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Effect of chitosan on interfacial polymerization of aniline

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ABSTRACT

In this study, a chemical oxidization method was utilized to prepare nanostructured polyaniline (PANI) via interfacial polymerization, which employed an immiscible interface formed using aqueous and organic solutions. The effect of the amount of chitosan on the morphology of the nanostructured PANI was elucidated. Transmission electron microscopy (TEM) results demonstrate that PANI nanofibers were only fabricated via interfacial polymerization of aniline when the amount of chitosan was <1.5 wt%. However, when the amount of chitosan was exceeded 2.5 wt%, only PANI nanoparticles were obtained, not nanofibers. When the amount of chitosan used was 1.5–2.5 wt% during interfacial polymerization of aniline, the morphology of the PANI products was a mix of nanofibers and nanoparticles.

1. Introduction

Polyaniline (PANI) is an important member of the family of intrinsically conducting polymers (ICPs). Because of its excellent environmental stability and unique electrochemical property, PANI has been widely studied and applied in, for example, secondary batteries, biosensors, anti-static packaging materials, and for corrosion protection. Generally, chemical oxidization and electrochemical syntheses are the two major routes for PANI preparation (Cao, Andreatta, Heeger, & Smith, 1989; MacDiarmid, Chiang, Huang, Humphery, & Somasir, 1985).

In particular, PANI nanotubes and nanofibers with diameters <100 nm can be fabricated by template-guided polymerization within channels of zeolites (Wu & Bein, 1994) or nanoporous membranes (Martin, 1995; Wang, Chen, & Li, 2002; Wang, Wang, Li, & Li, 2001). Adding structure-directing molecules, such as surfactants (Yu, Lee, Shin, Park, & Holze, 2003) or polyelectrolytes (Liu & Yang, 1991), to a chemical polymerization bath is another method for fabricating nanostructured PANI. Since these methods require a template or specific complex chemical reagent, post-synthetic treatments are needed to remove the template or reagent from products to recover the nanostructured PANI. Therefore, a novel synthesis process that does not rely on templates, structure-directing molecules, or specific dopants is needed, especially for producing large quantities of nanostructured materials.

Kaner et al. (Huang & Kaner, 2004; Huang, Virji, Weiller, & Kaner, 2003) examined an interfacial polymerization route and successfully synthesized PANI nanofibers with diameters roughly 50 nm, which is among the smallest reported for PANI nanofibers and nanowires without using a template. The interfacial polymerization method has been demonstrated as a general route for producing PANI nanofibers.

Chitosan is a fully or partially deacetylated form of chitin. The degree of deacetylation (DD) of chitosan is typically 70–95%. The amount of amine group on the backbone of chitosan molecule is proportional to the DD of chitosan. Chitosan, a natural cationic polyelectrolyte, is also a polyaminosaccharide with many important biological (i.e., biodegradable, biocompatible, and bioactive) and chemical properties (polycationic and hydrogel containing reactive groups such as –OH and –NH). Hence, chitosan has many applications, such as in wastewater treatment, enzyme immobilization, drug-delivery systems and for chromatographic support (Nam, Kim, & Ko, 2001).

In this work, a chemical oxidization method was employed to prepare nanostructured PANI via interfacial polymerization, which utilized an immiscible interface formed in water and organic solvent. Since chitosan is a strongly hydrophilic polymer, the viscosity of the water phase can be controlled by adding different amounts of chitosan during water phase. Furthermore, the various viscosities of the water phase can affect the assembly of polyaniline molecules and result in different morphologies of nanostructured PANI synthesized by interfacial polymerization of aniline. Thus, the effect of the amount of chitosan in the water phase on the morphology of PANI is elucidated in this work.

