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Fabrication of Core–Shell Polymer Nanospheres in the Nanopores of Anodic Aluminum Oxide Templates Using Polymer Blend Solutions

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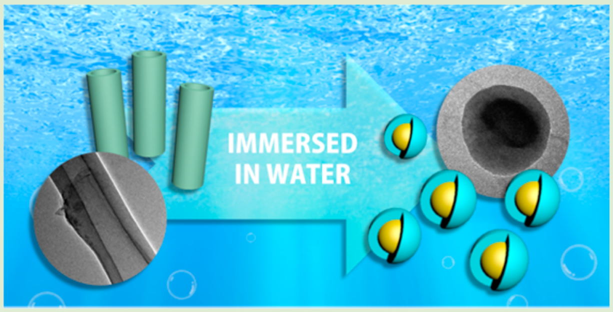
Supporting Information

ABSTRACT: Spherical core–shell structures have been widely investigated in recent years, and they can be used for various applications, such as drug delivery, biological labeling, and batteries. Although many methods have been developed to prepare core–shell structures, it is still a great challenge to fabricate core–shell structures in the nanoscale with well-controlled morphologies and sizes. In this work, we present a simple method to fabricate core–shell polymer nanospheres consisting of polystyrene (PS) cores and poly(methyl methacrylate) (PMMA) shells. The nanostructures are prepared by a solution-based template wetting method. After the nanopores of anodic aluminum oxide (AAO) templates are wetted sequentially by PS/PMMA blend solutions and water, the core–shell nanostructures can be formed. The formation process is related to the Rayleigh-instability-type transformation. Selective removal techniques are also used to confirm the morphologies of the core–shell nanostructures.



Spherical core–shell structures have attracted significant attention in recent years. Because of the special morphology and the characteristic of multicomponents, they can be used in different applications, such as drug delivery, biological labeling, and batteries.[1−3] For polymers, most researches focus on preparing core–shell structures in micrometer sizes.[4−9] Preparation of spherical polymer core–shell structures in the nanometer sizes with controlled morphologies, however, is still a great challenge. Here, we present a feasible template wetting method to fabricate core–shell polymer nanospheres using polystyrene (PS)/poly(methyl methacrylate) (PMMA) blend solutions.

The template wetting method, pioneered by Martin et al., is a powerful approach to prepare one-dimensional nanomaterials.[10,11] One of the most commonly used templates is the anodic aluminum oxide (AAO) template, which can be prepared by the anodization of aluminum foils.[12,13] In general, there are three major ways to use the template wetting method to introduce polymers into the nanopores of porous templates, including the melt method, the solvent annealing method, and the solution method.[14−20] Compared to the other two methods, the solution method is more versatile considering the various experimental parameters that can be used. In the solution method, polymer chains are first dissolved in suitable solvents, and the polymer solutions wet the nanopores via capillary force. Tunable parameters such as the type of solvent, the concentration of solution, the interfacial tension, the immersing time, and the drying condition can be changed in the solution method.[15,21−23]

Here, we use the solution method to fabricate the core–shell polymer nanospheres, which is related to the confinement effect of the cylindrical nanopores, the nonsolvent effect, and the surface-induced phase separation. For the confinement effect, the sizes of polymer nanostructures are controlled by the pore sizes of the templates. For the nonsolvent effect, we have previously studied the morphologies of polymer nanostructures by adding water (nonsolvent) in the nanopores containing polymer solutions, and nanospheres instead of nanotubes can be formed.[24] For the surface-induced phase separation, the polymer with stronger interactions to water can segregate near the interfaces of polymer solutions and water, while the polymer with weaker interactions to water is isolated in the center of the nanostructures.

In this work, polymer blend solutions are prepared by dissolving polystyrene (PS) and poly(methyl methacrylate) (PMMA) in dimethylformamide (DMF). First, the polymer blend solutions are infiltrated into the nanopores of AAO templates. Subsequently, water, which acts as a nonsolvent of the two polymers, is introduced into the nanopores.[24] Due to the stronger interactions between water and surfaces of the AAO nanopores, the polymer blend solutions are isolated in the center of the nanopores. The cylindrical solution domains transform to spherical domains to reduce the interfacial energies between polymer solution and water, driven by the Rayleigh-instability-type transformation.[25,26] After the solvents are evaporated and the templates are removed, the core–shell polymer nanostructures composed of PS cores and PMMA

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shells can be obtained. To confirm the morphologies of the nanostructures, PS cores and PMMA shells can be removed selectively using cyclohexane and acetic acid, respectively.

