Research Paper Physics

# Synthesis of Iron-Doped Polyaniline (PANI) & its Characterization

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**ABSTRACT**

This paper describes the synthesis and characterization of polyaniline (PANI) doped with iron. The composites were characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). The variation in dc conductivity of these composites was also studied as a function of temperature and concentration and the results were compared with pure PANI. The XRD, FTIR and SEM. PANI show lower dc electrical conductivity its conductivity increases with the increase of temperature. Metals and semiconducting nanostructure materials are used as stabilizers or capping agents of these conducting polymers. These nanocomposites exhibit many new characters, such as electrical, optical, catalytic and mechanical properties that the single material does not have.

**KEYWORDS** Polyaniline (PANI), XRD, Chemical synthesis, Conductive polymer

## 1. Introduction

Electronically conducting polymers such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy) have become the subject of increased research interest due to a great variety of applications in many fields suchelectrochromism,electroluminescence, sensors and energy storage systems, OLEDs etc. Among these conducting polymers special interest has been focused on polyaniline (PANI) due to its excellent thermal and environmental stability combined with relatively high level of electrical conductivity. Extensive studies on theoretical modeling have demonstrated that Polyaniline differs from other conducting polymers because of the important role of phenyl rings along with the presence of nitrogen heteroatom within the conjugation path. The conducting properties of polyaniline can be made to vary over a very wide range starting from insulating to semiconductor and towards metallic by varying concentration of dopant. In the present contribution polyaniline is subjected to structural modification by doping it with one of the d-block metal salt solution containing Sn2+ ions to study its dynamic electrical, mechanical and optical properties. Polyaniline and modified polyaniline was synthesized by chemical oxidative polymerization method which is further characterized by FTIR and H1 NMR spectral analysis.

Sputter deposition is one of the most important techniques for preparing the thin film because the purity of the film can be easily controlled and the adhesion of the film to the substrate can be enhanced. The magnetron sputtering technique can trap electrons in the region near the target and can effectively ionize working gas, leading to fast deposition of the film at room temperature. It was reported that sputter deposition could prepare dense and pure Fe thin films and islands .On the basis of the above-mentioned advantage of sputter deposition, it is desirable to prepare PANI-Fe composites by sputter-depositing Fe islands or particles on the PANI.

### 1.1 Synthesis & Characterization of Iron-doped Polyaniline (PANI)

The required synthesis is given in section 1.1.1 and characterization in 1.1.2.

#### 1.0.1 Synthesis of Iron-doped PANI

The iron-doped samples of PANI were prepared as described. For iron doping, ferric chloride solution was added to aniline solution, before the process of synthesis and protonation.

#### 1.0.2 Preperation of Iron-doped PANI thin films

The discs of iron doped PANI were first prepared and then heated in a vacuum chamber. The resulting vapours were allowed to condense over a cool glass substrate, when a thin film appeared over it after some time. The thickness of the film was monitored to be around 1700 A°.

#### 1.0.3 Characterization of Iron-doped PANI

The results of different characterizations are given as in the following:

##### 1.0.3.1 UV-Visible spectrum of Iron-doped PANI powder

The UV-Visible spectrum of chemically synthesized iron-doped PANI powder, when dissolved in NMP solvent was recorded with the help of a U-3900 Hitachi spectrophotometer. Fig. (a) shows the spectrum thus recorded for the iron-doped PANI samples as above.

Two absorption peaks of good oscillator strength are clearly seen in the optical absorption spectrum (Fig. a) at 334 nm and 631 nm. These peaks are characteristics of emeraldine base form of PANI. It is obvious that present iron-doped sample had got deprotonated due to the action of NMP solvent and hence the sample appeared like an emeraldine base.

The observed 334 nm band can now be assigned to the $\pi$-$\pi^*$ transitions in the benzenoid structure [10] and the absorption at 631 nm is further due to exciton formation in the quinoid rings [11].

Finally, the highest energy shoulder peak observed at 295 nm may be attributed to $\pi$-$\pi^*$ charge transfer in aniline monomer [12], left over even after the polymerization process.