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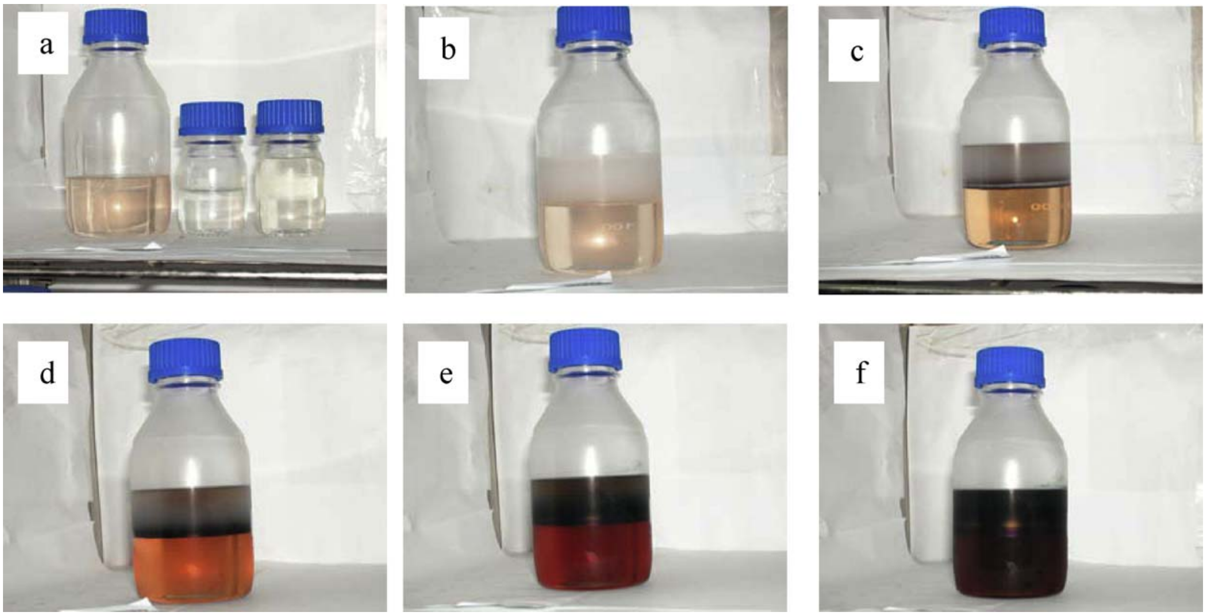

Fig. 1. Photographs showing interfacial polymerization of aniline in a water/chloroform system. From (a) to (f), reaction times are 0, 0.5, 30, 70, 180, and 360 min, respectively. The top layer is an aqueous solution of ammonium peroxydisulfate with 0.1 wt% chitosan; the bottom layer is aniline dissolved in organic solvent (i.e., chloroform).

2. Experimental

2.1. Materials

Chitosan (degree of deacetylation >95% and molecular weight is roughly 60,000 g/mol) was purchased from Cheng-Li Ltd., Taipei, Taiwan. Aniline ($C_6H_5NH_2$) and ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) (APS) were purchased from Merck, Germany. Nitric acid (HNO_3) was purchased from Union Chemical Works Ltd., Taiwan. All reagents were used as received.

2.2. Synthesis process

Aniline (0.1 mol) was dissolved in chloroform to form a 200 ml homogeneous solution in a 500 ml glass bottle. Ammonium peroxydisulfate (0.05 mol) was dissolved in distilled water to form a 50 ml homogeneous solution. To determine the influence of amount of chitosan in the water phase on formation of nanostructured polyaniline (PANI), various amounts of chitosan were dissolved in 100 ml of distilled water to generate chitosan solutions of 0.1, 0.5, 1.0, 1.5, 2.25, 2.5, and 3.0 wt%. Since chloroform density exceeds that of water, the aniline/chloroform solution formed the bottom organic phase and the APS/chitosan solution formed the top aqueous phase. The resulting two-phase system was well covered to eliminate solvent evaporation. This two-phase system was then left undisturbed for 24 h. After 24 h, the reaction mixture in the top layer was purified and collected.

2.3. Characteristic analyses

2.3.1. Fourier-transform infrared (FTIR) analysis

The chemical structure of the synthesized PANI was identified using a Fourier-transform infrared (FTIR) spectrometer (Spectrum One; Perkin Elmer, USA). The wave number range was 400–4000 cm^{-1} and scanning rate was 32/s. The powdery PANI samples and potassium bromide (KBr) (weight ratio of 1:99) were ground together into fine powders; the homogenous mixture was then pressed into a pellet for analysis.

