Inorganic/Organic Nanocomposites of Polyaniline and Fe₃O₄ with Hollow Cluster Structures using Polystyrene Template

Youngmin Chung,† Su Ryeon Yun,† Chan Woo Lee,‡ Nam-Ju Jo,§ Chul-Hyun Yo,§ and Kwang-Sun Ryu*†

†Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea. *E-mail: krsryu@ulsan.ac.kr
‡Department of Polymer Science and Engineering, Busan National University, Busan 609-735, Korea
§KISTI ReSEAT Program Senior Fellow, Seoul 130-741, Korea

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Polymeric nanostructures have attracted considerable attention because of their wide range of potential applications.¹ Polymeric spheres with core-shell structures offer physical and chemical properties that are superior to those of any of their component materials alone.² Due to their unique structural, optical, and surface properties, and extensive potential applications, hollow spheres of nanometer to micrometer sizes are of particular interest.³ A variety of methods have been employed to fabricate composite and hollow spheres. Their structures enable hollow polymeric spheres to encapsulate large quantities of guest molecules and create large surface areas.⁴ Therefore, hollow spheres can be used as carriers of catalysts or as delivery vehicles for removing contaminants from heavy metal and for the controlled release of substances such as drugs, cosmetics, dyes, and inks.⁵

Conducting polymers have received special attention because of their excellent electronic properties and tunable conductivities in addition to their superior polymer properties.⁶ The multifunctionality of conducting polymers is an important subject in the field of material science. In particular, polyaniline (Pani) has been the subject of intense study during the past two decades because of its excellent electronic and chemical properties.⁷ Pani displays many novel and interesting properties such as simple doping mechanisms, high environmental stability, and easy processing. It shows great potential for applications such as light-emitting diodes, chemical sensors, and electronic devices.⁸

In particular, magnetic composite spheres and hollow spheres both have potential applications in the ferrofluid and separation sciences. Iron oxides are important magnetic materials, and composites with core-shell structures have successfully been prepared with iron oxides as the shell or core.⁹ Magnetite or Fe₃O₄ is a common ferrite-possessing material with a cubic inverse spinel structure. Stable Fe₃O₄ with high crystallinity and magnetic responses can be easily manufactured.¹⁰ Furthermore, Fe₃O₄ has numerous potential applications in ferrofluids, catalysts, biological assays, chemical sensors, and electrophotographic developers.¹¹

The synthesis of magnetic nanoparticles or nanocomposites is currently one of the most interesting and challenging areas of scientific research.¹² Pani/Fe₃O₄ nanocomposites, in particular, are used as new materials in applications such as electrical magnetic shields, electrochemical display devices, and microwave absorbing materials.¹³ Pani hollow spheres can be synthesized by using latex spheres or emulsion templates. Typically, polystyrene (PS) spheres are used as templates in the latex sphere method.¹⁴ Pani hollow spheres have certain advantages such as large surface area and excellent conductivity.

Recently, a new method has been proposed for preparing composite capsules and hollow spheres using core-shell sulfonated PS spheres as templates.¹⁵ The template spheres are prepared by a simple sulfonation reaction of PS spheres. The PS cores can then be removed by solvent extraction. Pani is synthesized on the shells of sulfonated PS, and the PS cores can be removed by solvent extraction from the core shell structure to yield Pani hollow spheres.⁶ After removing PS, Fe₃O₄ nanoparticles can be synthesized on the surface of Pani hollow spheres.

In this study, we describe the fabrication of Pani hollow spheres, which involves microemulsion polymerization using PS as the template. We synthesized Pani/Fe₃O₄ nanocomposites with Fe₃O₄ on the surface of the Pani hollow cluster structures by in-situ and ex-situ methods and compared the two. To confirm and characterize the formation of Pani/Fe₃O₄ nanocomposites, we performed FT-IR, XRD, FE-SEM, FE-TEM, and EDS analyses.

Experimental Section

For polymerized PS, we mixed 20 g of styrene monomer, 0.2 g of potassium persulfate (K₂S₂O₈, KPS), and 200 mL of water under a N₂ atmosphere at 80 °C for 4 h. After polymerization, 80 mL of the emulsion PS template was diluted five times with water. Subsequently, 0.6 mL of aniline and 0.06 mL of divinylbenzene (DVB) were added into the PS emulsion and dispersed for 30 min in order to arrange aniline monomer on the surfaces of the PS cores. DVB plays an important role in improving the stability of Pani in the shells. 20 mL of a mixed solution of 1 M HCl and 1.51 g ammonium persulfate ((NH₄)₂S₂O₈, APS) was added to the other solution, and the polymerization of Pani proceeded at room temperature for 24 h. Pani hollow spheres were fabricated via PS using core microemulsion polymerization for the PS/Pani with a core-shell structure. PS/Pani was separated by centrifugation and dried.
under vacuum at 60 °C for 24 h. To fabricate Pani hollow spheres, PS cores were removed by excess acetone several times and washed and dried under 50 °C for 10 h.