There are four main advantages of using this strategy to fabricate core−shell polymer spheres. First, the diameters of the core−shell spheres can be easily controlled by using templates with different pore sizes. Second, the relative thickness of the core and shell layers of the core−shell spheres can be finely adjusted by tuning the ratios of the polymers in the polymer blend solutions. Third, the sizes of the polymer spheres can range from micrometers to nanometers, depending on the type of the templates. Forth, the cylindrical pores of the templates also provide a possibility for making curved particles by annealing the polymer spheres in the presence of the templates.[27]

The SEM images of the AAO templates are shown in Figure S1 (Supporting Information). The average diameter of the nanopores of the AAO templates is ~240 nm. PS and PMMA, two commonly used polymers, are chosen here. PMMA has a stronger interaction to water than PS does, causing the formation of the PMMA shells and the PS cores. The choice of solvent and nonsolvent is critical in this work. DMF, a solvent with a relatively high boiling point (~153 °C) and miscible with water, is selected as the solvent. When water (nonsolvent) is introduced into the nanopores, the stronger interaction between water and aluminum oxide than that between DMF and aluminum oxide causes the polymer solution to be isolated in the center of the nanopores.

The experimental scheme is shown in Figure 1. When an AAO template is immersed in a PS/PMMA polymer blend solution, the nanopores are wetted by the solution via capillary force. The wetting process only requires a few seconds because of the low viscosity of the polymer blend solution and the small pore diameter of the nanopores. After the immersion process, the samples are taken out and wiped by Kimwipes, which can avoid the formation of polymer thick films on the surface of the templates. Subsequently, the samples are dipped in deionized (DI) water for 10 s and dried by a vacuum pump for several hours to ensure that the solvents are evaporated completely. The AAO template is then removed selectively by 5 wt % NaOH(aq), and the polymer nanostructures can be obtained.

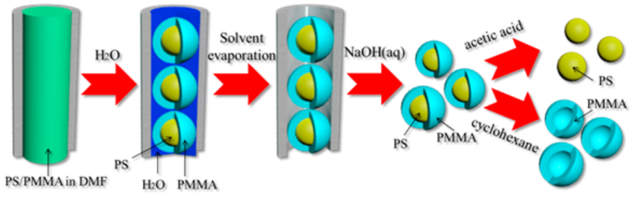

Figure 1. Graphical illustration of the experimental processes to prepare core−shell polymer nanospheres.

First, the viability of preparing polymer nanostructures using homopolymer solutions is confirmed, as shown in the Supporting Information. We then study the fabrication of polymer nanostructures using polymer blend solutions. The polymer blend solutions used in this work are composed of PS and PMMA, which possess different polarities. Figure 2a−c shows the SEM images of PS/PMMA blend nanotubes by dipping an AAO template into a PS/PMMA polymer blend solution for 10 s, followed by an evaporation process. The tubular structures can be confirmed further by TEM, as shown in Figure 2d.

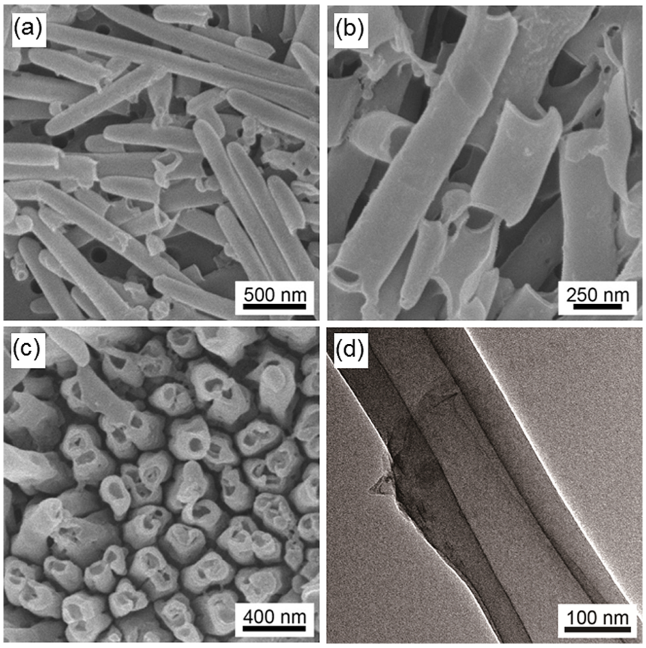

Figure 2. PS (M_w: 35 kg/mol)/PMMA (M_w: 97 kg/mol) blend nanotubes: (a and b) side-view SEM images at lower and higher magnifications, (c) top-view SEM image, and (d) TEM image.