2.3.2. Transmission electron microscopy (TEM) analysis

Samples for TEM (JEM-1230, JEOL Ltd., Japan) analysis were prepared on carbon-coated copper grids with Formvar film (Ted-Pella). The TEM acceleration voltage was 80 kV.

3. Results and discussion

Fig. 1 shows the photographs of interfacial polymerization of aniline using the water/chloroform system. Reaction times were 0, 0.5, 30, 70, 180, and 360 min (Fig. 1(a)–(f)). Fig. 1(a) shows three-glass bottles used to prepare interfacial polymerization of aniline. From left to right in Fig. 1(a), three-glass bottles are aniline/chloroform solution, APS solution, and chitosan solution with 0.1 wt% chitosan, respectively. For interfacial polymerization of aniline, the chitosan solution was carefully spread onto an organic solution i.e., the aniline/chloroform solution followed by adding the APS solution to the chitosan solution to form an aqueous/organic interface (Fig. 1(b)). During the 30-min reaction,

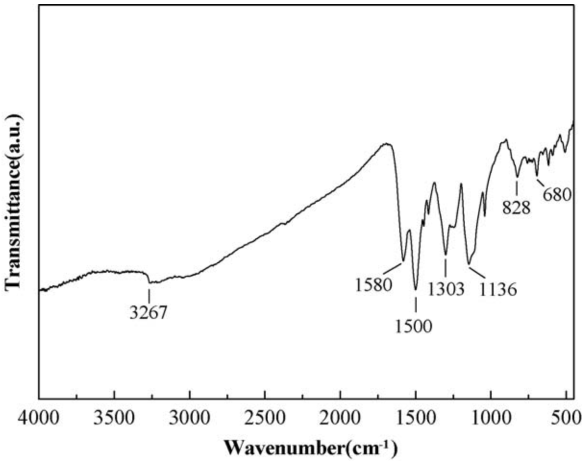

Fig. 2. The FTIR spectrum of PANI synthesized by interfacial polymerization with 0.1 wt% chitosan.

