

Research Article

Effect of Hydrochloric Acid Concentration on Morphology of Polyaniline Nanofibers Synthesized by Rapid Mixing Polymerization

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Polyaniline (PANI) nanofibers with diameters ranging from 60 nm to 190 nm were successfully synthesized by rapid mixing polymerization method at room temperature. The effects of synthesis conditions such as concentration of hydrochloric acid (HCl), ammonium persulfate (APS), and aniline monomer (Ani) on the morphology of PANI nanofibers were investigated using scanning electron microscopy (SEM). FTIR and UV-Vis analysis were performed to characterize the PANI nanofibers. The effect of polymerization time and electrical properties of PANI nanofibers was also discussed. A rapid mixing polymerization method is found to be advantageous in producing bulk quantities of nanofibers.

1. Introduction

In the past decades, conducting polymers had been considered an important organic material for various fields of research due to their wide range of applications. Among conducting polymers, PANI has been extensively studied due to its excellent conductivity, ease of synthesis, environmental stability, low cost, and highly reversible redox properties. These properties are beneficial for many applications such as rechargeable batteries, sensors, anticorrosion coatings, photovoltaic cells, and light emitting diodes (LED) [1–3].

Recently, one-dimensional (1D) nanostructured PANI such as nanotubes, nanorods, nanofibers, nanowires, nanobelts, nanoribbons, nanosticks, and nanoflowers has attracted the attention of many researchers due to its unique properties and new potential applications [4]. These 1D nanostructured materials usually offer very high surface area to volume ratio, homogeneous morphology, and tunable conductivity when compared to bulk or solid film material synthesized by traditional chemical or electrochemical polymerization.

In particular, various methods have been used to synthesize 1D nanostructured PANI including hard template [5, 6], soft template [7, 8], and template-free such as interfacial polymerization [9–11] and rapid mixing polymerization [12–14]. Currently, a rapid mixing polymerization method has been considered to be a better choice in the synthesis of PANI nanofibers due to its simplicity, large-scale affordability, cost effectiveness, being environmental friendly, and pure nanofibers production [15].

In this research, HCl at high concentration was investigated in synthesis of PANI nanofibers using a rapid mixing polymerization method at room temperature. The effects of oxidant (APS) and monomer (Ani) concentrations ratio on PANI morphologies are also discussed.

2. Experimental

All chemicals were of analytical grade and were used as received without further treatment. The following method