As the present optical absorption peaks were for iron-doped PANI sample dissolved in NPM, protonation and apparently disappeared and no corresponding peaks were observable.

##### 1.0.3.1.1 UV-Visible spectrum of Iron-doped PANI thin films

Fig. (b) shows the UV-Visible absorption (UV-Vis-NIR V670JASCO) spectrum of iron-doped PANI thin films, recorded in the wavelength range from 300 nm to 800 nm. The spectrum is obviously quite different from the spectrum of the fig.(a) for iron-doped samples dissolved in NMP.

In the thin film spectrum of fig.(b), two well resolved peaks are seen at 330 nm and 445 nm. The first peak at 330 nm corresponds to the similar peak at 305 nm for cobalt doped PANI. However the peak at 330 nm for iron doped PANI is much broader than the corresponding peak for cobalt doped sample. The second peak at 445 nm however did not present any broadening as above. Further, no peaks of higher wavelengths up to 800 nm were observed.

The thin film samples over the glass substrate were obviously protonated and had a greenish yellow tinge.

The interpretation of the observed peaks in the thin film spectra as above has been done as per the theoretical model of Stafstrom et al [13]., as done for the cobalt-doped sample. The level scheme of Fig. (c) shows the level "c" and "b" each to be fully occupied in the polaron lattice of iron doped PANI. The level "a" is however only half filled due to usual 50% protonation done to get conducting polymer of PANI. The level "a" is thus filled upto the half height at Fermi level Ef. Finally on the upper energy side there is a flat upper polaron band (x*) which is nearly degenerate with the conduction band (x). In the model of Stafstrom et al [13], the transition from band "c" to band "a" should have an absorption energy of 2.6 eV implying a wavelength of level at band "a" to "x" and "x' " involving energy differences of nearly 4.1 eV each, should be reflected by a peak at 301 nm. However, presently we obtain a quite broad band and it seems that the bands "x" and "x' " are quite well separated in iron-doped PANI to yield the features as above.

The transition from band 'b' to 'a' is not observed, as its lies in I.R. beyond the range of present observations. Further, any intra band transitions within a band are not seen, as these must lie in infra rad. The observed band positions at 330 nm thus seem to support the polaron lattice picture.

1.0.3.2 **Fourier Transform Infra Red**

Fig. (c) shows the FITR spectrum of chemically synthesized PANI with iron doping. The curves in the figure show the vibration bands at 3435. 1637, 1565, 1290, 1070, 610 and 495 $cm^{-1}$. The 3435 cm band is assigned to the stretching vibration of secondary amine.THE 1637 $cm^{-1}$ band is due to C=C bond of quinoid structure, whereas 1565 $cm^{-1}$ band arises due to vibrations of C=C bond associated with benzenoid structure. The 1290 $cm^{-1}$ vibration may be attributed to stretching associated with noral C-N linkage. The vibration at 1128 $cm^{-1}$ is also due to C=N vibration but in the structure. B-NH+ = Q and is indicative of protonation [14] of iron-doped PANI. Again, the vibration at 1070 $cm^{-1}$ and 610 $cm^{-1}$ may be attributed to C-H aromatic in – plane and out of plane vibrations of para-linked phenyl rings in PANI. Finally, the band at 495 $cm^{-1}$ is attributed to iron linkage in PANI.

The results as above thus suggest that the nature and positions of vibration bands are maintained even after iron doping of PANI.

1.0.3.3 **X-Ray Diffraction**

The X-ray diffractograms for iron-doped PANI has been found to exhibit peaks at 2θ values of 9.5°, 14.5°, 20.5°, 25.5°, 27.0° and 29.0°. The strongest peak is obviously for 2θ as 25.5°. The main crystalline order for protonated iron-doped PANI therefore corresponds to this peak. The corresponding inter-chain distance as calculated by the use of Bragg's equation is as before is 3.19 A°. The 2θ values of 9.5°, 14.5° and 20.5° must now corresponds to crystalline order in other ordered arrangements of oligomers.

