3.1 Introduction

The electrical and optical properties of polyaniline (PANI) can be tuned to the appropriate region by doping with protonic acids [1-4]. The doped PANI samples have decent electrical conductivity and excellent stability under ambient conditions. Recently various nanoscale applications have motivated the research on one dimensional (1D) nano scale materials such as nano rods, nano fibers and nano tubes [5-7]. PANI nano materials, in particular have caught much attention due to their enhanced electrical conductivity, environmental stability and colour change corresponding to diverse redox states [8-10]. In this chapter, a comparative study of the structural, morphological, electrical
and thermal properties of PANI and PANI nano rod samples are outlined. The variation of photoluminescence emission intensity and D.C electrical conductivity of micro sized PANI, with the nature of the dopants used, are also studied.

### 3.2 Synthesis

Freshly distilled aniline (A.R grade) is dissolved in 1.5M dopant acid solution. Ammonium persulphate(APS) dissolved in water is added drop wise to the mixture with continuous stirring for 4-5 hours (Aniline to APS weight ratio is fixed at 3.37). The precipitate obtained is filtered, washed and dried.

### 3.3 FTIR studies

The FTIR spectra of PANI doped with hydrochloric acid(HCl), camphor sulphonic acid(CSA) and orthophosphoric acid (H₃PO₄) are given in figures 3.1-3.3 below.

![FTIR spectrum of HCl doped PANI](image)

**Fig. 3.1** FTIR spectrum of HCl doped PANI
Fig. 3.2 FTIR spectrum of CSA doped PANI

Fig. 3.3. FTIR spectrum of H$_3$PO$_4$ doped PANI

The major peaks are at around 3500 cm$^{-1}$(NH stretching vibration), 2900 cm$^{-1}$ (CH stretch), 1570 cm$^{-1}$(C=N stretch of the quinonoid unit of PANI), 1470 cm$^{-1}$ (C=C stretch of the benzenoid unit of PANI) and 1100 cm$^{-1}$(quinonoid unit vibration of doped PANI) as reported earlier. [1, 5, 11]
3.4 Raman Studies

The Raman spectra of PANI doped with HCl, CSA and H₃PO₄ are given in figure 3.4.

The major peaks of PANI (HCl) are at 1192 cm⁻¹ (C-H bending of the quinonoid ring), 1481 cm⁻¹ (C-C in plane deformation of quinonoid ring), 1616 cm⁻¹ (C-C stretching of benzene ring) and 1338 cm⁻¹ (C-N band of polarons) [12-16]. CSA and H₃PO₄ doped PANI samples exhibit a slight shift in vibrational wave numbers and their corresponding intensities. For example, the position corresponding to C-N band of polarons is shifted to 1390 cm⁻¹ and 1409 cm⁻¹ respectively in CSA and H₃PO₄ doped PANI. Both the FTIR and Raman spectra exhibit all the major peaks corresponding to acid doped PANI.

![Figure 3.4 Raman spectra of PANI doped with various acids](image-url)

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3.5 X.R.D Analysis

The X.R.D spectra of PANI doped with HCl, CSA and \( \text{H}_3\text{PO}_4 \) are given in figures 3.5-3.7. All the samples are taken in powder form.

**Fig. 3.5** X.R.D spectrum of HCl doped PANI

**Fig. 3.6** X.R.D spectrum of CSA doped PANI
3.5 X.R.D Analysis

The X.R.D spectra of PANI doped with HCl, CSA and H₃PO₄ are given in figures 3.5-3.7. All the samples are taken in powder form.

