Synthesis of Polymer Hollow Spheres with Holes in Their Surfaces

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The chemical synthesis of polymeric materials with unusual and complex forms has attracted considerable attention owing to the obvious importance of the shape and texture of materials in determining their properties.[1,2] Polymer hollow spheres have stimulated great interest because of their hollow core structure with the ability to encapsulate large quantities of guest molecules and potential applications in controlled delivery systems, lightweight fillers, catalysis, and so on.[3−5] Polymer hollow spheres are mostly obtained with the aid of a hard template.[6−9] In this approach, the core template has to be removed by dissolution or thermolysis in order to create a hollow interior. Recently, the soft template, such as micelles[10−14] and lipid vesicles,[15,16] has been successfully applied to the synthesis of polymer hollow spheres. By using the soft template, large quantities of surfactants or functionalized organic acids are often required. Therefore, an inexpensive and environmentally friendly one-step strategy to uniform polymer hollow spheres is highly desirable. Herein, we demonstrate a facile and environmentally friendly approach for the fabrication of poly(*o*-methoxyaniline) hollow spheres. The chemical polymerization of *o*-methoxyaniline monomer was conducted in aqueous solution. The droplets formed by the monomers themselves are considered to be templates that lead to the formation of resultant polymer hollow spheres.

In a typical synthesis, *o*-methoxyaniline (0.30 g) was dissolved in deionized water (20 mL) with magnetic stirring at room temperature for 10 min. After that, the mixture was maintained at 0−5 °C for 0.5 h before oxidative polymerization. Then the aqueous solution of ammonium persulfate (APS) was added to the above mixture in one portion. The resulting solution was stirred for another 0.5 min to ensure complete mixing, and then the reaction was allowed to proceed without agitation for 12 h at 0−5 °C. Finally, the product was washed with deionized water until the filtrate became colorless and then dried in a vacuum at 60 °C for 24 h.

The morphologies of poly(*o*-methoxyaniline) were confirmed by scanning electron microscopy (SEM) analysis. The low-resolution image (Figure 1A) clearly indicates that the products are uniform hollow microspheres with an average size of 3.5 μm. From the magnified SEM image in Figure 1B, we can see evidently that most of the time there is one hole in the surface of each microsphere, which confirms the hollow interior of the polymer microspheres. The sizes of holes range from 0.7 μm to 2 μm, and the shell thickness is approximately 200 nm.

The schematic illustration of the formation of hollow polymer spheres is given in Figure 2. On account of the amphiphilic structure of the *o*-methoxyaniline monomer, droplets formed by the monomers themselves will exist in the aqueous solution. Such droplets will act as templates in the formation of polymer hollow spheres. When starting the polymerization after addition of APS, the polymerization takes place at the water/droplet interfaces because of the hydrophilicity of APS,[13,14] which results in the formation of original hollow nanospheres, followed by the aggregation and fusion process of such hollow nanospheres to form micro-sized hollow spheres. With the consumption of monomers in the outer surfaces of hollow spheres, monomers will diffuse from the droplets to the external surfaces to continue the polymerization reaction. Therefore, it is reasonable to believe it is the diffusion flux of monomers that leads to the formation of the hole in the shell of each hollow microsphere.

The concentration of monomer is found to have significant influence on the sizes of polymer hollow spheres; that is, both the sizes of hollow spheres and the sizes of holes decrease with the decreasing concentration of monomer. As seen in Figure 3, when the concentration of monomer decreases from 0.10 to 0.02 M, the size of the hollow spheres decreases from 3 μm to 0.7 μm and the size of the hole decreases from 800 to 200 nm, respectively. Also, with the decreasing monomer concentration, the uniformity of products increases. However, when the concentration of monomer is relatively low, for example, 0.02 M, the resulting polymer hollow spheres often fuse together (Figure 3D).

