Polyaniline Doped with Protonic Acids: Optical and Morphological Studies

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Abstract

In this work, polyaniline (PANI) and its doped state with microfiber morphologies were easily synthesized by a chemical route under the oxidative polymerization, in which the polymerization was performed in an acidic medium (protonic acids). In situ polymerization of aniline reacted with the chloride and sulfate ions of hydrochloric and sulfuric acid, respectively. The microfiber-like morphology of undoped and HCl doped PANI was observed. The X-Ray diffraction patterns represented that H$_2$SO$_4$ doped PANI was crystalline in nature. The effects of dopant acids on its optical properties were discussed. The strong interaction between chloride and sulfate ions with the ammonium group of PANI has been explained. The microfiber and granular morphology for HCl and H$_2$SO$_4$ doped PANI were observed. The redshifts were observed for the microfiber nature of doped PANI. These analytical results confirmed that the prepared PANI was in the doped state. Further, we found that the prepared PANI can be used for the fabrication of polymer solar cells.

Keywords: Polyaniline; Microfibers morphology; Doped PANI.

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1. Introduction

Polyaniline (PANI) is one of the most useful among the family of conjugated polymers as it is air and moisture stable in its conducting form (doping state) and insulating form (dedoped state). [1] In the conjugated PANI polymers, the chemical bonding contains one unpaired $\pi$-electron having sp$^2$-pz configuration per carbon atom which leads to the electronic delocalization along the backbone of the polymer chain of PANI and provides the “highway” for the charge mobility to its doped structure. [2] PANI is generally prepared by the chemical oxidative polymerization of aniline in the presence of strong oxidants such as ammonium persulfate (APS). [1] Polymerization of aniline is an exothermic process, therefore the reaction is carried out at low temperatures (0-10 °C) with one reactant (aniline) slowly added into APS under gentle stirring. [3]

Optical properties of parent PANI are different from those doped PANI due to the introduction of -SO$_2$H and Cl$^-$ groups along with the backbone structure of PANI. -SO$_2$H and Cl$^-$ ions create a more acidic medium, which is required for the polymerization of aniline. Recent theoretical calculation shows a strong steric interaction between the hydrogen atoms on adjacent rings of PANI because, after the doping of H$_2$SO$_4$, hydrogen atoms of PANI are replaced by -SO$_2$H groups which lead to an increase of the steric hindrance. [4] This steric hindrance limits the polymerization process of PANI. The size and amount of dopants play an important role in influencing the morphology of conducting polymers. The reported morphology of doped PANI (sulfonated porphyrin) can be changed from nanofibers to three-dimensional cauliflower structure. [5] PANI exhibits emeraldine salt structure when the PANI is obtained as a protonated form. [6] Most of the PANI derivatives do not show a well-defined fiber shape if it is prepared under the normal synthetic conditions. [7]

Previous synthesis of PANI (with its doped form) was carried out at low-temperature conditions (4 to 0 °C). [3-5,7] Here in this experiment we have synthesized PANI and its doped form at room temperature ($\approx$ 27 °C). The objective of the present study is to investigate the changes observed in PANI after the doping with protonic acids (HCl and H$_2$SO$_4$), and based on the reaction mechanism, the morphology of doped PANI has been studied.

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2. Experimentation
PANI was prepared by the direct addition of aniline into the APS solution. The molar ratio of aniline and APS (acts as an oxidizing agent) was 1:1 at room temperature (25 °C). PANI was doped with protonic acids viz. HCl and H2SO4 having different molarities (0.5 and 0.25 M). The solution was gently stirred (50-70 rpm) until it turned into a dark green and maintained overnight at room temperature. Then it was filtered using one filter paper. After filtration, the precipitate was dried. Accordingly, with increasing molarities, doped PANI was labeled as follows: “sample - b and c” for 0.25 and 0.5 M H2SO4 doped PANI, respectively whereas “sample - d and e” for 0.25 and 0.5 M HCl doped PANI, respectively; undoped PANI was labeled as “sample a”.