We then apply the strategy of adding water (nonsolvent) to polymer blend solutions. After the AAO templates are dipped in the polymer blend solution, water is introduced into the nanopores and wets the surface of the nanopores preferentially. The polymer blend solution is squeezed to the center of the nanopores and transforms from cylindrical domains to spherical domains to reduce the interfacial energies between water and polymer blend solutions, driven by the Rayleigh-instability-type transformation process. After the spherical domains of the polymer blend solution are dried, polymer blend nanospheres can be obtained.

The morphologies of the polymer blend nanospheres are mainly determined by the interactions between polymers (PS and PMMA), solvent (DMF), water, and aluminum oxide walls. The stronger interactions between water and the aluminum oxide walls than those between DMF and the aluminum oxide walls cause the polymer solution to be isolated in the center of the nanopores. Moreover, the interactions between water and PMMA are stronger than those between water and PS because of the different polarities: water > PMMA > PS. Therefore, the PMMA chains in the polymer blend solutions aggregate to the solution/water interface, resulting in the formation of PS/PMMA core−shell nanospheres after the evaporation of the solvents.

The SEM images of the PS/PMMA core−shell nanospheres are shown in Figure 3a,b. The core−shell morphologies can be confirmed further by TEM after the polymer nanostructures are stained by ruthenium tetroxide (RuO_4), which stains the PS domains of the nanostructures selectively. The darker PS domains in the PS/PMMA nanospheres can be observed in the TEM image (Figure 3c). The sizes of the core−shell nanospheres can be measured by analyzing the nanospheres in the SEM images. Figure 3d shows the histogram of the size distribution of the PS/PMMA core−shell nanospheres. The average size of the PS/PMMA nanospheres is ~230 nm, which

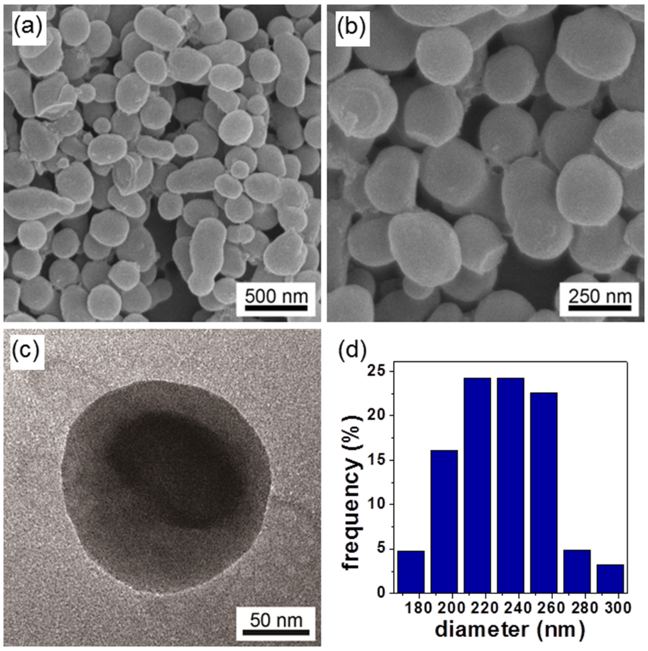

Figure 3. PS (M_w: 35 kg/mol)/PMMA (M_w: 97 kg/mol) core−shell nanospheres. (a and b) SEM images at lower and higher magnifications. (c) TEM image. The TEM sample is stained by RuO_4, which stains the PS core selectively, resulting in the darker PS domain. (d) Histogram of the size distribution of the PS/PMMA core−shell nanospheres. The average size of the PS/PMMA nanospheres is ∼230 nm. The nanostructures are prepared by dipping AAO templates in a PS/PMMA polymer blend solution in DMF and water sequentially.

is similar to that of the nanopores of the AAO templates (∼240 nm).

