Alkali-guided Synthesis of Polyaniline Hollow Microspheres

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Polyaniline hollow microspheres with conductivity of 9.7×10^{-3} S/cm were synthesized with alkali-guided method. The alkali (NaOH)-guided oxidation of aniline with ammonium peroxydisulfate as well as doping sulfate anion onto polyaniline.

In recent years, there has been increased interest in synthesizing hollow microspheres of functional materials mainly because of their application for encapsulation, drug delivery, development of artificial cells, and protection of biologically active agents.[1,2] As one of functional materials, polyaniline (PANI) hollow microspheres have been synthesized by both template[3] and template-free method[4] because of its favorable properties, such as conducting, oxidation- or protonation-adjustable electrical properties, good process ability, and environmental stability. In the template method, polyaniline wrapped on the template to result in a core-shell structure, and the template must be removed after reaction. However, in the template-free method, hollow microspheres could be prepared directly without any final treatment.

As we know, Wan et al. have reported micro- or nanostructures of polyaniline and their functionalized composites synthesized by the self-assembly method,[4,5] i.e., template-free method. Their attentions focused on researching the micro- or nanostructures doped with various acids[5,6] and the electric,[7] optic,[8] and magnetic[9] properties. The products were doped with acids and only a few organic acids were valuable for hollow microspheres because of existence of the hydrogen bond[4] so far as I know. Then a novel seeding method[10] has recently reported by Manohar's groups to control the overall morphology of PANI-containing nanospheres. In the seeding method, PANI was synthesized in one step without large organic dopants, surfactants, and/or large amounts of insoluble templates. Though all those micro- or nanospheres were well prepared either alone or using organic dopants, the samples were always synthesized in acid condition with ammonium peroxydisulfate (APS) as the oxidant. It is well known that APS was reduced to sulfate or hydrosulfate radical[11,12] which did not participate in the doping process during the polymerization in conventional opinions. But it was suggested us to use these sulfate or hydrosulfate radical as dopants directly. The equation[11,12] suggests us on this subject. What will happen when we add alkali to the system instead of acid? Can the hydroxy ion bind ammonium to drive the equation? Thus we made an attempt to synthesize polyaniline micro- or nanostructures with alkali.

In this work, we describe an extremely simple alkali (NaOH) guided method to synthesize polyaniline hollow micro spheres in one step without needing large amounts of organic dopants or other acids. It is an easier and cheaper way than conventional method. The experimental details of the synthesis are described in supporting information.[13] With the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images, we noted the average diameter of the hollow microspheres (Figures 1a and 1b) was about 1 μm. Remarkably, these hollow microspheres were guided by sodium hydroxide (NaOH), and only when the molar ratio of aniline (An) monomer to alkali was much higher, for example 10:1 or more, the hollow microspheres can be formed. When the molar ratio was lower, to our surprise, multimorphology of PANI-containing nanotubles, micrograins, and solid microspheres were synthesized within the same alkalinity of sodium hydroxide, and the morphology could be controlled from nanotubes to microspheres by simply changing the molar ratio of the aniline monomer to alkali (Table 1). The average size of the nanotubes (Figures 1c and 1d) is about 200 nm, micrograins is about 2 μm and solid spheres is about 2–5 μm.[13]

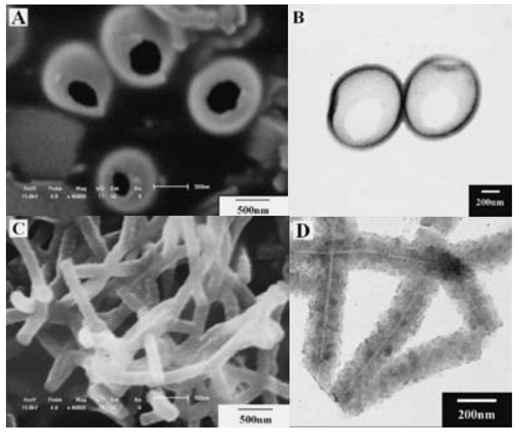

Figure 1. Typical SEM images (A and C) and TEM images (B and D) of the polyaniline micro/nanostructures: (A and B) hollow microspheres; (C and D) nanotubes. Micrograins and solid spheres were shown in supporting information.

