Polyaniline Hollow Microspheres Constructed with Their Own Self-Assembled Nanofibers

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ABSTRACT: Polyaniline (PANI) hollow microspheres constructed with their own nanofibers were prepared by inversed microemulsion polymerization associated with a template-free method in the presence of β-naphthalene sulfonic acid (β-NSA) as the dopant. The hollow microspheres were 4.0–6.0 μm in outer diameter and 150–250 nm in shell thickness; they consisted of the nanofibers (20–30 nm in diameter and 150–250 nm in length). We propose that the coordination effect of the reversed emulsion and the dopant or dopant/aniline micelle might have been a driving force in the formation of the special microstructures/nanostructures, where the reversed microemulsion acted as a soft template in the formation of the microspheres and where NSA or the aniline/NSA micelle was regarded as a soft template in the formation of the nanofibers. The molar ratio of water to the aniline/NSA salt and ultrasonic irradiation were critical in the control of the formation yield and the diameter of the uniform microspheres. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3050–3054, 2006

Key words: emulsion polymerization; fibers; microstructure

INTRODUCTION

Hollow microspheres of functional materials have received great attention because of their empty interiors, which give them wide application in controlled release drugs, the development of artificial cells, and the protection of light-sensitive components, catalysis, and biologically active agents.[1] So far, various methods, such as nozzle–reactor systems,[1,2] emulsion/phase separation techniques coupled with sol–gel processing,[1,3] and template against colloidal particles methods,[1,4] have been applied to prepare hollow microspheres of functional materials. Among these methods, the template synthesis method has been the most effective approach in the preparation of hollow microspheres. In a typical procedure, a thin coating of the target material or its precursor is formed on the template to create a core–shell composite followed by the removal of the template by calcinations at an elevated temperature in air or selective etching in an appropriate solution.[5] Usually, the template size controls the inner diameter of the resulting hollow spheres. However, it seems difficult to control the homogeneity and shell thickness, and sometimes,

clumping and heterocoagulation may occur. Reversed microemulsion polymerization has also been applied to prepare hollow spheres of functional materials.[6] This method has several distinct advantages. First, a reversed microemulsion can be considered a microreactor that allows a polymerization reaction to be carried out in its inside. Moreover, thermal and viscosity problems are much less significant than they are in bulk polymerization. In addition, the product can be directly obtained without further separations. Therefore, reversed microemulsion polymerization is simple and inexpensive compared with the aforementioned methods. Because emulsions are thermodynamically unstable systems that tend to break down over time due to a variety of physicochemical mechanisms, including gravitational separation, flocculation, and coalescence,[7] efficient steric stabilizations are usually required in traditional inverted emulsion polymerizations. In general, small molecules or polymeric surfactants are used as steric stabilizers in order to enhance the formation yield and stability.[8] However, surfactants may have some negative impacts on the product solubility and impurity, and it is especially difficult to control the shape of the resulting products.[9]

In addition, ultrasonic irradiation has been applied extensively in the dispersion, crushing, and activation of particles and the synthesis of nanoscaled materials;[10] moreover ultrasonic irradiation is an excellent method for emulsifying a reaction system because it

acts as a cavity that can be used to causes a large number of microbubbles to form in a very short time.[11]

In our previous studies, we demonstrated that conducting polymer nanotubes or nanofibers can be synthesized by chemical polymerization[12] without an external membrane (e.g., Al_2O_3 or polycarbonate) as a template. This method is a self-assembly process because the dopant or dopant/monomer acts as a soft template in the formation of the nanotubes.[13] Therefore, it is accepted that the previous self-assembly process combined with a reversed microemulsion polymerization, can be constructed microspheres of conducting polymers with their nanotubes or nanofibers. In other words, microspheres constructed their nanofibers or nanotubes are new bright microstructured/nanostructured conducting polymers that differ from either spheres or fibers/tubes published in the literature. To our knowledge, however, no article dealing with the previously mentioned microstructures/nanostructures has yet been published.

In this study, polyaniline (PANI) hollow microspheres constructed with their own nanofibers doped with β-naphthalene sulfonic acid (β-NSA) were prepared with a reversed microemulsion polymerization associated with a template-free method. The effects of the polymerization conditions on the morphology and electrical properties of the new microstructures/nanostructures were investigated. The formation mechanism of the new microstructure/nanostructure is discussed.