To confirm the morphologies of the PS/PMMA core−shell nanospheres, the selective removal technique is applied. Acetic acid is chosen as the solvent to remove the PMMA domains selectively, while the PS domains are retained. After the PS/PMMA core−shell nanospheres are immersed in acetic acid for 24 h, the PMMA shells are dissolved, leaving the PS nanospheres, as shown in the SEM and TEM images (Figure 4a−c). From the histogram of the size distribution of the PS nanospheres (Figure 4d), the average size of the PS nanospheres (∼175 nm) is measured to be smaller than that of the average size of the PS/PMMA core−shell nanospheres (∼230 nm). The size reduction indicates the removal of the PMMA shells, proving that the core−shell nanospheres are composed of PS cores and PMMA shells. The narrower size distribution of the PS nanospheres than that of the PS/PMMA core−shell nanospheres is probably due to the effect of the electron beam during the SEM measurements.

To confirm the morphologies of the PS/PMMA core−shell nanospheres further, we also try to remove the PS cores selectively. Cyclohexane is chosen as a solvent to remove the PS domains selectively while the PMMA domains are retained. After the PS/PMMA core−shell nanospheres are immersed in cyclohexane for 24 h, the PS cores are dissolved, leaving the PMMA shells, as shown in Figure 5a,b. For some PS/PMMA core−shell nanospheres in which the PS cores are not covered by the PMMA shells completely, hollow PMMA shells with cavities on the walls can be observed after the selective removal process.

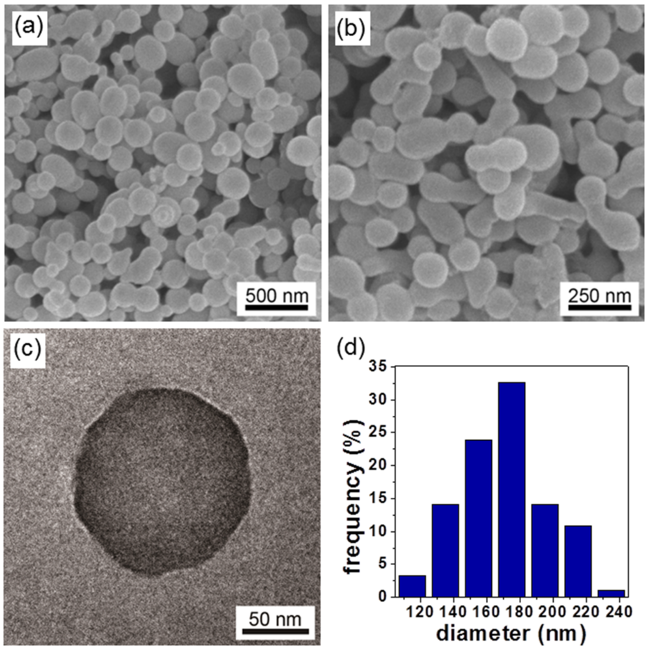

Figure 4. PS (M_w: 35 kg/mol) nanospheres. (a and b) SEM images at lower and higher magnifications. (c) TEM image. (d) Histogram of the size distribution of the PS nanospheres. The average size of the PS nanospheres is ∼175 nm. The nanostructures are prepared by dipping the PS/PMMA core−shell nanospheres in acetic acid to remove the PMMA shells.

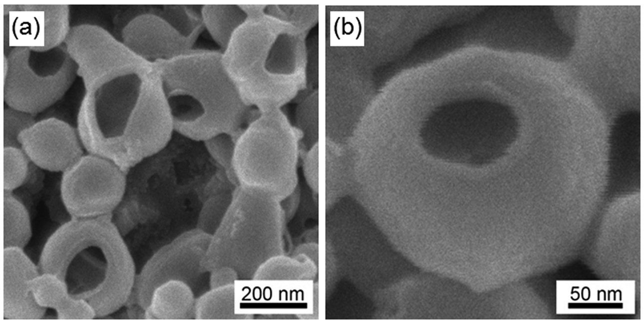

Figure 5. PMMA (M_w: 97 kg/mol) shells. (a and b) SEM images at lower and higher magnifications. The nanostructures are prepared by dipping the PS/PMMA core−shell nanospheres in cyclohexane to remove the PS nanospheres.

In conclusion, we present a novel method to fabricate PS/PMMA core−shell nanospheres containing PS cores and PMMA shells. The formation mechanism of the nanomaterials is related to the nonsolvent effect of water, the Rayleigh-instability-type transformation, and the phase separation in confined geometries. For possible future works, we will apply this strategy to fabricate organic/inorganic multicomponent nanomaterials that may be used in applications such as organic solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and the images of the AAO templates and the polymer nanostructures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00297.

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Notes

The authors declare no competing financial interest.

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