The structures of the samples were firstly studied by ultraviolet–visible spectrometry (UV–vis). Figure 2 (left) shows the solution UV–vis spectra of the hollow microspheres in *N*-methyl-2-ketopyrrolidine (NMP) and the doped curve with hydrochloric acid (HCl). In general, the peaks around 320 and 620 nm (curve A) represent the emeraldine base (EB) form of PANI[14] owing to the NMP base. In order to clarify the doped

Table 1. Effect of the An/NaOH molar ratio

An/NaOH[a]	10:1	2:1	1:1	1:2
Morphology	Hollow sphere	Nanotube	Grain	Solid sphere
Conductivity (S/cm)	9.7×10^{-3}		10^{-8}–10^{-9}	

[a]The PANI synthesized in deionized water solution of NaOH (pH = 12.6), $t = -5\,°C$, An/APS = 1:1, 24 h with different An/NaOH molar ratio.

form, we doped the sample with HCl solution. The doped PANI have major absorptions around 412 nm, which related to the π–π^* transition on the polymer chain.[14] The absorption around (or after) 800 nm is attributed to polaron after doping and corresponds to localization of electron[15] as shown in curve B. The peak at 620 nm of the original sample (curve A) has disappeared. These proved the doped structures of polyaniline. However, only the hollow microspheres were in the doped form. The micro/nanostructures synthesized in lower molar ratio of An/NaOH were in the oxidized state as shown in Figure 2 (right). The peaks around 620 nm are blue-shifted and more weakened. This phenomenon just proved the PANI chains to be more in the quinoid structures.[16]

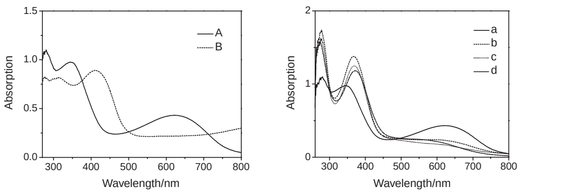

Figure 2. (Left) Typical UV–vis spectra of the polyaniline hollow microspheres in NMP (curve A) and the sample doped with HCl (curve B); (Right) The UV–vis spectra of the polyaniline (a) hollow microspheres; (b) nanotubles; (c) micrograins and (d) solid microspheres in NMP.

To farther prove that the polyaniline hollow microspheres were doped with sulfate, three test steps were carrying out. (i) After polymerization, the mother liquid was strongly acidic with pH test paper, and the addition of aqueous barium chloride gave a white precipitate; (ii) The samples were filtered and washed with water until no white precipitate was given by adding aqueous barium chloride; (iii) The dedoped sample with ammonia was filtered and aqueous barium chloride was added to the filtrate. It gave a white precipitate, confirming the presence of sulfate anion. These results indicate that polyaniline hollow microsphere contains sulfate group as dopant ion and this sulfate ion was generated from ammonium persulfate which was used for the oxidant originally.

It is well known that the conductivity of polyaniline is increased with the doping level and it is also an evidence of doped form. So we measured the conductivity of original samples, samples doped with HCl and samples dedoped with ammonia by four-probe method. The room-temperature conductivity (Table 1) of the compressed pellets of polyaniline hollow microspheres was found to be 9.7×10^{-3} S/cm due to low doping degree in our points. The conductivity of doped samples was found to be 1.8×10^{-2} S/cm, which are twice over that of the original samples. The conductivity of dedoped samples was found to be 3.7×10^{-9} S/cm, which are six orders of magnitude lower than that of the original samples. As expected, the micro- or nanostructures synthesized in lower molar ratio of An/NaOH were insulators. Their conductivities were around 10^{-8}–10^{-9} S/cm. These properties confirm our belief that a little alkali can guide oxidation of aniline with ammonium peroxydisulfate as well as doping sulfate anion onto polyaniline.

The Fourier transform infrared spectroscopy (FTIR) was also used to testify the backbone structure. The typical FTIR spectra are shown in Figure 3. The characteristic peaks of the polyaniline hollow microspheres were at 3448, 3257, 1581, 1500, 1301, 1145, and 823 cm^{-1}. The intensity of the bands at 1300 (C–N stretching vibration) and 1145 cm^{-1} (the same vibration mode of positive nitrogen species $-NH^+=$) weakened with the decrease of the molar ratio of An/NaOH, and this also proved the redox forms showed by the UV–vis spectra.

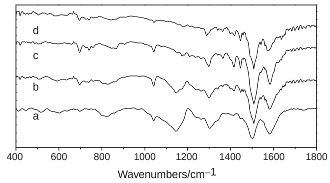

Figure 3. FTIR spectra of PANI (a) hollow microspheres; (b) nanotubles; (c) micrograins and (d) solid microspheres.

In summary, we have succeeded in synthesizing polyaniline hollow microspheres with conductivity of 9.7×10^{-3} S/cm using alkali (NaOH)-guided method. These spheres were doped with sulfate anions which were generated from ammonium peroxydisulfate. Ammonium peroxydisulfate acts as both oxidant and dopant in the polymerization. In addition, multi-morphology of polyaniline, such as nanotubes, micrograins and solid microspheres, were obtained by changing the molar ratio of An/NaOH. Therefore, this alkali-guided method affords an easy way to get polyaniline structures without any need of large amounts of organic dopants or other acids used by conventional techniques.

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