In the traditional synthetic method,[17] HCl is used in the reaction system in order to get high conductivity of conducting polymer. However, we found that if HCl was used in

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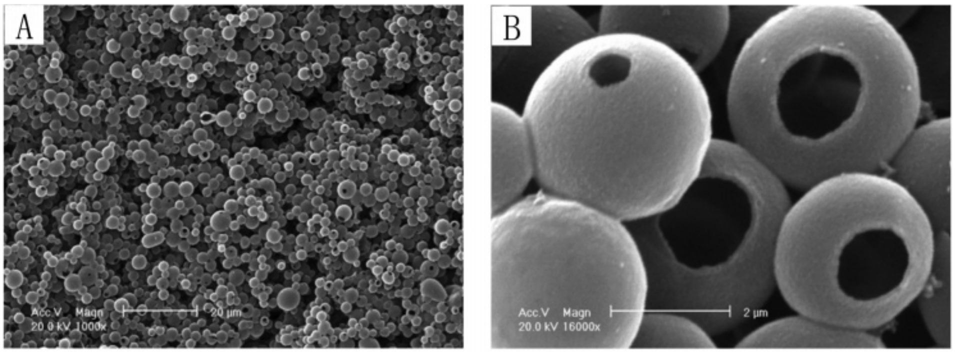

Figure 1. (A) Low-magnification and (B) high-magnification SEM images of poly(*o*-methoxyaniline) hollow spheres synthesized in aqueous solution with $C_{\mathrm{monomer}} = 0.12$ M.

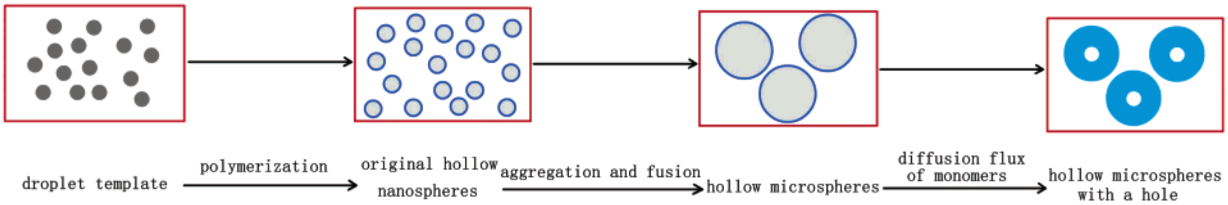

Figure 2. Schematic illustration of the formation of hollow polymer spheres with holes in their surfaces.