3. Characterization
X-ray diffraction (XRD) patterns for all dried powder samples of PANI were recorded on a Rigaku D/max-2400 X-ray Diffractometer (Tokyo, Japan) using copper Kα radiation at λ=0.154 nm. Filtered liquid of all PANI samples was used for UV-visible spectra. Fourier transforms infrared (FTIR) spectra of the PANI were recorded on a Thermo Fischer FTIR spectrometer. FTIR spectra were collected from 4000 to 400 cm⁻¹, with a 4 cm⁻¹ resolution. The UV-visible absorption spectra were recorded on Perkin Elmer Lambda 950 spectrophotometer with 2 nm spectral resolution at room temperature in the range of 200-1000 nm. Scanning electron microscope (SEM) images of PANI were recorded using a JEOL JSM-6360A.

4. Results and Discussion
4.1 FTIR study
The presence of doping elements in the PANI was studied by FTIR as shown in Fig. 1. In the FTIR spectrum of PANI, Lesiak et al.[9] ascribed 832 cm⁻¹ bands to the out-of-plane bending vibration of C-H on para disubstituted rings. FTIR spectrum of undoped and doped state of PANI shows a redshift of 37 cm⁻¹ for the 795 cm⁻¹ w. r. t. the 832 cm⁻¹.

This redshift may be the indication of disturbed C-H bending vibration in PANI. The band of 1030 cm⁻¹ in all samples is correlated with sulfate ion from the APS (oxidant).[9] The incorporation of protonic acids with PANI leads to the shifting of FTIR bands e.g. 1087 cm⁻¹ is corresponding to C-N⁺ = C radical cation stretching modes.[10] which is observed for sample - a, b, and c. The stretching mode 1146 cm⁻¹ in HCl doped samples (d and e) has blue shifts around 60 cm⁻¹. Seeger et al.[11] stated that such blue shifts are due to the band vibrations in phenyl rings of PANI, which are strongly perturbed by the charged polymers (H⁺ Cl⁻ dopant ions). The perturbed mode, 1140-1146 cm⁻¹ for sample - c and e, is attributed to C-N stretching mode.[12] However, in the sample-b and c, this stretching mode of 1146 cm⁻¹ is absent which must be due to sulfate ions present in the chemical structure of the carbon chain of PANI. 1301 cm⁻¹ mode is observed for both undoped and doped state of PANI, which is due to C-N delocalized polarons.[13] This concludes that C-N delocalized polaron of PANI are not disturbed by the presence of protonic acids. FTIR spectra show 1486 cm⁻¹ mode for the sample-a, d, and e which is assigned for C=C of benzenoid rings,[14] but the sample-b and c having redshifts of 66 cm⁻¹ (1420 cm⁻¹) and 54 cm⁻¹ (1432 cm⁻¹) respectively w.r.t. the C=C benzenoid rings as shown in Fig. 1.

Redshifts indicate a strong interaction between SO²⁻ ions and the carbon chain of PANI. The 1562 cm⁻¹ band is assigned for the C=C bond in quinoid rings of PANI.[14] This band was observed in both the undoped and doped state of PANI. Since sample -b and -c are doped by H2SO4, SO²⁻ ions may have more influences on the quinoid rings of PANI. Due to the influence of this SO⁴²⁻, sample-b, and -c might have the lowest transmittance inverse peak for this mode as compared to its undoped and HCl doped PANI. 1562, 1486, 1302, 1146, and 792 cm⁻¹ are the characteristic transmittance inverse peaks for doped PANI.[15][16]

4.2 UV-visible spectra
The UV-vis spectra of PANI and its doped form are shown in Fig. 2(a) and 2(b). The broader peaks in UV vis spectra were observed at 378 and 530 nm for sample-b and 500 nm for sample-c as shown in Fig. 2(a). The broadening of these peaks revealed the transformation of PANI from its coiled to the extended coil form.[17]

