Research Paper Physics

Synthesis of Cobalt – Doped Polyaniline (PANI) and Its Characterization

Ankit Gupta Inspire Fellow, Department Of Physics

Dr. Mahendra Kumar Assistant Professor , Department Of Physics

ABSTRACT

This paper deals with synthesis & characterization of Cobalt – doped Polyaniline. This Cobalt – doped Polyaniline were characterized by UV–Visible (UV-Vis-NIR V670JASCO), FTIR spectroscopy and XRD analysis techniques and the various results obtained have been explained. Due to the advantages of material abundance and synthetic simplicity, polyaniline can be used as a high capacity cathode material. However, its practical application in battery has been hindered by poor electrochemical utilization and cycling instability.

KEYWORDS Polyaniline (PANI), doping, FTIR, Spectrophotograph, XRD

1. Introduction

Polyaniline (PANI) has been in the forefront of the global search for commercially viable conducting polymers because of its unique proton dopability, excellent redox recyclability, chemical stability, variable electrical conductivity (which can be varied by changing the pH at which it is prepared), low cost and ease of synthesis. Polyaniline have been studied as materials for industrial products, such as rechargeable batteries, conductive coatings, light emitting diodes, gas sensors and antistatic materials. However, the major problem in applying these polymers is their poor processibility by solvent or multitechniques. Most of them are insoluble in common solvents and undergo degradation before reaching the melting point. Polymers have traditionally been considerd good electrical insulators and a variety of their applications have been relied on their this insulating property. 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. Polyaniline (PANI) and its derivatives have been extensively studied in the last decade with improved processing and intrinsic electrical properties. They have received great attention owing to its ease of synthesis, good stability in the presence of oxygen and possessing electrochemical properties of unique conducting mechanism.

1.1 **Synthesis and Characterization of Cobalt – doped Polyaniline (PANI)** The Synthesis and characterization are described under separate headings, as in the following:

1.1.1 Synthesis of Cobalt doped PANI

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

1.1.2 Preparation of Cobalt – doped PANI thin films by vacuum evaporation technique

A glass substrate was used in this work for deposition of PANI films over it. The glass slides to be used were first cleaned by a solvent. This was followed by deionized water (DI) rinse, then a mild acid clean & further again a DI rinse. Finally the substrate was dried using a blower.

The discs of Cobalt – doped PANI was then prepared and heated inside a vacuum deposition unit. The substance got evaporated and resulting vapours condensed over the glass substrate, the schematic arrangement being shown in fig. (a). The thickness of the film deposited over the substrate was monitored and controlled by quartz film thickness monitor to be around 1600 A°.

1.1.3 Characterization of Cobalt – doped PANI

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

1.1.3.1 UV-Visible spectrum of Cobalt-doped PANI powder

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

Two absorptions peaks of good oscillator strength are clearly seen in the optical absorption spectrum (Fig. b) at 329 nm and 628 nm. These peaks are characteristics of emeraldine base form of PANI. It thus seems that cobalt-doped samples of PANI had got deprotonated before the recording of spectra. This deprotonation is in conformity with the studies of Pruneanu et al [8] on PANI dissolved in NMP.

The 329 nm band can now be assigned to the π-π^* transition in the benzenoid structure [10]. The absorption in the visible range at 628 nm is further described to excitation formation in the quinoid rings [11]. Finally, the highest energy shoulder peak at 287 nm may be attributed to π-π^* charge transfer in aniline monomer [12], left over after the polymer formation. The present optical studies were for the samples dissolved in NMP. Such a dissolution has led to deprotonation of PANI samples and thus no polaron assisted peaks [13] could be observed.

1.1.3.1.1 UV-Visible spectrum of cobalt-doped PANI thin films

Fig.(c) shows the UV-visible absorption spectrum of cobalt-doped PANI thin films, recorded in the wavelength range from 300 nm to 800 nm using Hitachi 331 spectrophotometer. This spectrum is seen to be quite different from that of fig. (b) for cobalt-doped PANI samples dissolved in NMP.

In the spectrum of fig. (c), well identified peaks are seen at 328 nm and 445 nm. No peak of appreciable strength was, however, seen for higher wavelengths up to 800 nm. The thin film sample over the glass substrate was obviously protonated and had an expected greenish yellow shade.

Stafstrom et al [13] have presented energy level calculations for highly conducting polyaniline. The typical energy levels (in atomic units) for the polaron lattice responsible for optical absorption are shown in fig. (d).