Pani/Fe₃O₄ nanocomposites with a hollow cluster structure were synthesized by the *in-situ* method for forming Fe₃O₄ on the surface of Pani. Pani/Fe₃O₄ hollow nanocomposites were easily fabricated by coating Fe₃O₄ onto the surface of Pani hollow spheres directly via chemical reaction. Pani hollow spheres were dispersed in 100 mL of 0.4 M HCl solution for 30 min. 0.26 g of FeCl₃·6H₂O and 0.1 g of FeCl₂·4H₂O were added to the mixed solution. 250 mL of 1.5 M NaOH was dropped into solution under a N₂ atmosphere. On the other hand, Pani/Fe₃O₄ nanocomposite could be produced simply by mixing Pani hollow spheres and Fe₃O₄ nanoparticles, which were already made by the above method. Here, we refer to this as the *ex-situ* method. We compared the distribution and formation of Fe₃O₄ on the surface of Pani hollow spheres in the *in-situ* and *ex-situ* methods.

Pani/Fe₃O₄ nanocomposites with a hollow cluster structure were analyzed by Fourier transform infrared spectroscopy (FT-IR; Varian 2000), X-ray diffraction (XRD; Rigaku ultra-X), field emission scanning electron microscopy (FE-SEM; Supra40), field emission transmission electron microscopy (FE-TEM; JEM 2100F, JEOL), and energy dispersive X-ray spectroscopy (EDS; JEM 2100F).

The overall synthetic procedure for producing Pani/Fe₃O₄ hollow nanocomposites is shown in Scheme 1. The success of encapsulation for Pani might have been limited due to differences in polarity between PS and water. However, a high concentration of emulsifier and the lower interfacial energy between PS and water promote the formation of a core-shell morphology. The surface of diluted PS has residual KPS, which plays an important role in core-shell synthesis. Its anion, which contains a sulfate group, attracts monomer aniline onto the surface of PS. Therefore, KPS serves an emulsifier-like role in this process, and its polarity attraction causes Fe₃O₄ nanoparticles to coat the surface of the Pani hollow spheres.

The FT-IR spectra of the overall process materials are shown in Fig. 1. The Pani/Fe₃O₄ hollow nanocomposites (Fig. 1(d) and (e)) exhibit peaks at 1587, 1487, 1440, 1308, 1137, 747, 687, and 523 cm⁻¹. The characteristic peaks at 747 and 687 cm⁻¹ in Fig. 1(a) can be attributed to PS. These peaks arise from the out-of-plane hydrogen and ring deformation of a mono-substituted phenyl group, whereas the two peaks at 1487 and 1440 cm⁻¹ are caused by C-H stretching. The peaks at 1587 and 1487 cm⁻¹ are caused by C=O and C=C stretching, respectively, of the quinoid and benzoid rings of Pani in Fig. 1(b). The peaks at 1308 and 1137 cm⁻¹ correspond to C-N stretching (N-benzoid-N) and C=O stretching (N=quinoid=N), respectively.

The weak peak at 523 cm⁻¹ is attributed to that of the Fe₃O₄ nanoparticle in Fig. 1(c). The spectra of the Pani/Fe₃O₄ hollow nanocomposites (Fig. 1(d) and (e)) are similar, with each showing these PS, Pani, and Fe₃O₄ peaks. Strong PS peaks remain due to the residual PS in the Pani hollow nanocomposites. Since DVB and styrene have a very similar structures, similar peaks are obtained in the FT-IR spectra.

The XRD patterns of PS, Pani, and Pani/Fe₃O₄ hollow nanocomposites (*in-situ* and *ex-situ*) are shown in Fig. 2. PS (Fig. 2(a)) and Pani hollow-spheres (Fig. 2(b)) have only a broad band at a 2θ value of 19°, which is ascribed to the periodicity parallel to the polymer chains. The characteristic diffraction
Fe₃O₄ nanoparticles are aggregated on the surface of the Pani hollow spheres. However, Fe₃O₄ nanoparticles synthesized with the ex-situ method (Fig. 3(d)) are more widespread on surface of Pani hollow spheres as compared to those with the Fe₃O₄ nanoparticles synthesized with the in-situ method (Fig. 3(g) and (h)).

The existence of Fe₃O₄ nanoparticles on the surface of Pani hollow spheres was analyzed by energy dispersive X-ray spectrometry (EDS) and elemental mapping analysis. The components of the Fe₃O₄ nanoparticles were identified by using the mapping method together with spectral lines on each Pani/Fe₃O₄ hollow nanocomposite sphere, as shown in Fig. 4(a) and (b). The components were also analyzed by EDS. Fe and O elements were found to exist on the surfaces of Pani hollow spheres (Fig. 4(a) and (b)). Thus, the results of FT-IR, XRD, and EDS analyses confirmed the presence of Fe₃O₄ nanoparticles on the surface of Pani hollow spheres.

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