EXPERIMENTAL

Aniline monomer (Beijing Chemical Co, Beijing, PRC) was distilled under reduced pressure. Ammonium persulfate [$(NH_4)_2S_2O_8$; APS; Beijing Yili Chemical Co, Beijing, PRC], β-NSA (Beijing Yucai Chemical Co, Beijing, PRC), and other reagents were used as received without further treatment. The reaction proceeded at room temperature. Aniline (5.5×10^{-4} mol) and NSA (precalculated with a molar ratio of 1:1) were dissolved in 3.0 mL of deionized water; then, 20 mL of 1,2-dichloroethane was added to this mixture. The mixture was emulsified under ultrasonication for 0.5 h. To the previous emulsion, we quickly added 0.55 mL of an aqueous solution of APS ($1.0M$) as an oxidant, and the mixture was kept under ultrasonication stirring for 10 min. Then, the mixture was allowed to react for 12 h without ultrasonication. The product was washed with deionized water, methanol, and diethyl ether several times and finally dried *in vacuo* for 24 h to obtain a dark blue powder of PANI/β–NSA.

The structure of PANI/β-NSA was characterized by Fourier transform infrared (FTIR) spectra (with a PerkinElmer system, Beijing, PRC). A field emitting scanning electron microscope (JSM-6700F, Beijing, PRC) and a transmission electron microscope (JEM-20°CX, Beijing, PRC) were used to measure the morphology of PANI/β-NSA. A high-intensity ultrasonic probe (Sonics, model CX-100, 1.25 Ti horn, 20 kHz, 100 W/cm², Beijing, PRC) was used as the source of ultrasonic irradiation. The conductivity of the compressed pellets of the PANI/β-NSA hollow microspheres at room temperature was measured by a four-probe method with a Keithley 196 SYSTEM DMM digital multimater (Beijing, PRC) and an ADVANTEST R6142 programmable direct-current voltage/current generator (Beijing, PRC) as the current source.

RESULTS AND DISCUSSION

In general, reversed microemulsions have core–shell structures. In this study, water was regarded as the core, and the aniline/NSA micelle was regarded as the shell. The core–shell structure was considered a microreactor that allows the aniline polymerization to be carried out in its inside due to the hydrophilicity of APS. The reaction mixture was emulsified enough with ultrasonic irradiation before oxidation to form a uniform reversed microemulsion. Ultrasonic irradiation fashion and time during the polymerization played critical roles in the formation of the completed microspheres. To obtain a high yield and quality hollow spheres, ultrasonic irradiation was required as follows: once the polymerization took place, ultrasonic irradiation during the initial polymerization was only performed for a short time (e.g., 10 min). After that, the polymerization process was carried out without ultrasonic irradiation; otherwise, the resulting the spheres were destroyed due to the high ultrasonic energies. Scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) confirmed the resulting PANI/β-NSA microspheres, as shown in Figure 1(a); as shown, spheres (4.0–6.0 μm in average diameter) at a high formation yield were obtained. Moreover, some broken spheres were also observed [see Fig. 1(b)], which indicated that the spheres were hollow. TEM measurements further proved that the microspheres were empty and that their shell was about 150–250 nm (see Fig. 2). Interestingly, the shell of the hollow microspheres consisted of final fibers 20–30 nm in average diameter and 150–250 nm in average length, as shown in Figure 3. Moreover, the insides of those hollow microspheres were rougher than that the outsides, which suggested that the oxidation reaction took place within the reversed emulsion. In particular, those nanofibers aggregated to form junctions at the center of the microspheres. The microstructures/nanostructures were bright new morphologies that were different from spheres or
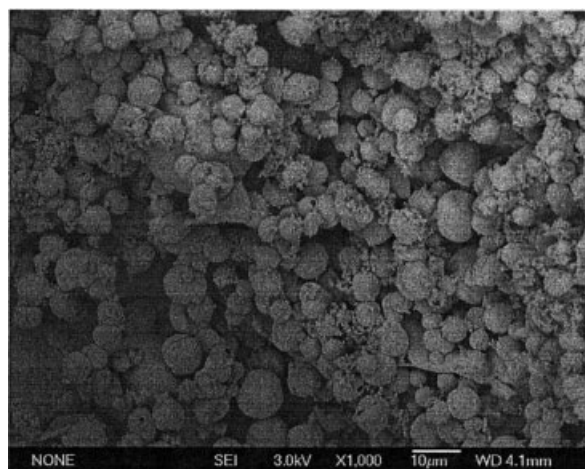
(a)
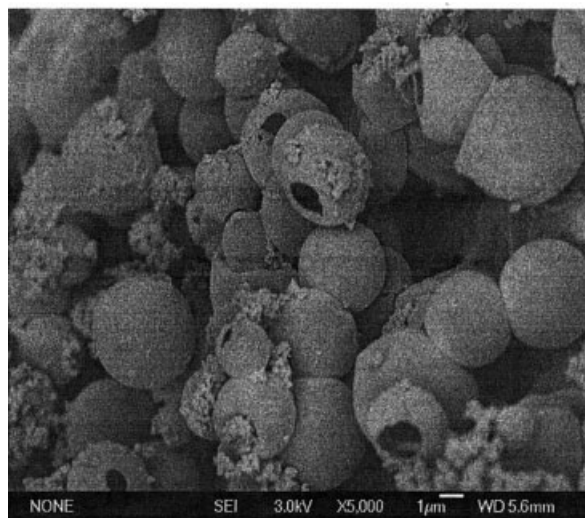
(b)

