A Facile Method for Preparation of Hollow Polyphenylsilsesquioxane Microspheres

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Hollow polyphenylsilsesquioxane microspheres were fabricated under mild conditions from a mixture of water and phenyltriethoxysilane (PTES) with ammonia as catalyst. The pH value and the temperature of the reaction mixture are the crucial factors contributing to the formation of stable and regular polyphenylsilsesquioxane hollow spheres. A possible mechanism for the formation of hollow structure was proposed.

The preparation of hollow microspheres is of much importance for applications in catalysis, chromatography, cosmetics, coating, drug-release, lightweight fillers, etc.[1–5] In the past decades, many methods have been developed to prepare hollow microspheres including dual-nozzle reactor processes,[1] spray-dried droplets,[2] and hydrothermal method.[3] Recently, two strategies are especially attractive and widely employed to fabricate hollow microspheres. One representative approach is templating against colloid particles;[4–6] the other typical method utilizes emulsion or reverse emulsion as templates to prepare hollow spheres.[7–11] However, the removal of the core particles often results in fractures of the shells that usually led to a poor mechanical strength, and the residual surfactant often induces a weak optical performance, these are disadvantageous for potential applications. Therefore, developing facile and feasible methods to prepare hollow spheres continue to be a great challenge. Phenylsilsesquioxanes which have a siloxane structure with phenyl groups have attracted considerable interests in organic–inorganic hybrid materials because of their unique optical, mechanical, and thermal properties.[12–15] The preparation of polyphenylsilsesquioxane hollow spheres with phenylsilsesquioxane has been also attempted by a simple two-step method using phenyltrimethoxysilane (PTMS), hollow sphere were prepared without utilization of core template and any surfactant.[16–18]

In this paper, we report a facile method for the fabrication of hollow polyphenylsilsesquioxane microspheres in an oil-in-water system with ammonia as catalyst. Hollow polyphenylsilsesquioxane microspheres were prepared as follows: 0.54 g of phenyltriethoxysilane (PTES) was added to 150 mL of water which was kept at 40–90 °C through an isothermal water bath. Ammonia solution was added into the reaction mixture to adjust pH value at 9–10.5. The mixture was further stirred at 300 rpm for several hours, and the transparent mixture became milky gradually. The hollow polyphenylsilsesquioxane spheres could be obtained after centrifugation of suspension at 7000 rpm and drying at 85 °C in a vacuum oven for 24 h.

SEM image of microspheres is given in Figure 1, which indicates the good spherical shape and smooth surface of the microspheres. Simple analysis of the image shows that the diameters of the microspheres have a wide distribution in the range of 200 to 400 nm. Light scattering was used to determine the particle size distribution of the microshperes. The result is shown in Figure 2, which is in good agreement with the SEM result.

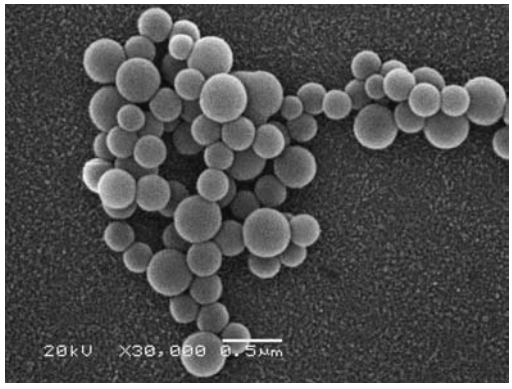

Figure 1. SEM image of the polyphenylsilsesquioxane particles obtained at 80 °C and pH 9.0.

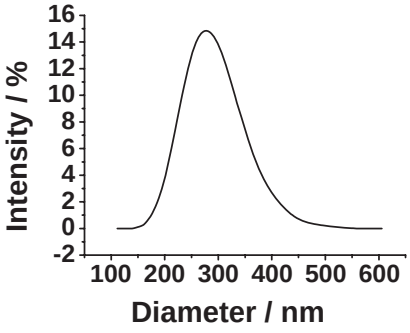

Figure 2. The particle size distribution (from dynamic light scattering) of the polyphenylsilsesquioxane spheres obtained with pH at 9.0 and temperature at 80 °C.

Figure 3 shows the TEM images of microspheres prepared at different pH value. It could be concluded that the pH value of the reaction mixture affects the percentage of microspheres with hollow structure. The lower the pH value of the reaction mixture, the more hollow spheres were obtained.