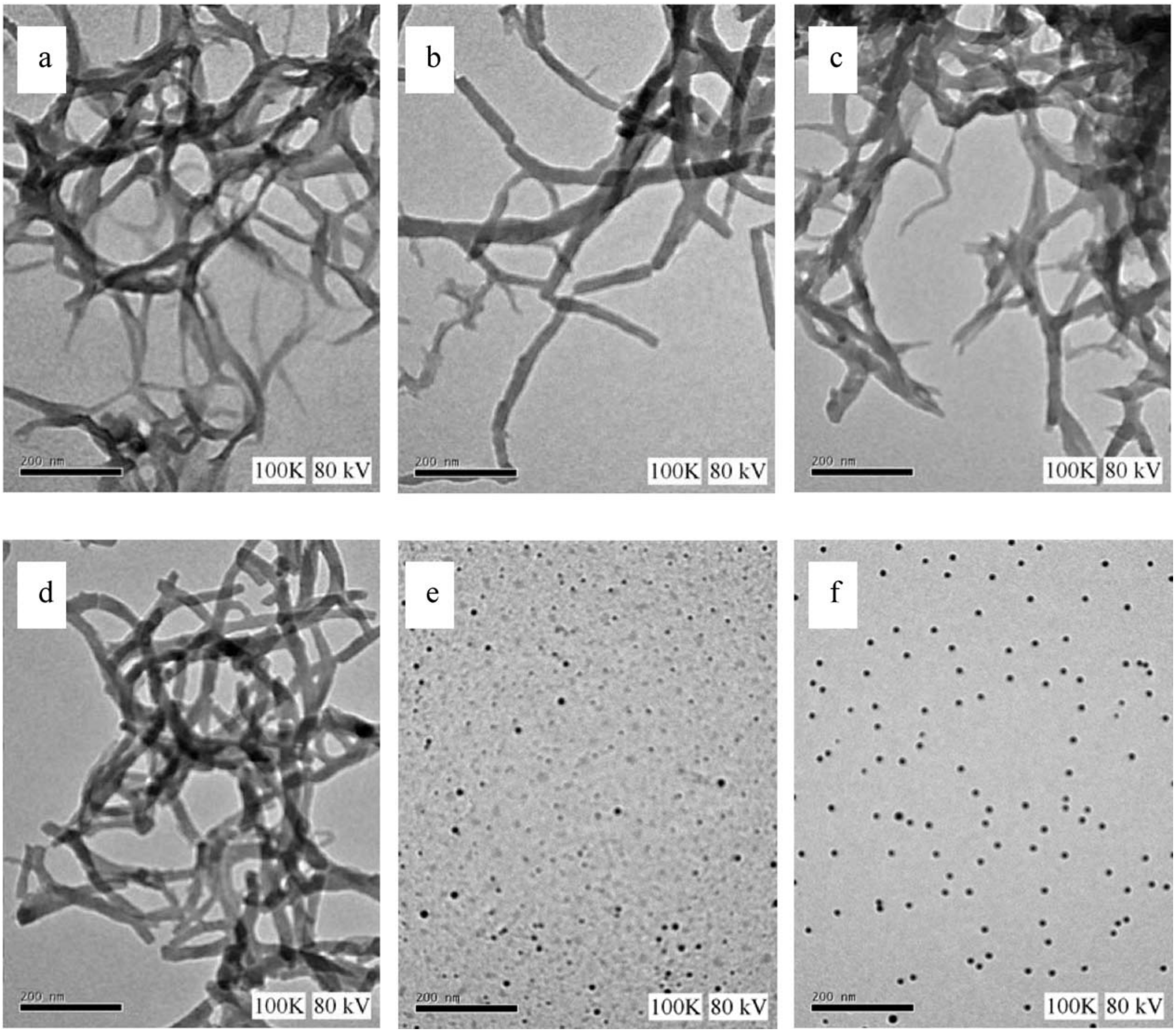

Fig. 3. The TEM images (from (a) to (f)) of PANI synthesized by interfacial polymerization with 0.1, 0.5, 1.0, 1.5, 2.5, and 3.0 wt% chitosan, respectively (scale bar = 200 nm).

polyaniline appeared rapidly at the interface (Fig. 1(c)), migrated into the water phase (Fig. 1(d) and (e)), and finally filled the entire water phase (Fig. 1(f)). As the reaction proceeded, the colors of the water and organic phases darkened and finally stopped changing. Thus, color change can be used as an indication of the degree of completion of interfacial polymerization of aniline. An overnight reaction time (i.e., 24 h) was generally sufficient for interfacial polymerization of aniline. The end product was then collected and purified through filtration.

Fig. 2 shows the FTIR spectrum of PANI synthesized by interfacial polymerization with 0.1 wt% chitosan. The characteristic peaks at roughly 1580 and 1500 cm^{-1} corresponded to stretching vibrations of the N=Q=N ring and N–B–N ring, respectively. The peak at 1303 cm^{-1} was attributable to C–N stretching vibration of the secondary amine in the PANI main chain. The peak at roughly 1136 cm^{-1} corresponded to the characteristic of the B–NH–Q bond or B–NH–B bond, and in-plane bending vibration of benzenoid or quinonoid C–H (where B refers to benzenic-type rings and Q refers to quinonic-type rings). The peaks at 828–680 cm^{-1} corresponded to the characteristic of the B–NH–Q bond or the B–NH–B bond, and out-of-plane bending vibration of benzenoid or quinonoid C–H and N–H bonds. Furthermore, for the peak located at roughly 3267 cm^{-1} resulted from the stretching vibration mode of the N–H bond. The locations of these characteristic peaks are in good agreement with those in literature (Zhang & Wan, 2002; Zhou, Wu, & Kan, 2007).

