Acid doped polyaniline nanofibers synthesized by interfacial polymerization

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Acid-doped polyaniline (PANI) nanofibers have been successfully synthesized by interfacial polymerization and characterized by TEM, FT-IR and UV-vis spectra and thermal analysis. The TEM results show that the type of dopant acid: acetic, phosphoric, hydrochloric and perchloric acids, and the concentrations of aniline monomer and acid affect the morphology and diameter of the nanofibers. The diameters of the nanofibers are in the range of 30-50 nm, which increase with the increase in acid strength. The electrical conductivity of nanofibers varies in the order: HAC-PANI< H₃PO₄-PANI< HClO₄-PANI< HCl-PANI, which is closely related to the acid type and the size of its negative ion. Thermal stability of acid-doped PANI is different from that of EB PANI, which is attributed to the strong interaction between PANI and doped acid.

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Experimental

Aniline monomer (AR grade) was purified prior to its use. All the other reagents, including ammonium persulfate (APS), HClO₄, HCl, H₃PO₄, HAC, dimethylsulfoxide (DMSO), ammonia, toluene and acetone were of analytical grade. Doubly distilled water was used.

APS (0.58 g) was added to 250 ml beaker, containing aqueous solution (100 ml) of 1.0 mol/L HClO₄, HCl, H₃PO₄, HAC, dimethylsulfoxide (DMSO), ammonia, toluene and acetone were of analytical grade. Doubly distilled water was used.

APS (0.58 g) was added to 250 ml beaker, containing aqueous solution (100 ml) of 1.0 mol/L HClO₄, HCl, H₃PO₄ or HAC, respectively, to form the aqueous phase. Aniline monomer (1 ml) was dissolved in 100 ml of toluene to form the organic phase. Then the organic phase was carefully added along the side of the beaker to the aqueous phase to produce a clear interface of aqueous –organic phase. Then the organic phase was carefully added along the side of the beaker to the aqueous phase to produce a clear interface of aqueous –organic phase. The polymerization of aniline occurred at the interface. After 12 h, the upper organic phase was carefully removed and the lower mixture was filtered. The solid, which filtered out was washed with water and acetone until the washings were colorless. The solid samples were dried in a vacuum oven at 80°C for 12 h to obtain acid-doped PANI sample. These samples were named as HClO₄-PANI, HCl-PANI, H₃PO₄-PANI, and HAC-PANI, respectively.

Emeraldine base polyaniline (EB) was obtained by rinsing the HCl-PANI in 1 mol/L of aqueous
ammonia. By varying the concentrations of the monomer (0.1-0.2 mol/L) and dopant acid (0.2-1.0 mol/L), the effect on the morphology, size and conductivity of the samples was studied.

The samples were dispersed in ethanol and cast on carbon-coated copper grid and their morphology was observed on a JEM-100SX transmission electron microscope (TEM). FT-IR spectra were recorded on a DIGILAB-FTS3000FX FT-IR spectrometer with the samples pelletized with KBr. The UV-vis absorption spectra of the samples dissolved in DMSO were recorded on an Hp3518 UV-vis spectrophotometer in the range of 275-900 nm. TG-DTA was carried out on a PE-PYRIS Diamond TG-DTA instrument at a heating rate of 20°C min⁻¹ in air atmosphere. Conductivity of the sample was measured by a SDY-4 four probe at 25°C. The sample was compressed to a pellet of thickness about 13 mm.

**Results and discussion**

The particular acid used affects the morphology and diameter of PANI remarkably. In this study, four acids, HClO₄, HCl, H₃PO₄ and HAC were used. The TEM images of the samples are shown in Fig. 1 (a-d). It can be observed that flocky nanofibers are formed when the acid used is HClO₄ and nanofibers are uniquely uniform when HCl and H₃PO₄ are used, while long nanorods are obtained when HAC is used.

![TEM images of PANI nanofibers obtained under different conditions.](image)
Note that the traditional chemical polymerization using common mineral acids yields granular PANI. Figure 1 (a-d) also shows that the dopant acids affect the diameters of the nanofibers. The mean diameters of nanofibers in the presence of HAC, H₃PO₄, HCl and HClO₄ are 30, 35, 40 and 50 nm, respectively. Thus, the mean diameter of doped polyaniline nanofibers increases with the increase in the acid strength.

The dopant concentration affects the morphology of PANI. For example, branched nanofibers are produced when HCl is used and its concentration is in the range 0.2-0.5 mol/L as shown in Fig. 1 (e). Highly uniform nanofibers are obtained and yield of the nanofibers increases with the increase in the acid concentration in the range 0.5-1.0 mol/L. A similar result is obtained when H₃PO₄ is used. Therefore, sufficiently high concentration of the acid is necessary for obtaining uniform polyaniline nanofibers. This is consistent with the usual chemical polymerization, where concentration above 0.5 mol/L HCl is used.