Temperature of the reaction mixture is a crucial factor in the preparation of hollow polyphenylsilsesquioxane microspheres. Figure 4 shows the TEM images of microspheres prepared at different temperature. Only anomalous particles were obtained with the temperature at 40 °C. Regular spheres were fabricated when the temperature was kept between 60 and 90 °C. However, the higher temperature, the more solid spheres were obtained. Almost all of the microspheres had a hollow cavity in the center, when the temperature was at 60 and 80 °C.

The mechanism for the formation of hollow structure is not very clear. Based on the experimental results and the reports before,[9,16,19] we proposed a possible formation mechanism as

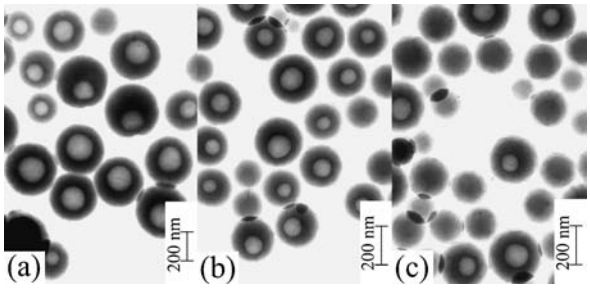

Figure 3. The TEM images of the polyphenylsilsesquioxane particles prepared at 80 °C with different pH values (a) pH 9, (b) pH 10, and (c) pH 10.5.

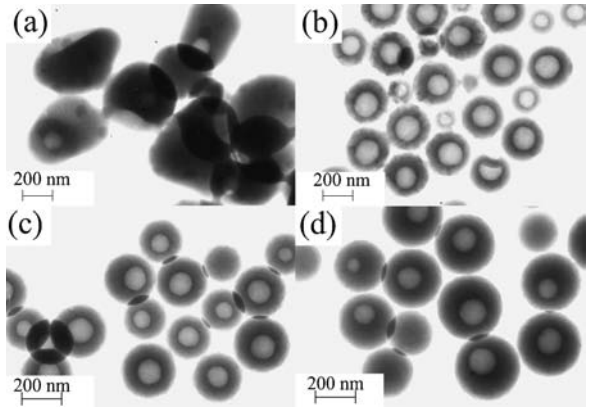

Figure 4. The TEM images of polyphenylsilsesquioxane particles prepared at pH 9.0 with different temperature (a) 40, (b) 60, (c) 80, and (d) 90 °C.

follows. Because PTES is immiscible with water, during the preparation of the polyphenylsilsesquioxane hollow spheres, it is just dispersed as monomer droplets in the aqueous solution under agitation. There are four main steps in the whole process: First, the hydrolysis of PTES took place at interface of oil–water to generate hydrolysate which dissolved in water subsequently.[14] Second, the condensation started in the water phase and also at the interface of oil–water to yield oligomer immediately. Third, the resulted reaction mixture forms stable oil-in-water emulsion by associating with the oligomer and hydrolysate molecules. This is the key step for the formation of the hollow polyphenylsilsesquioxane microspheres. Emulsion droplets and monomer droplets coexist at this stage. At last, with the migration of hydrolysate from the monomer droplets to the surface of the emulsion droplets, the emulsion droplets kept growing outward. Eventually, all the monomer in the monomer droplets was consumed and the monomer droplets disappeared, the core–shell (liquid–solid) type particles were prepared. Hollow polyphenylsilsesquioxane spheres were obtained after drying in the vacuum oven to remove the liquid cores.

The mechanism of the hydrolysis and condensation of PTES are mostly the same as TEOS.[15,20,21] The formation of the oil-in-water emulsion depends on the competition between hydrolysis and condensation reaction. When the pH value is less than 9, the rate of hydrolysis and the rate of condensation are both relatively slow, which do favor for the spontaneous emulsification involving the oligomer and hydrolysate molecules and results in hollow spheres as shown in Figure 3a. When the pH value is greater than 9, the rate of condensation is much greater than that of hydrolysis. It is more helpful to the nucleation occurrence in the water phase, and hollow structure is affected as shown in Figure 3c.

In conclusion, hollow polyphenylsilsesquioxane microspheres were successfully prepared by a facile and efficient approach without the utilization of core template and any surfactant. With the introduction of a small amount of ammonia as catalyst, organic–inorganic hybrid hollow microspheres were obtained. By controlling the pH value and the temperature, hollow polyphenylsilsesquioxane microspheres with uniform wall thickness can be prepared. Since this process under mild conditions, it can be facilely extended to the fabrication of hollow microspheres containing other organic pigment.

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