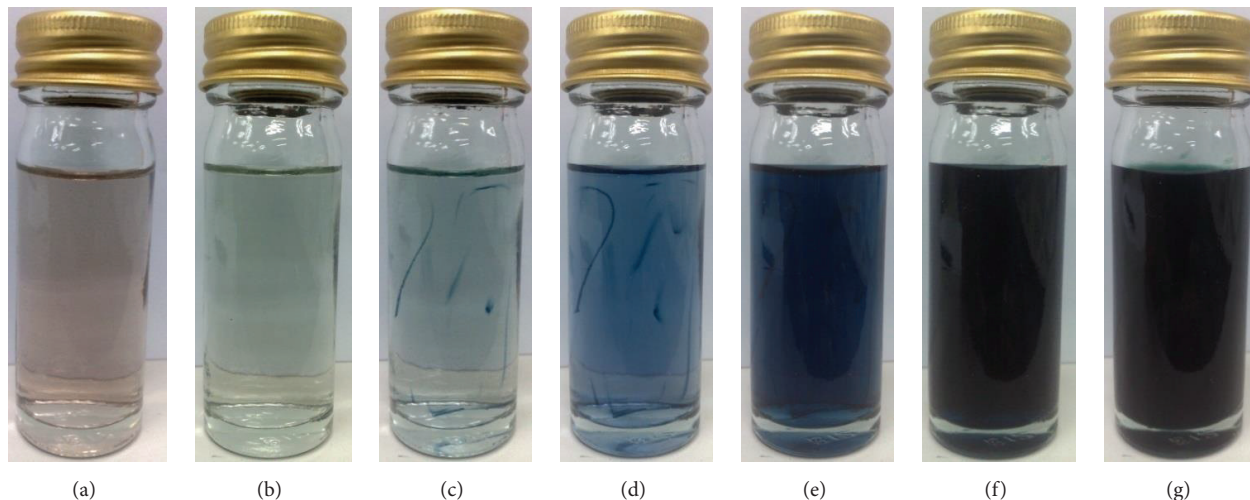


FIGURE 1: Snapshots showing the rapid mixing polymerization of PANI nanofibers in 1.0 M of HCl concentration at room temperature. The reaction times are (a) 15 s, (b) 60 s, (c) 180 s, (d) 240 s, (e) 300 s (f) 420 s, and (g) 480 s.

was adopted for preparing PANI nanofibers [16]. A 4 mmol (0.36 mL) Ani and 1.0 mmol (0.23 g) APS were dissolved in two glass vials containing 10.0 mL of HCl at room temperature (25.0°C). The solutions were poured rapidly into a 30.0 mL glass vial and shaken vigorously for about ~15 s. The mixture was left unagitated for a day. In a 30.0 mL glass vial, the HCl concentration and APS/Ani molar ratio were varied from 0.5 to 3.0 M and 1/4 to 4/1, respectively, to investigate the effects of PANI nanofibers formation. The crude product was purified by dialysis against deionized water for 3 days using tube with a 12000–14000 MW cutoff (Fisher Scientific) to remove excess acid and by-products.

The polymerization time of PANI nanofibers is measured through colour change from pink to sky blue. Samples for scanning electron microscopy studies (SEM, JEOL JSM 6460 LA) are prepared by drop-casting an aqueous dispersion of PANI nanofibers onto glass substrate and it was sputtered with gold (Auto Fine Coater, JEOL JFC-1600). The electrical conductivity of compressed PANI nanofibers was measured by four-point probe resistivity measurement (SR-4 resistivity, Everbeing) using a Keithley 2400 source meter. The circular pellets were prepared by uniaxial pressing at room temperature with 13 mm of diameter and ~3 mm of thickness. UV-Vis spectra and Fourier-transform infrared spectra (FT-IR) were recorded on a Varian, Cary 50 UV-Vis Spectrophotometer and Perkin Elmer, Spectrum 400, respectively.

3. Results and Discussion

The conventional PANI synthesis tends to produce agglomerate and irregular particulate products due to a secondary growth or overgrowth of irregular particles during polymerization. To prevent this from happening, a new method discovered by Huang and Kaner that utilizes a rapid mixing reaction was adopted [12]. Basically, the reaction is performed in an acidic solution with oxidant and monomer mixed rapidly together.

TABLE 1: Reaction conditions of synthesized PANI nanofibers by rapid mixing polymerization at room temperature.

Number	[APS]/[Ani]	HCl concentration (M)	Polymerization time (s)
1	1:4	0.5	370
2	1:4	1.0	300
3	1:4	1.5	250
4	1:4	2.0	170
5	1:4	2.5	120
6	1:4	3.0	40
7	1:1	1.0	220
8	4:1	1.0	70

Figure 1 showed the synthesis of PANI nanofibers in 1.0 M of HCl concentration at room temperature. After the two reactants (concentration of APS and Ani) were mixed, the solution turned into pink colour. The colour change signified that the reaction had commenced. The colour of the solution continued to change to clear, sky blue, dark blue, and finally green indicating that the reaction had completed. The effect of polymerization time in various HCl concentrations and APS/Ani molar ratios is shown in Table 1. The results showed that the polymerization time of PANI nanofibers is decreased by increasing the HCl concentration and APS/Ani molar ratio. For example, in the polymerization condition of APS/Ani molar ratio at 1/4, with the increase of HCl concentration from 0.5 to 3.0 M, the time for reaction completion of PANI nanofibers was 370, 300, 250, 170, 120, and 40 s, respectively. Meanwhile, in the polymerization condition of 1.0 M of HCl concentration, with the increase of the APS/Ani molar ratio from 1/4 to 4/1, the time for reaction completion of PANI nanofibers was 300, 220, and 70 s, respectively. It was