Figure 1 SEM images of PANI/β-NSA hollow microspheres prepared under the following reaction conditions : aniline = 5.5×10^{-4} mol, NSA/aniline = 1, APS/aniline = 1, [water]/[NAS/aniline] = 358, 1,2-dichroloethane = 15 mL, and reaction temperature = 25°C.

nanotubes/nanofibers prepared by the template-free method[12] or template method.[5]

In general, β-NSA is an amphiphilic molecule due to its lipophilic —$C_{10}H_7$ and hydrophilic —SO_3H groups, which is also a counterion for the doped PANI. As a result, the β-NSA dopant in this study played doping and surfactant functions at the same time. Moreover, aniline/NSA micelles were formed in an aqueous solution through an acid/base reaction. Therefore, the reversed microemulsion with a core–shell structure was regarded as a microreactor. In the microreactor, water (the core) was a soft template in the formation of the microspheres, whereas NSA or the aniline/NSA micelle in the
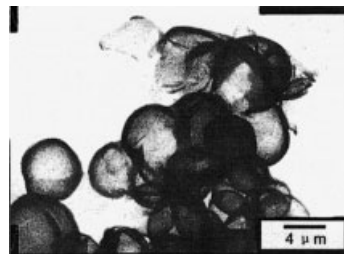

Figure 2 TEM of PANI/β-NSA hollow microspheres prepared under the following reaction conditions: aniline = 5.5×10^{-4} mol, NSA/aniline = 1, APS/aniline = 1, [water]/[NAS/aniline] = 358, 1,2-dichloroethane = 15 mL, and reaction temperature = 25°C.

shell acted as a soft template in the formation of the nanotubes or nanofibers. Once APS was added as the oxidant, aniline oxidation polymerization only took place inside close to the water phase of the microreactor because of its hydrophilicity. This is why the outside surface of the microspheres was smoother than the inside surface.

Second, the microreactor also consisted of NSA or aniline/NSA micelles. On the basis of our previous reports,[13] those micelles were regarded as soft templates in the formation of the nanotubes or nanofibers and which was allowed by elongation[14] or accretion processes.[15]

Third, the shell, composed of NSA or aniline/ NSA micelles, was also considered a bielectrical layer, where the anilinium cation acted as a positive charge layer and the β-NSA ion acted as a negative charge layer close to the water phase of the microemulsions due to the —SO_3H group of NSA. Such a bielectrical layer structure probably resulted in the oriented arrangement of the micelles facing the cen-
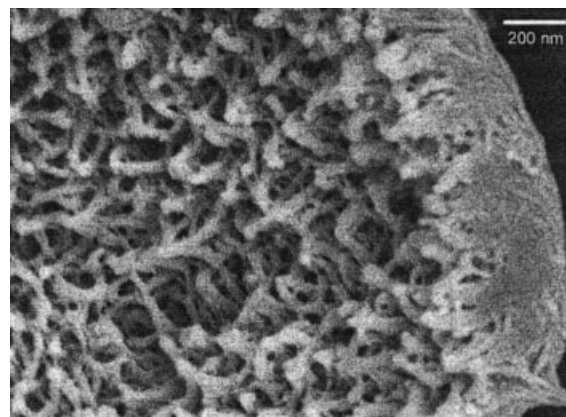

Figure 3 Magnification SEM of broken hollow microspheres of PANI/β-NSA prepared under the following reaction conditions: aniline = 5.5×10^{-4} mol, NSA/aniline = 1, APS/aniline = 1, [water]/[NAS/aniline] = 358, 1,2-dichroloethane = 15 mL, and reaction temperature = 25°C.

ter of the microemulsions. In the polymerization process, the growth of the nanofibers would be along on those formed nanofibers through elongation and accretion[14,15] processes, or the nanofibers would aggregate to form junctions through interaction, such as π–π interactions, hydrogen bonds, and even ionic bonds, along the polymers.[16] That is why the nanofibers formed in inner of the shell of microspheres seemed to be oriented to the center of the hollow spheres (see Fig. 3). In conclusion, the coordination effect of the reversed-emulsion polymerization with the dopant or dopant/aniline micelles might have been a driving force in the formation of the special microstructures/nanostructures.