Figure 1(c & f) shows the TEM images of PANI under different monomer concentrations. It is observed that the monomer concentration affects the morphology and diameter of the nanofibers and the diameter increases with increase in the concentration in the range 0.1 ~ 0.2 mol/L.

Further, the effects of reaction temperature and time were also investigated. No significant effect on morphology was observed when the temperature was in the range of 5-80°C and the duration was from 12-24 h. Thus, synthesizing PANI nanofibers by the IP method is simple. The reaction conditions are mild and the method is suitable for the large-scale synthesis of the material.

**Electrical conductivity**

The conductivity of nanofibers increases in the order: HAC-PANI(0.06 S/cm) < H₃PO₄-PANI(2.22 S/cm) < HClO₄-PANI(9.02 S/cm) < HCl-PANI(21.04 S/cm). This may be due to some different chemical reaction of the polymer chains with different dopant and the morphological changes. PANI is doped easily with strong acids and results in a stabilized structure, which will provide a more effective channel for the movement of charges than the channels in PANI doped with weak acids. The different morphologies probably provide different electric channels. Another reason may be that charge carriers can hop along the chain, from one chain to another or among fibers in the PANI samples. Thus, larger ions would increase the chain separation resulting in weakening the coupling between chains, leading to loss in the conductivity.

**Spectral characterisation**

Figure 2 shows the FT-IR spectra of EB PANI and doped PANI nanofibers. The characteristic bands of EB PANI (Fig. 2a) are as follows: the peaks at 1580 and 1505 cm⁻¹ are associated with C=N and C=C stretching mode of the quinonoid and benzenoid rings, respectively. The peaks at 1303 and 1248 cm⁻¹ are attributed to C–N stretching mode of the benzenoid ring while the peak at 1167 cm⁻¹ is due to the quinonoid unit of doped PANI. The peak at 836 cm⁻¹ is assigned to an out of plane C–H bending of 1,4...
disubstituted benzenoid rings. These assignments confirm the formation of PANI. Comparing with Fig. 2a, we find that the spectrum of doped PANI shows all the characteristic bands of PANI and shifts to the lower wavenumber resulting from the strong interaction between PANI and doped acid. These results confirm that acid-doped PANI is synthesized by IP.

The UV-vis absorption spectra of EB PANI and doped PANI nanofibers, dissolved in DMSO, are given in Fig. 3. The spectrum of EB PANI exhibits two absorption maxima at 340 and 638 nm. These peaks represent the transition and the charge-transfer excitation-like transition bands of the emeraldine base form of PANI, respectively. The peaks (spectrum b-e) at 340 and 430 nm and the broader absorption at 830 nm correspond to the electronic transitions from the valence band to polaron band characteristic of the doped emeraldine oxidation state of PANI, indicating the conducting state of PANI. This is consistent with the green color of the product. The emeraldine oxidation state of PANI contains half imine and half amine nitrogens, which may be represented by the formula \([-\text{C}_6\text{H}_4-\text{N}=\text{C}_6\text{H}_4-\text{N}=\text{C}_6\text{H}_4-\text{NH}=\text{C}_6\text{H}_4-\text{NH-}n\]. The imine nitrogens may be completely protonated on exposure to strong acids, leading to fully doped polyaniline.

**Thermal analysis**

The TG-DTA of the EB PANI shows weight loss from room temperature up to 250°C, corresponding to the removal of water molecules/moisture from the polymer matrix and the degradation of the low molecular weight and small chain fragments (Fig. 4). Then, the weight loss from 250°C onwards represents the degradation and decomposition of the polymer backbone. The TG-DTA of PANI doped with HCl shows significant weight loss, which includes the elimination of the acid doped in PANI above 300°C. However, complete decomposition occurs between 460-505°C for EB PANI. These results suggest the existence of a strong interaction between PANI and the dopant as noted from FT-IR and UV-vis spectra. The TG-DTA properties of PANI doped with other acids are similar to that of PANI doped with HCl.

The present study shows that doped PANI nanofibers have been synthesized by the interfacial polymerization. The dopant type and the concentrations of aniline monomer and the dopant affect the polyaniline morphology, size as well as conductivity. The diameters of the nanofibers are in the range of 30 ~ 50 nm, which increase with the increase in acid strength. The conductivity of nanofibers increases in the order: HAC-PANI < H₃PO₄-PANI < HClO₄-PANI < HCl-PANI, which is closely related to the acid type and the size of negative ion. Thermal stability of acid-doped PANI is different from that of EB PANI which is attributed to the strong interaction between PANI and doped acid.

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