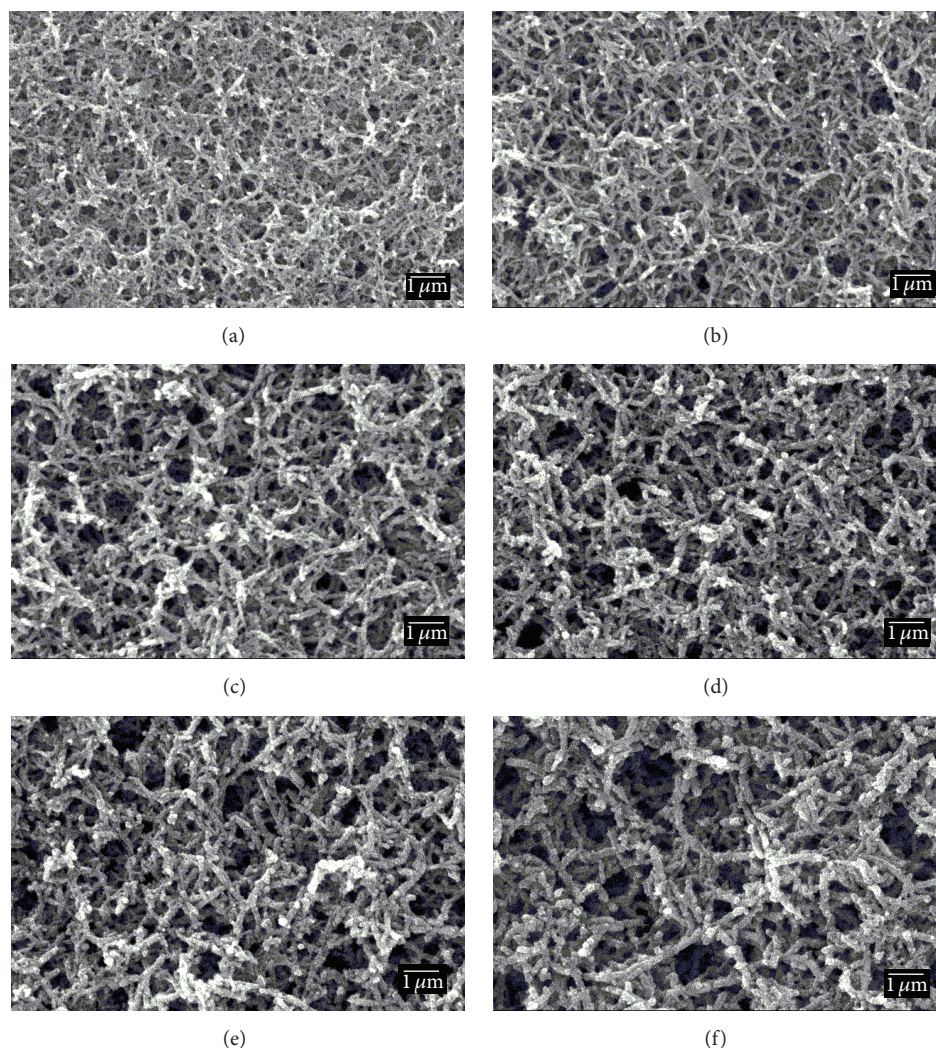


FIGURE 2: SEM images of the PANI nanofibers prepared at different HCl concentration. (a) 0.5 M, (b) 1.0 M, (c) 1.5 M, (d) 2.0 M, (e) 2.5 M, and (f) 3.0 M.

found that the time of colour changes was dependent on the HCl concentration and the APS/Ani molar ratio. Thus, the polymerization time of PANI nanofibers should be faster at higher acid and oxidant concentrations.