Fig.3.5 X.R.D spectrum of HCl doped PANI

Fig. 3.6 X.R.D spectrum of CSA doped PANI
Orthophosphoric acid doped polyaniline shows a crystalline, sharp peak at $25^\circ$. The peak shown by CSA doped PANI at the same position is less sharp and reduced in intensity, while HCl doped PANI shows only an amorphous peak at the same position. Additionally, orthophosphoric acid doped PANI shows crystalline peaks at $27^\circ$ and $21^\circ$ and amorphous peaks at $15^\circ$ and $30^\circ$. Peak exhibited by CSA doped PANI at $27^\circ$ is less crystalline. All other peaks of this sample are amorphous. The peak shown by HCl doped PANI at $15^\circ$ is also amorphous [16, 17]. Evidently orthophosphoric acid doped PANI shows more crystallinity compared to PANI doped with the other two protonic acids. Accomodating large sized dopant ions such as $\text{PO}_4^-$ demands greater rearrangement of bonds along the polymer backbone, leading to better crystallanility [1, 18]. This is strongly supported by the fact that the increase in crystallanility of the three PANI samples is in the ascending order of the size of the dopant ion attached. The graphite-
like diffraction peak at around $25^0$[1, 16, 19] is common to all the samples and is characteristic of the extent of $\pi$ conjugation in PANI. Since orthophosphoric acid doped PANI shows the sharpest and the most crystalline peak at $25^0$, it has the longest order of $\pi$ conjugation. In short, the benzenoid and quinonoid units are more orderly arranged in orthophosphoric acid doped PANI compared to PANI doped with the other two acids.

3.6 Photoluminescence studies

The samples in powder form, are excited at 365nm. This is because the $\pi-\pi^*$ transition of the benzenoid unit, the unit responsible for photoluminescence in PANI, falls around 330 nm. [20-21]. The samples are excited using a high intense, 450W xenon lamp. The corresponding spectra are shown in figure 3.8.

![Photoluminescence emission spectra of PANI doped with three different dopants excited using a high intense, 450W xenon lamp (excitation wavelength is 365 nm).](image)
For the three samples, the photoluminescence emission is observed at around 450nm. This corresponds to the HOMO/LUMO transition in the $\Pi-\Pi^*$ energy gap [20].

Orthophosphoric acid doped PANI shows the highest luminescence intensity followed by PANI doped with HCl and CSA respectively. The better crystallinity in orthophosphoric acid doped PANI, as evident from its X.R.D spectrum implies that the benzenoid and quinonoid units in it are more orderly arranged, without any unfavourable clustering of quinonoid units. Generally the quinonoid unit quenches the photoluminescence emission due to intrachain energy dissipation [20-22]. The higher extent of $\Pi$ conjugation coupled with the more orderly arrangement of the benzenoid and quinonoid units observed in orthophosphoric acid doped PANI favours the formation of excitons. The singlet exciton thus formed decays to the ground state with the emission of light [1]. There is another important reason for the observed high P.L emission in orthophosphoric acid doped PANI. As the conjugation length increases, probability for singlet exciton formation increases[23]. This is because, the delocalization length of singlet exciton in conjugated polymers is comparable to its conjugation length[23]. But triplet exciton is confined. In conjugated polymers, singlet excitons are mostly responsible for P.L emission, because conjugated polymers do not have the mechanism to produce the spin flip necessary for an optical transition [24-25]. Hence one should expect higher photoluminescence emission from orthophosphoric acid doped PANI which has a higher extent of $\Pi$ conjugation. HCl doped PANI
shows slightly better photoluminescence emission compared to the more crystalline CSA doped PANI. The possible reason may be the presence of lighter dopant ions in HCl doped PANI(Cl), with greater mobility compared to the heavier dopant ions(SO₃⁻) in CSA doped PANI. This favours increased exciton formation and its decay to the ground state results in light emission with enhanced intensity[1].

3.7 D.C electrical conductivity studies

The variation of D.C electrical conductivity with temperature of PANI doped with three different dopants is given in fig 3.9. The temperature range chosen is from 303K to 413K. All the samples are taken in the form of pressed pellets, applying uniform pressure. 4-probe technique has been used to measure the D.C electrical conductivity.

![Fig. 3.9 Temperature dependent D.C electrical conductivity plots of PANI doped with various acids](image-url)
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HCl doped PANI shows a flat temperature dependence of D.C electrical conductivity up to about 373K (room temperature conductivity is 2.17S/cm). The reasonably high electrical conductivity of HCl doped PANI is attributed to the high molarity of dopant acid solution used and low mass of Cl ions. Actually only less than 1% of the available charge carriers contribute to the conductivity of doped PANI. If all the charge carriers contribute, the room temperature conductivity of doped PANI would be comparable to that of copper [20]. In fact PANI is only partially crystalline, with conducting metallic islands separated by large amorphous regions as evident from the X.R.D spectrum (Fig 3.5-3.7). The characteristic metallic conductivity in doped PANI is limited by strong disorder [20, 26].

