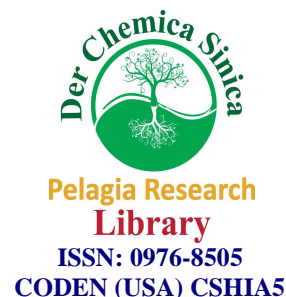




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Synthesis of Nanostructured Polyaniline (PANI) using Chitosan by Chemical Oxidation Method *via* Interfacial Polymerisation

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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. 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.

Keywords: Chitosan, Polyaniline, Interfacial polymerization, Nanofiber, Nanoparticle.

INTRODUCTION

Nanotechnology can be broadly defined as the creation, processing, characterization and utilization of materials, devices and systems with dimensions on the order of 0.1-100 nm exhibiting novel and significantly enhanced physical, chemical and biological properties and processes due to their nano scale size [1]. 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.

Polyaniline (PANI) has received much attention as a popular kind of conducting polymer with various exceptional properties, such as environmental stability, ease of synthesis, and low cost of raw materials [2]. Particularly, the ability of PANI to change electrical conductivity and colour upon exposure to acidic / basic or redox environment makes it useful in the field of chemical sensor and indicator [3–7]. Until now, various kinds of PANI and their composite sensors based on the electrochemical property have been fabricated to detect vapors and liquids like ammonia [8], carbon dioxide [9], carbon monoxide [10], nitrogen dioxide [11], chlorine gas [12], ozone [13], and even the growth of bacteria [14].

Generally, chemical oxidization and electrochemical syntheses are the two major routes for PANI preparation [15,16]. In particular, PANI nanotubes and nanofibers with diameters < 100 nm can be fabricated by template-guided polymerization within channels of zeolites [17] or nanoporous membranes [18-20]. Adding structure-directing molecules, such as surfactants [21] or polyelectrolytes [22], 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.* [23,24] 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 [25].

Chitin, poly (β -(1-4)-N-acetyl-d-glucosamine), is a natural polysaccharide of major importance, first identified in 1884 (Fig. 1). This biopolymer is synthesized by an enormous number of living organisms; and considering the amount of chitin produced annually in the world, it is the most abundant polymer after cellulose. Chitin occurs in nature as ordered crystalline micro fibrils forming structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast. It is also produced by a number of other living organisms in the lower plant and animal kingdoms, serving in many functions where reinforcement and strength are required.

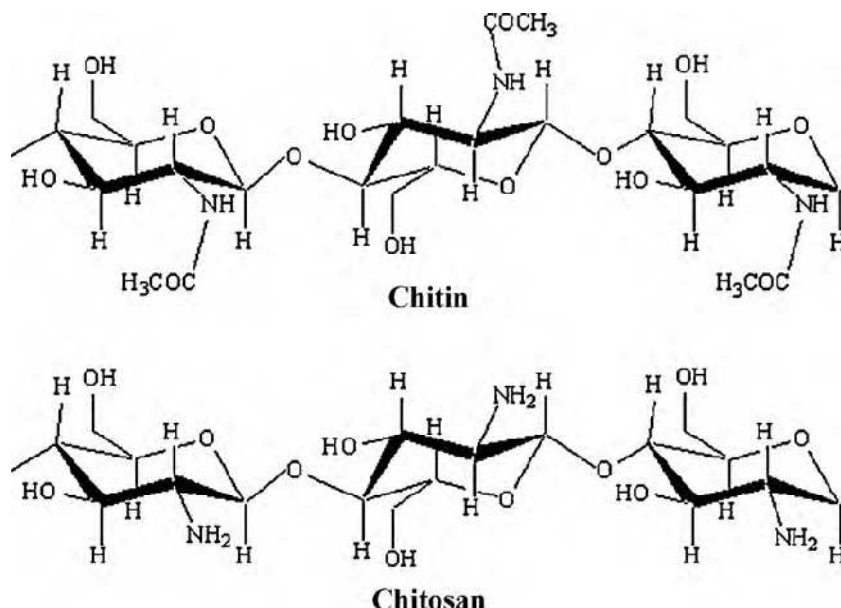


Figure 1 : Structure of Chitin and Chitosan

The most important derivative of chitin is chitosan (Fig. 1), obtained by (partial) deacetylation of chitin in the solid state under alkaline conditions (concentrated NaOH) or by enzymatic hydrolysis in the presence of chitin deacetylase. 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 poly amino saccharide with many important biological (*i.e.*, biodegradable, biocompatible, and bioactive) and chemical properties (polycationic and hydrogel containing reactive groups such as $-\text{OH}$ and $-\text{NH}$). Hence, chitosan has many applications, such as in wastewater treatment, enzyme immobilization, drug-delivery systems and for chromatographic support [26].

Because of the semi-crystalline morphology of chitin, chitosan obtained by solid-state reaction has a heterogeneous distribution of acetyl groups along the chains. Chitin and chitosan are biocompatible, biodegradable and non-toxic polymers. These properties, find several biomedical applications in tissue engineering [27, 28], wound healing [29], as excipients for drug delivery [30] and also in gene delivery [31, 32]. Chitin and chitosan are easily processed into gels [33], membranes [34], nanofibers [35, 36], beads [37], microparticles [38], nanoparticles [39] and scaffolds [40, 41]. The above forms provide a wide variety of biomedical applications in tissue engineering, wound dressing, cancer drug delivery and targeting, in the area of nano biotechnology [42].