In order to study the effects of HCl concentration, the morphology of PANI nanofibers was observed at fixed APS/Ani molar ratio, 1/4. As shown in Figure 2, it is observed that the PANI nanofibers are present in all HCl concentrations. From 0.5 to 3.0 M of HCl concentrations, the average diameters of PANI nanofibers are ~60, ~70, ~130, ~150, ~170, and ~190 nm, respectively. The SEM images show that acid concentration played an important role in PANI formation. With the increasing of the acid concentration, the large diameters and higher yields of nanofibers were obtained [12]. With further increasing of the acid concentration, the nanofibers would initiate aggregation. As illustrated in Figure 3, the precipitate of PANI nanofibers that were observed increases with increasing HCl concentration due to the heterogeneous nucleation in the polymerization process. PANI molecules

grows on the nanofibers leading to the formation of thicker and agglomerated particles [17].

To investigate the effects of oxidant (APS) and monomer (Ani) concentrations, the morphology of PANI nanofibers was observed at fixed acid concentration, 1.0 M HCl. From Figures 4 and 2(b), it is apparent that the PANI nanofibers obtained have both about similar diameters and uniformity. The diameters of the nanofibers are ~70 nm. The results show that rapid mixing is independent of both oxidant and monomer concentrations.

Tables 2 and 3 showed the effect of HCl concentration and APS/Ani molar ratio on the electrical conductivity of PANI nanofibers synthesized by rapid mixing polymerization at room temperature. As shown in Table 2, the electrical conductivity of the PANI nanofibers become higher with the increase of HCl concentration. Based on the results, the increase in the electrical conductivities is caused by doping degree and oxidation of PANI nanofibers. Besides, it was also due to aggregation and the yield of PANI nanofibers.

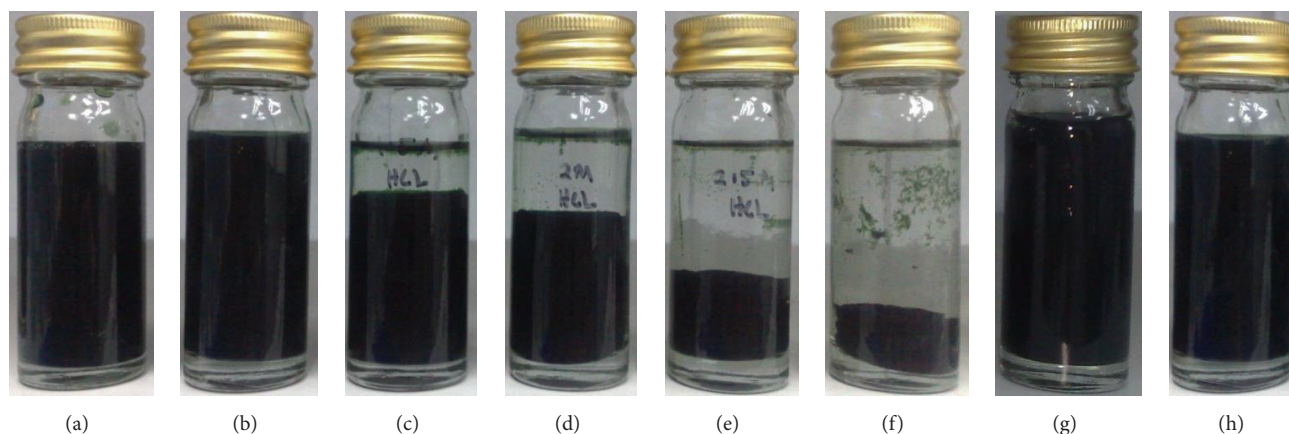


FIGURE 3: Snapshots showing the PANI nanofibers dispersion at different HCl concentration and APS/Ani molar ratio after standing for 24 hours at room temperature. (a) 0.5 M, (b) 1.0 M, (c) 1.5 M, (d) 2.0 M, (e) 2.5 M, (f) 3.0 M, (g) 1:1, and (h) 4:1.

