required to remove the particle core[7]. Herein, we describe a preparation of micrometer-sized, stable, and regular hollow particles by using a combination of these two approaches of emulsion polymerization and templating under rather mild safe conditions. This technique relies upon the emulsion polymerization of bi- and tri-functioned organosilicon onto the surface of preformed particles into spherical particles of core-shell morphological structure, followed by infiltration and extraction of the template core to leave the membrane as the hollow polysiloxane shells.

Preparation of polydiphenylsiloxane microspheres. In a 500 mL three necked flask, 3 g of the surfactant benzethonium chloride was dissolved in twice-distilled water (125.0 g) containing NaOH 40.0 mg. Diphenyldimethoxysilane (22.5 g) was added with

*E-mail: xmzheng73@hotmail.com

vigorous stirring, at room temperature over 1 h. The opalescent dispersion was continuously stirred for 12 h. The silanol end groups of the polydiphenylsiloxane were endcapped using methoxytrimethylsilane (1.0 g) .

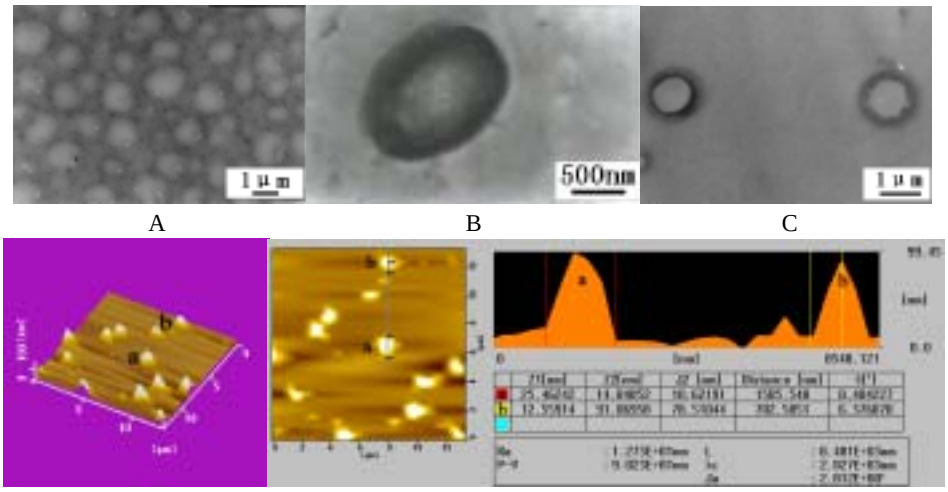
Preparation of core-shell structured particles. Under vigorous stirring, a mixture of diphenyldimethoxysilane (8.5 g) and methyltrimethoxysilane (10.0 g) was added slowly into the above-mentioned system within 1 h at room temperature and the resultant opalescent dispersion was stirred for a further 5 h. The active Si-OH groups were endcapped using methoxytrimethylsilane (3.0 g) twice. After stirring for a further 12 h the dispersion was destabilized by the addition of methanol and centrifuged to obtain the precipitate. In order to completely endcap the silanol groups, the above product dissolved in 50 mL toluene and 5.0 g of hexamethyldisilazane was added. The reaction mixture was stirred at room temperature for 12 h. The resulting product was precipitated with methanol, centrifuged to obtain the core-shell structured particles.

Preparation of hollow polysiloxane particles. The above product was dissolved in THF, infiltration and centrifugation twice to obtain the hollow particles. The particles were dissolved in benzene, and freeze-dried overnight. Yield: 10.4 g of white powder.

The transmission electron micrograph (TEM) photographs were measured with a JEM-200CX transmission electron microscope. The atomic force microscopy (AFM) photographs were recorded with a SPI3800N probe station operating in tapping mode.

Figure 1 A、B and C shows the transmission electron micrographs of the hollow polymer particles. One particle shown in A was deliberately magnified as shown in B. The sample C was stained by 2.5% uranyl acetate and lead citrate to make the particles to be stable and separated. It can be seen from **Figure 1** A, B and C that the particles of the sample possess obvious hollow structure as regular spheres. The particle size distribution is narrow and the mean diameter of the particles is 1.500±0.100 μm. **Figure 1** D and E shows the atomic force microscopes (AFM) of the samples. A tapping-mode AFM image of a hollow particle provided information on the diameter and height of the outer wall of the spheres. **Figure 1** D shows the three-dimensional surface graphics of the hollow polysiloxane particles. **Figure 1** E illustrates the topographical images of the sample (left) . Line profiles of topographical images were provided also (right). The diameter and height of a hollow sphere were measured by a pair of lines from cross-sectional line profiles which is corresponding to the pair of cursors shown in topographical images and the measured data were labeled in the table under the line profiles as shown in **Figure 1** E. The horizontal distance between the pair of cursors bestriding particle “a” is taken as the diameter of the hollow sphere. The vertical distance (⊿Z) between the pair of cursors bestriding particle “b” is taken as the height of the hollow sphere. The mean diameter and height of the hollow spheres, obtained from statistics of 100 particles data of AFM measurements, were approximately 1.497 μm and 0.079 μm respectively. **Figure 2** A and B show the diameter and height distributions of hollow spheres respectively. The mean diameter of the particles measured from AFM coincides well with the TEM results. The mean height of the particles, however, is significantly less than the mean diameter, which suggested that the dry spheres were collapsed a little, resulting in discus-like structures. This phenomenon is consistent with their hollow-core nature.

Figure 1 The TEM (A, B and C) and AFM (D and E) of the hollow polysiloxane particles

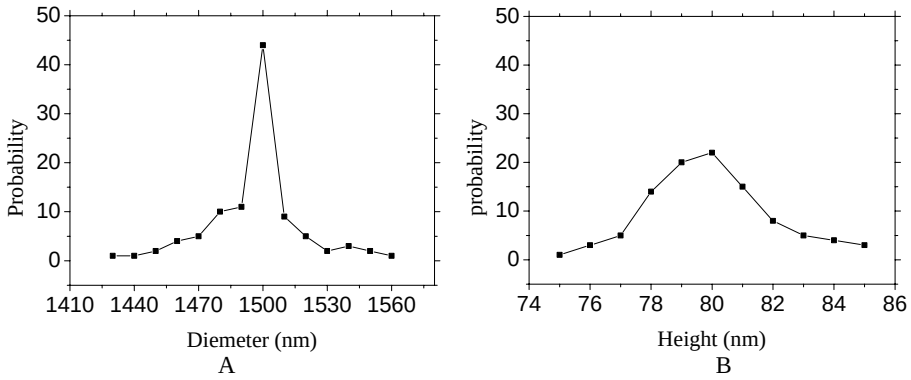


The images shown include: (A) d=1.500±0.100 μm; (D) Distance=1.505 μm; ⊿Z =0.078 μm.

From the TEM and AFM measurements, no holes or traces of polydiphenylsiloxane were identified in these samples, which indicate that solvent extraction is effective, mild and safe way for removal of the templated cores.

It has been demonstrated that the template technique, associated with emulsion polymerization, provides a successful pathway for fabricating polysiloxane hollow spheres in the micrometer size. The method is generally applicable to a wide variety of particles, thereby making possible the production of various hollow spheres. Experiments directed at the synthesis of hollow microspheres which fabricated with other polymers, are currently in progress.

Figure 2 The diameter distribution (A) and height distribution (B) of the hollow spheres



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