Fig. 3 shows TEM images of PANI samples synthesized by interfacial polymerization with different amounts of chitosan. In Fig. 3(a)–(d), the amounts of chitosan are 0.1, 0.5, 1.0, and 1.5 wt%, respectively. Notably, only PANI nanofibers were obtained with these amounts of chitosan. This phenomenon was due to insufficient viscosity of the aqueous phase for inducing polyaniline molecules to form PANI nanofibers. The morphology of the obtained polyaniline has an interconnected and branched network-like nanofibrous structure with nanofiber diameters of 10–40 nm. The diameters of polyaniline nanofibers were much smaller than those of PANI synthesized using a conventional polymerization process. No significant differences existed in the branched interconnected network structures of polyaniline nanofibers when syntheses were carried out by adding <1.5 wt% chitosan. Moreover, TEM results demonstrate that no significant differences existed among average diameters of polyaniline nanofibers when syntheses were carried out with 0.1, 0.5, 1.0, and 1.5 wt% chitosan. The average diameters of PANI nanofibers were approximately 25 nm in Fig. 3(a)–(d).

Fig. 3(e) and (f) shows TEM images of PANI samples synthesized by interfacial polymerization process with 2.5 and 3.0 wt% chitosan, respectively. Notably, PANI nanoparticles were obtained only when chitosan content exceeded 2.5 wt% during interfacial

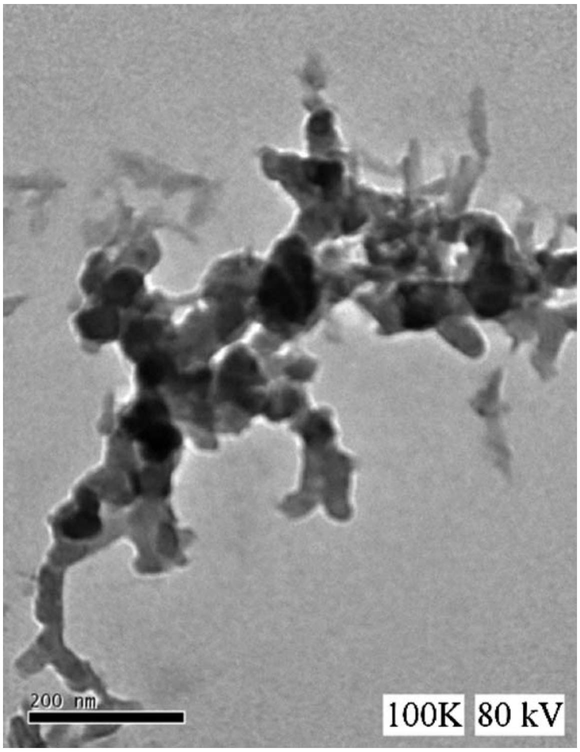

Fig. 4. The TEM image of PANI synthesized by interfacial polymerization with 2.25 wt% chitosan.

polymerization. This phenomenon resulted from sufficient viscosity of the aqueous phase for inhibiting formation of PANI nanofibers and inducing polyaniline molecules to form nanoparticles. Furthermore, TEM results demonstrate that no significant differences existed between average diameters of polyaniline nanoparticles when syntheses were carried out with 2.5 and 3.0 wt% chitosan. The diameters of PANI nanoparticles (Fig. 3(e) and (f)) were 5–15 nm.

Fig. 4 shows TEM images of PANI samples synthesized by interfacial polymerization with 2.25 wt% chitosan. Notably, PANI nanofibers and nanoparticles coexisted when 2.25 wt% chitosan was added during interfacial polymerization of aniline. According to this experimental result, the critical amount of chitosan was roughly 2.0 wt% for interfacial polymerization of aniline. That is, when 1.5 and 2.5 wt% chitosan was added to interfacial polymerization of aniline, the morphology of PANI products was a mix of nanofibers and nanoparticles.

4. Conclusions

Polyaniline nanofibers and nanoparticles were successfully fabricated by interfacial polymerization of aniline, which applied the immiscible interface formed via aqueous and organic solutions. The viscosity of the aqueous phase fully depended on the amount of chitosan added. The morphology of nanostructured PANI products was strongly dependent on the amount of chitosan in the water phase. The critical amount of chitosan in the aqueous phase was roughly 2.0 wt%. We conclude that PANI nanofibers can be obtained via interfacial polymerization of aniline only when <1.5 wt% chitosan is added. However, if the amount of chitosan added exceeds 2.5 wt%, only PANI nanoparticles can be obtained via interfacial polymerization of aniline.

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