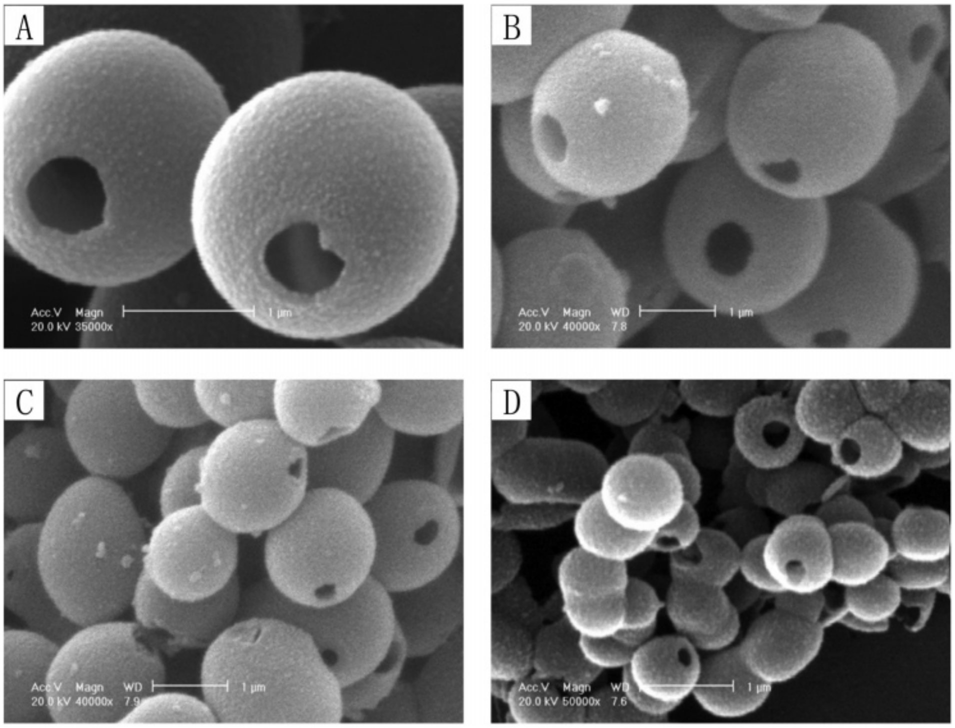

Figure 3. SEM images of poly(*o*-methoxyaniline) hollow spheres synthesized at different concentrations of the monomer: (A) 0.10 M; (B) 0.08; (C) 0.04; and (D) 0.02 M.

our reaction system, hollow spheres completely disappeared. This can be rationalized by the fact that, after the acid/base reaction between the acid and *o*-methoxyaniline when adding an acid, monomers will exist in the form of *o*-methoxyaniline hydrochloride which is unfavorable for the formation of monomer droplet. Here, the doping/dedoping experiments were also conducted to see whether the polymer hollow spheres can still be reversibly doped and dedoped. The corresponging Uv−vis spectra are shown in Figure 4. Doped poly(*o*-methoxyaniline) shows three characteristic absorption bands at 288, 458, and 878 nm. After dedoping with 0.1 M NH_4OH(aq), only two peaks at 320 and 738 nm, which are assigned to the $\pi-\pi^*$ benzenoid transition and the benzenoid to quinoid excitotic transition, respectively,[18] are observed. The results indicate that the conducting polymer hollow spheres synthesized in the absence of an acid can still be reversibly doped and dedoped. Furthermore, the hollow spherical morphology can be survived after several circles of doping/dedoping processes according to the SEM investigations.

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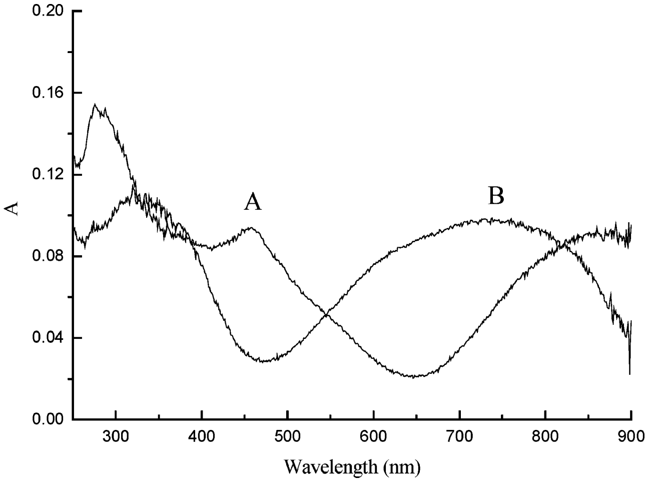

Figure 4. Uv−vis spectra of poly(*o*-methoxyaniline) hollow spheres after (A) doping with 1 M HCl(aq) and (B) dedoping with 0.1 M NH_4OH(aq).

In conclusion, poly(*o*-methoxyaniline) hollow spheres with holes in their surfaces can be successfully prepared by chemical polymerization in the absence of an acid. By simply changing the monomer concentration, the size of hollow sphere and the size of hole can be tuned in a wide range. The droplets formed by monomers themselves are proposed as template in the formation of hollow spheres, and the diffusion flux of monomers during the polymerization process is responsible for the formation of the hole. We have also successfully prepared poly(*o*-toluidine) hollow spheres with holes in their surfaces, which indicates that the proposed one-step solution route has potential applications in the synthesis of hollow spheres of other polyaniline derivatives. As the dispersion ability of our prepared hollow spheres in various systems, such as in a slurry, is an important aspect that determines their practical applications, our subsequent work will focus on this matter.

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