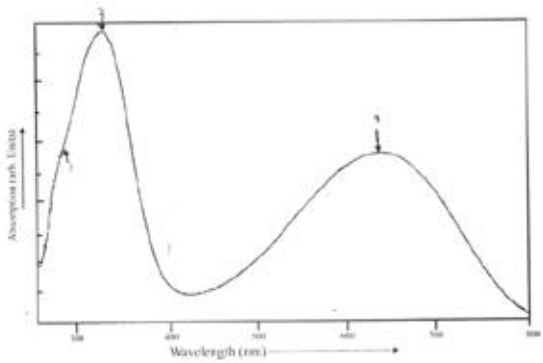


**Fig. (a) UV-Visible absorption spectra of PANI with iron doping**

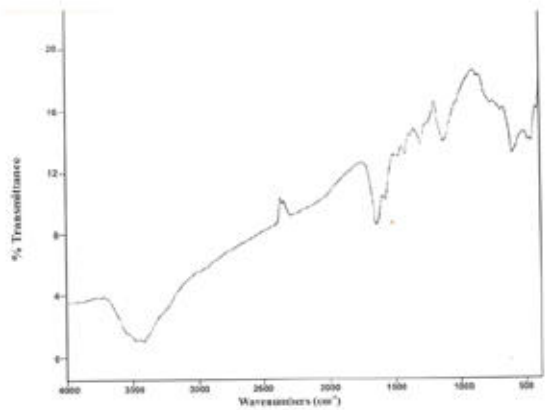


**Fig. (b) UV Visible spectra of PANI film (vacuum deposited) with iron doping**

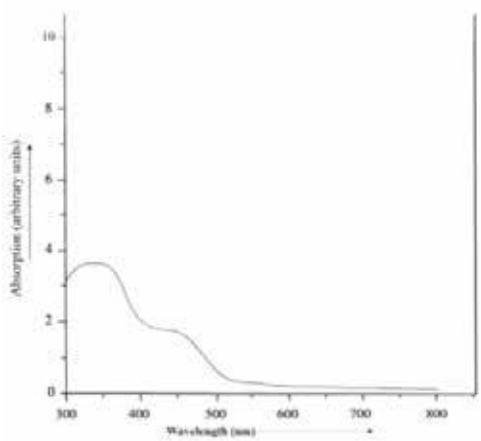


**Fig (c) FTIR spectra of PANI with iron doping**

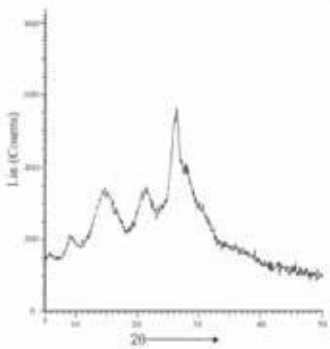


**Fig (d) X-ray diffractogram for PANI with iron doping**

### 1.1 Conclusions

The conclusions derived from various studies on characterization of PANI iron doped may be summarized as below.

#### 1.1.1 UV- Visible absorption

The UV-Visible absorption (UV-Vis-NIR V670JASCO) spectra obtained, after dissolving the iron in a solvent, indicate that these get modified in its character due to hydrogen-bond formation with the solvent molecules. The protonation had thus disappeared and the observed spectra represented the emeraldine base form of PANI in its iron metal-doped.The optical absorption spectra obtained however, for the film varieties of PANI support the theoretical predictions of Stafstrom et al [13].

#### 1.1.2 Fourier Transform Infra Red

The FTIR characterization studies indicate almost similar results for all samples of PANI and its derivatives. The aniline monomers which were left un-polymerized , were also seen to show up their presence. In metal doped PANI samples corresponding peaks of metal linkages are prominently seen.

#### 1.1.3 X-Ray diffraction

The studies on X-ray diffraction characterization indicate almost identical nature of all samples, being whether PANI or its derivative. The metal doping thus does not seen to change the major crystalline nature in the PANI samples and it seems that metal derivatives get trapped between PANI pockets.

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