HCl doped PANI shows the highest room temperature D.C electrical conductivity (2.17S/cm) as compared to CSA (0.30953S/cm) and orthophosphoric acid doped PANI (0.55S/cm). The comparatively higher D.C electrical conductivity of HCl doped PANI as compared to PANI doped with the other two acids may be due to the presence of lighter dopant ions(Cl ions) in HCl doped PANI as compared to the heavier counterparts in CSA(SO3) and orthophosphoric acid(PO4) doped PANI samples. The light weight Cl ions have greater mobility than the heavier SO3 and PO4 ions, resulting in enhanced conductivity. Although PO4 ions are heavier than SO3 ions, orthophosphoric acid doped PANI exhibits slightly greater D.C electrical conductivity than CSA doped PANI. The possible reason may be the better crystallinity of orthophosphoric acid doped PANI, due to the large sized PO4 ions,
demanding greater rearrangement of bonds as explained in the previous section. The more orderly arrangement of the benzenoid and quinonoid units facilitates easier charge transport, compensating for the greater weight of $\text{PO}_4^-\text{ ions. This enhances the D.C electrical conductivity.}$

The samples show negligible variation of D.C electrical conductivity with temperature, characteristic of polymer samples near the metallic region of metal-insulator transition [27-32].

3.8 **Studies on PANI nano rods**

Nanoscale materials and devices have grabbed the attention of the scientific community, thanks to their diverse applications [5-7]. PANI nano materials have the added advantage of higher conductivity and better environmental stability. A variety of techniques such as template method, self assembly method, electrochemical polymerization and electro spinning have been employed for the preparation of pani nano rods [8-10]. PANI nano rods could be produced in large scale without undesired byproducts using dispersion polymerization method [33].

3.8.1 **Synthesis of PANI nano rods**

PANI nano rods with different monomer to oxidant (APS) feed ratios are prepared using dispersion polymerization technique [5]. The synthesis procedure is briefly outlined below.

20 ml of 35 weight% HCl and 2 ml aniline (freshly distilled, A.R grade) are dispersed in 200 ml of distilled water. APS is added to the solution, at a definite monomer to oxidant feed ratio. The resulting mixture
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is stirred for 3h. The synthesis temperature is maintained at around \(-10^\circ\) C using freezing mixture. The precipitate obtained is filtered, washed and dried. Samples are prepared with different aniline to APS feed ratios. In this method, overgrowth is prevented by stopping the polymerization as soon as the nano rods form. When the reaction starts, the initiator molecules are consumed rapidly during polymerization and depleted after the nano rod formation. Therefore the overgrowth of polyaniline is suppressed due to lack of initiator molecules.

3.8.2 FTIR Analysis

The FTIR spectrum of PANI nano rods is given in figure 3.10.

![FTIR spectrum of HCl doped PANI nano rods](image)

Fig. 3.10 FTIR spectrum of HCl doped PANI nano rods

The spectra show all the characteristic peaks of doped polyaniline as already reported. [1,5] It is observed that peaks in the spectrum of PANI nano rods are sharper compared to those in micro sized PANI.
3.8.3 X.R.D Analysis

The X.R.D spectra of PANI (micro sized) and PANI nano rod samples (all in powder form) with different aniline to APS feed ratios are given in figure 3.11.

![X.R.D spectra of PANI (micro) and PANI nano rod samples](image)

**Fig. 3.11** X.R.D spectra of PANI (micro) and PANI nano rod samples

HCl doped PANI shows only amorphous peaks at 25° and 15°, while PANI nano rods show a sharp crystalline peak of much higher intensity at 25° and amorphous peaks at 9°, 15° and 21°. The peak at 25° is common to both the samples and is characteristic of the degree of II conjugation in PANI [1]. Since PANI nano rods exhibit a sharper and more intense peak at 25°, it has better II conjugation. It is also observed that, for PANI nano rod samples, the crystallinity decreases with increased addition of APS. As the APS content increases, the rate of polymerization as well as the chain length increases. If the
polymerization rate exceeds a certain limit, it may adversely affect the orderly arrangement of the benzenoid and quinonoid units.