According to the previous proposal, it seemed that water played a critical role in controlling the diameter and formation yield of the hollow microspheres. This is not only consistent with results published in the literature[17] but also agrees with our experimental results, which indicate that the diameter of the hollow microspheres was strongly affected by the molar ratio of water to the aniline/NSA salt ([water]/[aniline/NSA]). The hollow microspheres with 4.0–6.0 μm in diameter became dominant, for instance, when the [water]/[aniline/NSA] ratio was 358. When the ratio was higher or lower than 358, however, the proportion of the microspheres significantly decreased, indicating that the microspheres with high yield were only obtained in a narrow range of the [water]/[aniline/NSA] ratios. In addition, the microsphere diameter increased to 5.0–8.0 μm when the ratio increased to 452. These results indicate that the [water]/[aniline/NSA] ratio not only changed the formation yield but also the diameter of the microspheres. However, influence of the reaction temperature on the formation of the microspheres could be negligible because the formation yield was still high even when the polymerization was performed at room temperature.

The molecular structure of the hollow spheres constructed with their nanofibers was characterized by FTIR spectroscopy, as shown in Figure 4. All characteristic bands of PANI at the 1578 and 1495 cm^{-1} (benzenoid and quinoid rings, respectively), 1303 cm^{-1} (C—N stretching), 1141 cm^{-1} (C=N stretching), and 819 cm^{-1} (l,4-substituted phenyl ring stretching) were observed in the FTIR spectra of the hollow microspheres, which were identical to the emeraldine salt form of PANI.[18] The conductivity of the microstructures/nanostructures at room temperature measured by the four-probe method was about 6.2×10^{-2} to 1.3×10^{-1} S/cm, depending on the synthesis conditions. The poor conductivity of the micro/nanostructures might have been

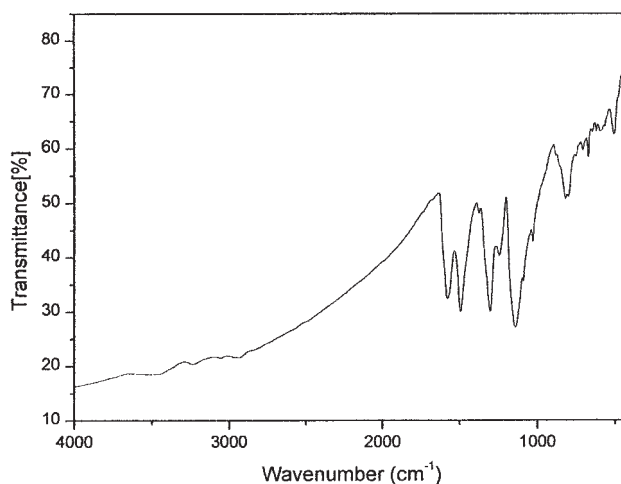**Figure 4** FTIR spectra of PANI/β-NSA hollow microspheres prepared under the following reaction conditions: aniline = 5.5×10^{-4} mol, NSA/aniline = 1, APS/aniline = 1, [water]/[NAS/aniline] = 358, 1,2-dichroloethane = 15 mL, and reaction temperature = 25°C.

caused by a low concentration of the dopant used in the polymerization.

CONCLUSIONS

PANI hollow microspheres (4.0–6.0 μm in outer diameter and 150–250 nm in shell thickness) constructed with their nanofibers (20–30 nm in diameter and 150–250 nm in length) were prepared by a reversed-emulsion polymerization associated with a template-free method. We propose that the reversed microemulsion acted as a soft template in the formation of the spheres, whereas the NSA or aniline/NSA micelle was regarded as a soft template in the formation of the nanofibers. The molar ratio of water to the aniline/NSA micelles, as well as the ultrasonic irradiation fashion and time, were critical parameters in the control of the formation yield and diameter of the microspheres. The method opened a simple and effective route to the preparation of conducting polymer hollow microspheres constructed with their own nanotubes or nanofibers.

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