In this work, a chemical oxidation 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.

MATERIALS AND METHODS

Materials

Chitosan (degree of deacetylation > 95% and molecular weight is roughly 60,000 g/mol) was purchased from Sigma-Aldrich. Aniline (C₆H₅NH₂) and ammonium peroxodisulfate ((NH₄)₂S₂O₈) (APS) were purchased from Merck, Germany. All reagents were used as received.

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.

Characterisation of PANI

Fourier-transform infrared (FT-IR) analysis

The chemical structure of the synthesized PANI was identified using a Fourier-transform infrared (FT-IR) 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.

Transmission electron microscopy (TEM) analysis

The TEM image of PANI, synthesized by interfacial polymerization with 2.25 wt% chitosan was carried out. Samples for TEM analysis were prepared on carbon-coated copper grids with Formvar film (Ted-Pella). The TEM acceleration voltage was 80 kV.

RESULTS AND DISCUSSION

Interfacial polymerization of aniline was carried out using the water / chloroform system. Reaction times were 0, 0.5, 30, 70, 180, and 360 min. Three-glass bottles were used to prepare interfacial polymerization of aniline. The three-glass bottles are (i) aniline / chloroform solution, (ii) APS solution, and (iii) 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.

During the 30-min reaction, polyaniline appeared rapidly at the interface, migrated into the water phase, and finally filled the entire water phase. As the reaction proceeded, the colours 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.

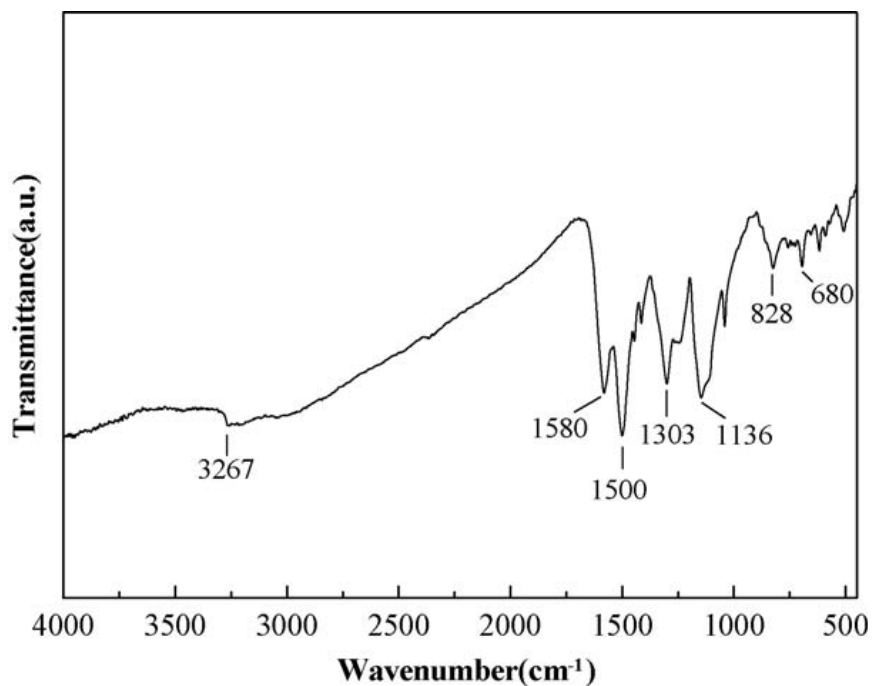


Figure 2 The FT-IR spectrum of PANI synthesized by interfacial polymerization with 0.1 wt % chitosan.

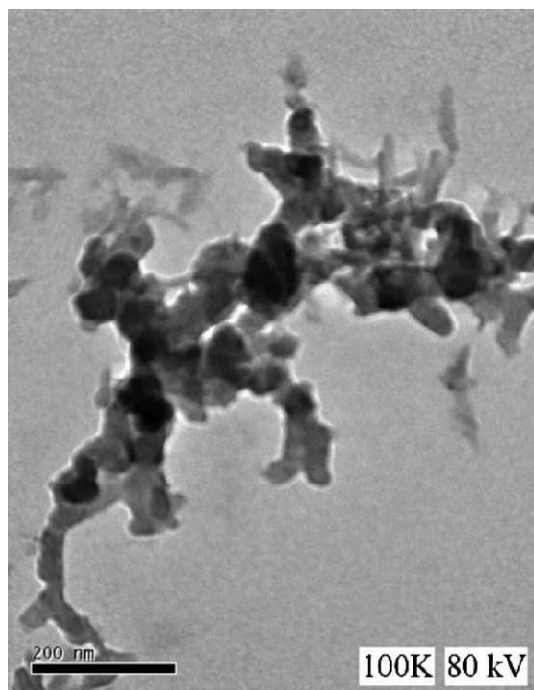


Fig. 3. The TEM image of PANI synthesized by interfacial polymerization with 2.25 wt% chitosan.

Significant, scientific and technological interest has been focused on polymer nano particles [43 - 45]. FT-IR study is useful for the characterization of polymers [46, 47]. Fig. 2 shows the FT-IR 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 $828 - 680\text{ cm}^{-1}$ 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 [48, 49].

Fig. 3 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.

CONCLUSION

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 nano structured 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 $< 1.5\text{ wt } \%$ 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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