### 3.8.4 TEM Analysis

**Fig. 3.12a** TEM image of a PANI nano rod  
**Fig. 3.12b** TEM image of another PANI nano rod

TEM images of PANI nano rods (in powder form) are given in figure 3.12a and figure 3.12b.

The average diameter of PANI nano rods is found out to be 10-15nm.

### 3.8.5 D.C Electrical Conductivity studies

The temperature dependent D.C electrical conductivity plots of PANI nano rod samples synthesized with various aniline to APS feed ratios are given in figure 3.13. The samples are taken in the form of pressed pellets, applying uniform pressure. The measurements are taken using 4-probe technique.
Fig. 3.13. Temperature dependent D.C electrical conductivity plots of HCl doped PANI nano rods synthesized with various aniline to APS feed ratios and HCl doped PANI (micro).

The PANI nano rods exhibit better D.C electrical conductivity than PANI (micro)(2.17S/cm). The better crystallinity of PANI nano rods implies greater long range order favouring effective charge transfer along the chains. This results in higher electrical conductivity. PANI nano rods synthesized with aniline to APS feed ratio 1:1.2 has better room temperature D.C electrical conductivity (16S/cm) than PANI nano rods with aniline to APS feed ratio 1:2.4(7S/cm). This is because of the improved crystallinity of the sample with lower APS loading as explained in section 3.8.3. The conductivity of PANI nano rods is observed to decrease almost exponentially with temperature, unlike the nearly flat temperature dependent behaviour of PANI(micro). The possible reason may be the
greater scattering of the charge carriers at the nano rod walls and at the intersections between different nano rods. The smaller aspect ratio (Length (of the order of nanometers) is not much large compared to diameter) of the PANI nanorods as compared to carbon nano tubes enhances the scattering probability.

3.8.6 T.G.A Analysis

The thermo grams of PANI (micro) and PANI nano rods (aniline to APS feed ratio is 1:1.2) and PANI nano rods (aniline to APS feed ratio is 1:2.4) are given in figure 3.14.

Fig. 3.14 Thermo grams of PANI (micro), PANI nano rods (1:1.2) and PANI nano rods (1:2.4)

Weight loss up to 100$^\circ$ C is mainly due to the evaporation of adsorbed water molecules. Loss of dopants become prominent from a
temperature of 250° C. Degradation of the polymer backbone starts at around 400° C [34].

Up to 300° C, PANI(micro) exhibits 50% weight loss, while the corresponding weight loss for PANI nano rods(1:2.4) is 31%, and that for PANI nano rods(1:1.2) is 27%. At 900° C, the weight loss for PANI(micro) is 86% and PANI nano rods(1:2.4) and PANI nano rods(1:1.2) are 57% and 52% respectively. Obviously PANI nano rod samples are more thermally stable than PANI (micro), possibly due to their better crystallanity. For the PANI nano rod sample with higher APS feed ratio, thermal stability decreases. This is because, as more amount of APS is added, the chain length increases. This slows down the heat transport along the chains, causing faster degradation. Another possible reason is the better crystallanity of the PANI nano rod sample with lower APS feed ratio.

3.9 Conclusions

Polyaniline (micro sized) samples doped with various acids are synthesized and their structural, electrical and photoluminescence properties are investigated. A comparative study of the photo luminescent properties of polyaniline doped with different acids are carried out. Orthophosphoric acid doped PANI exhibits the highest P.L emission, making it suitable for the fabrication of optoelectronic devices. Temperature dependent D.C electrical conductivity studies reveal that HCl doped PANI has the highest room temperature D.C electrical conductivity which stays almost constant with temperature (above room temperature).
The structural, morphological, electrical and thermal properties of polyaniline nano rod samples are investigated. The polyaniline nano rod samples exhibit better crystallinity as compared to micro sized PANI. TEM measurements reveal that they are rod like in shape. The entire polyaniline nano rod samples show better D.C electrical conductivity and thermal stability as compared to micro sized PANI. The crystallinity of the PANI nano rod samples is found to decrease with increase in the APS feed ratio. Obviously the polyaniline nano rod sample with the lowest APS feed ratio exhibits the highest room temperature D.C electrical conductivity and thermal stability.

References

Studies on PANI and PANI nano rods