The peak observed at 378 nm for sample- b is corresponding to π-π* transition in the benzenoid structure of PANI.[18][19] Another peak for PANI at 530 nm has been assigned for the “exciton” transition[20][21] from the highest.
occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). As reported earlier,[4] H$_2$SO$_4$ doped PANI has greater electron localization effects (induced by the -SO$_3$H groups) as compared to their parent PANI. The exciton transition peaks from 630 to 560 nm were reported by Stejska.[23]

In the present case, 500 and 530 nm absorption peaks were observed particularly for 0.5 M (sample-c) and 0.25 M (sample-d) H$_2$SO$_4$ doping concentrations, respectively. These excitons show the blue-shifts of 60 and 30 nm respectively w.r.t. the reported 560 nm. Thus, these peaks must be associated with the excitons that occur within H$_2$SO$_4$ doped PANI. Hence, we can say that these blue-shifted peaks are sensitive to the chemical structure of H$_2$SO$_4$ doped PANI. As reported, an absorption peak of 330 nm is the signature of the π*–π transition of benzenoid rings within the PANI structure.[23,26]

For sample-b and -d, we have observed such absorption peaks at 375 and 378 nm having redshifts of 45 and 48 nm w.r.t. the reported 330 nm. These redshifts confirmed the doping of PANI by protonic acids as shown in Fig. 2(b). As reported, the absorption peaks of 430 nm are attributed to the polaronic peak, indicating protonation of the backbone polymer chain of PANI. [20] Wu et al.[27] have studied the PANI nanofiber, they observed an absorption peak at 440 nm which is ascribed to the polaron-π* transition. Further, this peak indicates that PANI is in the doped state.[28]

In the present study, we have an absorption peak at 397 nm for sample-e (HCl doped PANI), which has blue shifts of 43 nm w.r.t. the polaronic peak. This blue shift of 43 nm should be due to the microfiber behavior of PANI as we have observed in the present study. The absorption tail as shown in both parts of Fig. 2 is the extended “free- carrier tail” (NIR region: 800-1000 nm) of PANI which are the characteristics of charge carrier delocalization in the conducting polymers.[29] Thus, due to –SO$_3$H- group, the charges are more localized in sample-b and -c as compared to their pristine or undoped form (sample-a).

4.3 SEM analysis

The mixed morphology of microfiber and granular coral type structures were observed for the undoped PANI (sample-a) as shown in Fig. 3(a). Hence, the nucleation of sample-a is not only homogeneous but also heterogeneous. Upon H$_2$SO$_4$-doping (sample-b and -c), the microfiber structure of PANI almost disappears. Sample-b and -c revealed large chunks of doped PANI as shown in Fig. 3(b) and 3(c). This granular morphology of H$_2$SO$_4$ doped PANI indicates a strong interaction between the H$_2$SO$_4$ and PANI during the polymerization. The interconnected network-like structures of HCl doped PANI microfibers are 1.6 ± 0.5 µm long. Jimenez et al.[30] suggested that the origin of microfiber structures of HCl doped PANI is due to spontaneous self-nucleation during oxidative polymerization. Hence microfiber structure of sample-a, -d, and -e must have a homogenous polymerization. Since during the heterogeneous polymerization, the polymerized monomers of PANI grow on the previously formed PANI particles, these hetero nuclei particles act as nano-scale sticky contact linked to the particles together, leading to the agglomerated morphology of sample-b and -c.[31,32] Heterogeneous nucleation leads to the granular particulates morphology, which is observed for the sample-b and c. Hence H$_2$SO$_4$ couldn’t help the monomers of PANI to form a microfiber structure as it has happened for HCl doped PANI as shown in Fig. 3(b) and 3(c). Diameters of undoped PANI microfibers are in the range of 0.12 ± 0.02 µm but after doping with HCl, their diameters are expanded to 0.18 ± 0.02 µm for the sample d and e as shown in Fig. 3(a), (d) and (f). The reasons behind the modification of the diameters of microfibers of sample d and e are still unclear, but Zhao et al.[33] explained that this may be due to different sizes of the anion of acids and the dopant structure of polymers (hydrochloride emeraldine salt of PANI). Mattoso et al.[34] stated that the elongation process of PANI during the