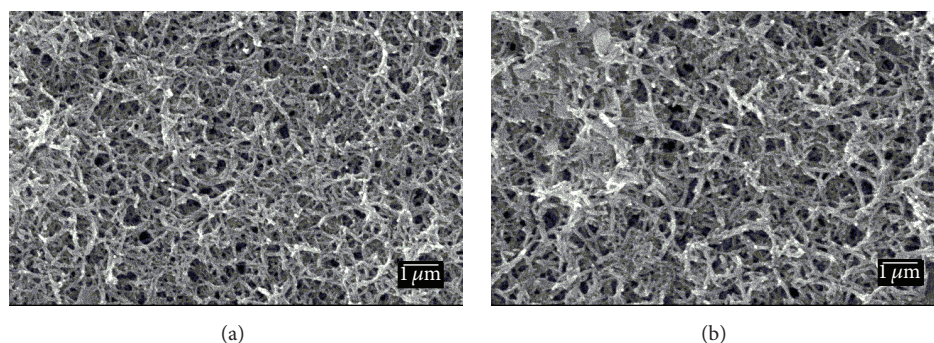


FIGURE 4: SEM images of PANI nanofibers obtained from different APS/Ani molar ratio. (a) 1:1 and (b) 4:1.

TABLE 2: The electrical conductivity of PANI nanofibers at different HCl concentration.

HCl (M)	0.5	1.0	1.5	2.0	2.5	3.0
Conductivity ($S \cdot cm^{-1}$)	0.2	0.6	1.4	2.8	4.2	7.6

TABLE 3: The electrical conductivity of PANI nanofibers at different APS/Ani molar ratio.

APS/Ani molar ratio	1/4	1/1	4/1
Conductivity ($S \cdot cm^{-1}$)	0.6	0.18	0.04

Table 3 depicted the effect of APS/Ani molar ratio on the electrical conductivity of PANI nanofibers. The increase of APS/Ani molar ratio would cause a decrease in the electrical conductivity of PANI nanofibers. It was found that the morphology of PANI nanofiber at different molar ratio did not affect its electrical conductivity. It was found that the higher content of oxidant would reduce the conductivity of PANI due to a decrease of doping degree and oxidation of nanofibers.

FTIR spectra of PANI nanofibers at different HCl concentration and APS/Ani molar ratio were shown in Figure 5(a).

From the figure, the characteristic absorption bands of PANI are revealed. The broad band of N-H stretching vibration of the amine group was observed at 3286 cm^{-1} . The bands at 1580 and 1490 cm^{-1} were assigned to C=C stretching vibration of both quinoid and benzenoid rings, respectively. The band at 1218 cm^{-1} corresponds to C-N stretching vibrations of secondary amine of PANI backbone [9]. The C-H aromatic amine appeared at 1146 cm^{-1} . Meanwhile, the band at 620 cm^{-1} relates to C-Cl stretching vibration. Figure 5(b) shows the UV-Visible spectra of PANI nanofibers at different HCl concentration and APS/Ani molar ratio. The figure depicts three typical PANI bands that are characteristic of the emeraldine salt (ES) form of the PANI nanofibers. At 340 nm and 420 nm , the $\pi-\pi^*$ and π -polaron band transitions appear; meanwhile, the localized polaron- π^* bands transitions appear in the range of $790-800 \text{ nm}$ [18]. Therefore, both of these FTIR and UV-Vis spectra results correspond to well-doped PANI nanofibers.