![Fig. 2 UV-visible spectra: (a) Undoped and H$_2$SO$_4$ doped PANI (sample b and c). (b) Undoped and HCl doped PANI (sample d and e). Sample-b and d both have absorption peaks at around 375 nm. The actual photograph of the undoped/doped PANI is shown in the inset of both Figures. Undoped states have a yellow color and doped states of PANI have red and dark red color solutions.](image-url)
oxidative polymerization of aniline in an acidic medium involves reactive intermediate species (H\(^+\) and Cl\(^-\)) rearranged from the protonated aniline. The low concentration of protonated aniline is not beneficial to the rearrangement and elongation of reactive intermediate species because of low concentration of H\(^+\) ions present in its acidic medium.\(^{[13]}\)

![Fig. 3 SEM: (a) Undoped PANI; (b) and (c) H\(_2\)SO\(_4\) doped PANI (sample- b and c); (d) and (e) HCl doped PANI (sample-d and e). H\(_2\)SO\(_4\) doping has forbidden the fiber growth of PANI while HCl doping is favorable for the growth of its fiber structure.](image)

4.4 Polymerization of undoped and doped PANI
The present observation in the polymerization of PANI is fiber-like structures that were generated without adding any protonic acids. When the polymerization of PANI just turned into green, the collected sample contains almost well-dispersed microfibers. If the oxidant (APS) is gradually added into the aniline with gentle stirring, the yielded microfibers become thicker and coarser and the final reaction solution contains mostly irregularly shaped microfibers of PANI. As the reaction moves on further, re-nucleation produces agglomerated microfibers of PANI. However, the study revealed that the homogeneous nucleation of PANI is responsible for the fiber structure of PANI. Zhang et al.\(^{[34]}\) found that the reaction temperature and the precursor ratio (1:1) of aniline/acid had an important influence on the morphology of the resulting PANI. As the polymerization of PANI is an exothermic reaction, lower temperature (0 - 4 °C) is required for the formation of fiber morphology of PANI. However, in the present case, we have the microfibers of PANI at RT (25 °C). The formation of PANI was initiated by some nuclei (a small molecular aggregate), these nuclei can be formed by homogeneously in the parent phase of nucleation, or they can be heterogeneously grown on other species such as composite surface particles.\(^{[31,32]}\) We propose that the kind of polymerization is controlled by the kind of dopant acids as well as the temperature because the polymerization in the present work changes due to dopant acids in PANI at RT. A similar result was observed by Stejskal et al.\(^{[35]}\) but they had explained the effect of acidity level of strong and weak acids on the PANI, in which organized nanotubular structures were obtained in a lower acidity at the lower temperature (0 - 4 °C). In the present work, we have observed microfiber morphology of undoped and HCl doped PANI at the RT (25 °C). Hence, reaction temperature plays an important role in getting the microfiber structure of PANI. The reported study revealed the fact that, as the aniline/acid ratio decreases (<1:1), nanostructured PANI was detected.\(^{[36,37]}\) The morphology of H\(_2\)SO\(_4\) doped PANI has a granular structure that is often found in the literature.\(^{[38,39]}\) But none of the paper explains the exact reason for the granular morphology of H\(_2\)SO\(_4\) doped PANI. However, the literature survey explained that the initial stage of polymerization of aniline oligomers is hydrophobic. These oligomers predetermine the directional growth of PANI. As the pH of the solution decreases, the hydrophobicity of the in-situ synthesized PANI decreases and the corresponding PANI oligomer becomes soluble in the reaction medium, which results in oligomer aggregation of PANI structure. For the stronger acid, the smaller the value of dissociation constant (pK\(_a\)), the higher is the dissociation of H\(^+\) ions in the solution.\(^{[40]}\) The pK\(_a\) values of H\(_2\)SO\(_4\) and HCl are - 3 and - 6.3,\(^{[41]}\) respectively. Thus, HCl is a stronger acid than H\(_2\)SO\(_4\). Hence HCl doped PANI retains its acidity in the in-situ polymerization of PANI, consequently its hydrophobicity is sustained for a long time which keeps the acidic environment for the polymerization of PANI even at RT. But as the reaction is exothermic and the temperature is...
not low, the diameters of fiber structure of the PANI are expanded and instead of nanofibers, microfiber morphology is observed for the undoped and HCl doped.

4.5 XRD Analysis
Dried undoped and doped PANI powder samples were examined by the XRD measurements as shown in Fig. 4. The sample -b and -c show diffraction peaks at 2θ = 23.5, 25.1, and 30.3° respectively. The peak of 25.1° is the only feature of XRD patterns of undoped PANI (sample -a). The X-ray reflection is at 25.1° observed for all the samples of PANI which is ascribed for the regular spacing between phenyl rings of adjacent chains in a parallel orientation. The extra peaks at 23.3, 26.3, and 30.3° for the sample −b and −c indicate that the doped PANI with H2SO4 is partially crystalline. In general, these extra peaks of sample −b and −c are influenced by the formation of a granular particle size of PANI as shown in Fig. 3(b) and 3(c). The X-ray peaks of PANI are the result of irregular arrangement of molecular chains whereas the regularity of the molecular chains does not show any X-ray peaks because, in this case, they are amorphous in nature. As the sample-a, d and e are microfibers, they have a regular arrangement of molecular chains of PANI polymers. Hence, there are not any noticeable X-ray peaks that are observed for sample −a,−d, and −e. However, the sample −b and −c have granular morphology of PANI and show the crystallinity behavior as to the amorphous nature of sample-a, d, and e. Hence there are X-ray peaks due to the randomly arranged aggregate polymer particles of PANI as shown in Fig. 4.

Fig. 4: XRD patterns of PANI prepared by the CBD method (a) undoped PANI, (b) 0.5 M H2SO4, (c) 0.25 M H2SO4, (d) 0.5 M HCl and (e) 0.25 M HCl doped PANI. The extra peaks are obtained for sample−b and −c which represents the crystallinity of aggregated particles of PANI produced due to the influence of H2SO4 doping.

5. Conclusion
The optical and morphological study of undoped PANI was modified by the doping of protonic acids (HCl and H2SO4). XRD analysis confirmed that the doped PANI with H2SO4 is partially crystalline. Microfiber morphology was observed for HCl doped PANI, it is proved that HCl concentrations were favorable for the microfiber nucleation of PANI whereas H2SO4 concentration forbid the microfiber nucleation of PANI. H2SO4 doped PANI produced large chunks of PANI and aggregation of PANI. Thus, it is easy to distinguish the HCl and H2SO4 doped PANI. Room temperature and aniline/acid ratio (1:1) were responsible for the microfiber nature of HCl doped PANI. The redshift was observed for protonic acid doped PANI. The doping effect has a strong impact on the phenyl rings of PANI as compared to its undoped form. The optical spectrum shows that the absorption peak of HCl doped PANI was observed at 397 nm, blue shifts of 43 nm was observed w.r.t. the polaronic peak at 440 nm. This blue shift of 43 nm is a result of the microfiber behavior of HCl doped PANI whereas the redshifts in H2SO4 in PANI represent that there are excitons trapped in the between π-π* transitions of benzenoid rings. These excitons moved in a conduction band. Further, we found that the prepared PANI can be used for the fabrication of polymer solar cells.

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