4. Conclusions

PANI nanofibers were successfully synthesized by a rapid mixing polymerization method. It has been found that increasing the HCl concentration and the APS/Ani molar

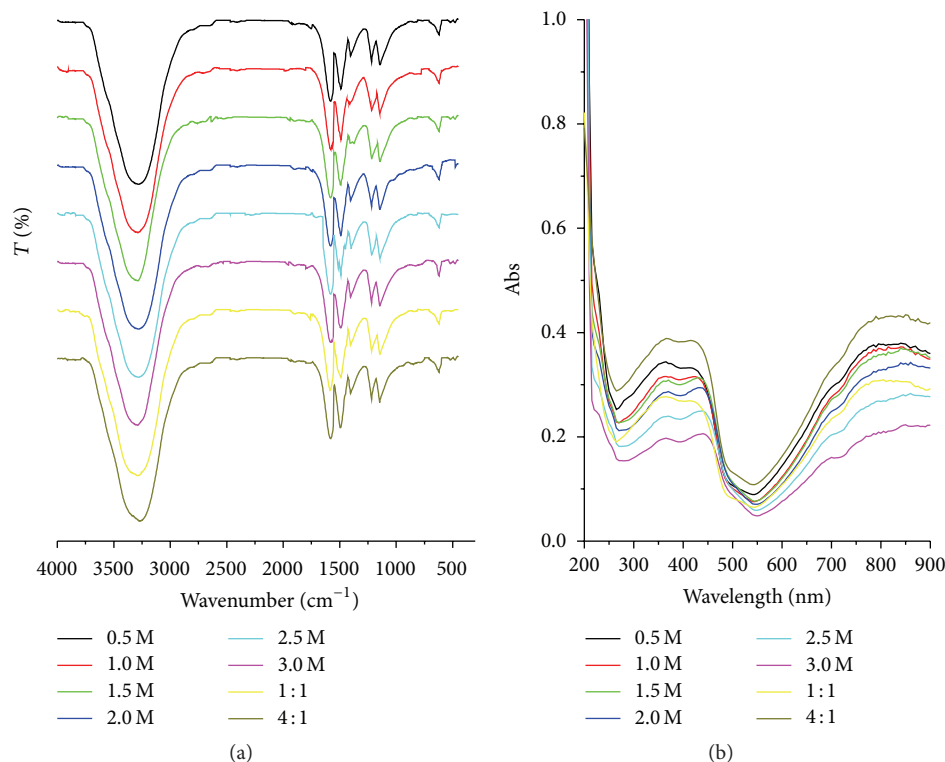


FIGURE 5: (a) FTIR spectra and (b) UV-Vis spectra of polyaniline nanofibers obtained at different HCl concentration and APS/Ani molar ratio, respectively.

ratio would take a shorter time for the PANI nanofibers to polymerize. A larger electrical conductivity of PANI nanofibers was measured at higher HCl concentration and lower APS/Ani molar ratio. FTIR and UV-Vis spectra results revealed that a well-doped characteristic of PANI nanofibers emeraldine salt is formed. SEM analysis showed that the morphology of PANI nanofibers is affected by the HCl concentration with the diameters of nanofibers increasing from ~60 nm to ~190 nm. An aggregation and thicker PANI nanofibers are obtained with the increasing HCl concentration. Meanwhile, there is no obvious effect on nanofibers from both the oxidant and monomer concentrations. This will give a huge advantage for rapid mixing polymerization to a scale-up process. Therefore, PANI nanofibers synthesized by this method could become an excellent material platform for vast applications in the near future.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

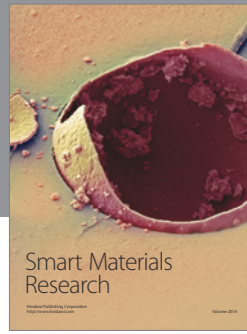
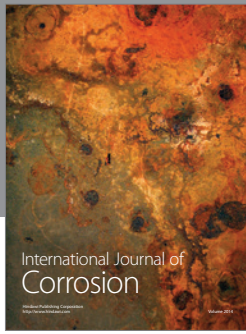
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