In the fig. the levels "c" and "b" each are fully occupied in polaron lattice of PANI, whereas the level "a" is only half-filled due to 50% proton doping, leading to the withdrawal of equivalent number of electrons. The level "a" is thus filled roughly up to half height indicating Fermi level (E_F). Finally, there is a flat upper polaron band (x') which is nearly degenerate with the conduction band (x). The different transitions which could yield optical absorption could be as under :

(a) A direct optical transition could occur from band b to the polaron band a.
(b) Further, a direct optical transition is expected from band c to the polaron band a.
(c) As polaron band a is only half occupied, an intrabond transition could occur within this band.
(d) Further, the electronic transitions are expected for the electrons at the Fermi level, leading to their transfer to the upper defect band (x') and conduction band (x). The other electronic transitions from bands b and c to x and x', will have quite high frequencies, not to be observed at all in the present work. The transition from band 'b' to the polaron band 'a' is calculated to be at 1.8 eV and thus expected at 823 nm. However, as our absorption measurements were only below 800 nm, this band is not at all observable in the present work. The optical transition from band 'c' to the polaron band 'a' is calculated to be at 2.8 eV and thus expected at 441 nm. The observed band at 445 nm, thus very well supports the theory of stafstrom et al [13].

The intra – band transitions will have much lower energy differences, with expected positions in far infra-red and thus again not observed at all.The electronic transitions from Fermi-level to x and x' bands with calculated energy differences of about 4.1 eV are expected at about 301 nm and very well account for the observed 328 nm band in UV absorption. Further transitions from band b and c to x and x' bands will have further higher energies, not to be observed in the present UV spectrum.

1.1.1.2 Fourier Transform Infra Red

Fig. (d) shows the FTTR spectrum of chemically synthesized PANI with cobalt doping. The curves in the figure show the vibration bands at 3415, 1640, 1556, 1300, 1115, 1050, 640 and 495 cm^{-1}. The 3415 cm^{-1} band is assigned to the stretching vibration of secondary amine. The 1640 cm^{-1} band is due to C=C bond of quinoid structure, whereas 1556 cm^{-1} band arises due to vibration of C=C bond associated with benzenoid structure. The 1300 cm^{-1} vibration may be linked to stretching associated with normal C-N linkage. The vibration 1115 cm^{-1} is also due to C=N vibration, but in the structure B-NH+ = Q and is indicative of protonation [14] of PANI. The vibration at 1050 cm^{-1} and 640 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 probably due to copper linkage.

1.1.1.3 X-Ray Diffraction

The X-ray diffractograms for PANI doped with cobalt are shown in fig. (e). The fig. shows peaks at 2θ values of 9.5°, 14.0°, 20.5°, 25.5°, 27.0° and 29.0°. The strongest peak is obviously for 2θ as 25.5°. The crystalline order for protonated cobalt-doped PANI, therefore corresponds to this peak for 2θ as 25.5°. The corresponding 'd' as 3.19 A° is thus the interchain distance between two nearest chains. The 2θ values of 9.5°, 14.0° and 20.5° must subsequently represent some other ordered arrangements, which could be due to oligomers. It may be now mentioned that the X-ray diffractograph are almost similar for undoped PANI and its cobalt doped variety.

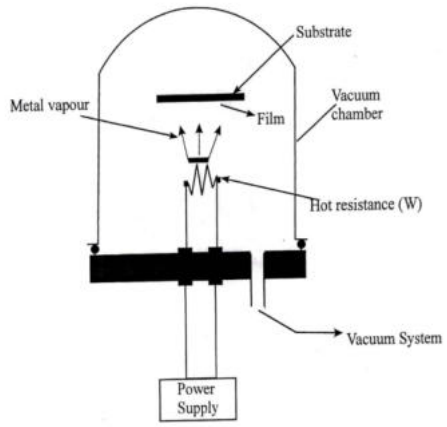

Fig. (a) Schematics of thin deposition equipment

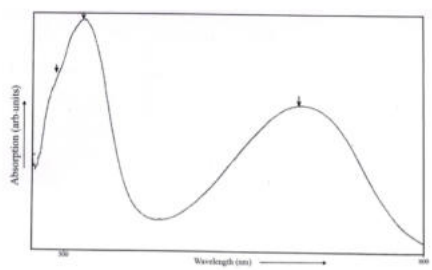

Fig. (b) UV-Visible absorption spectra of PANI with cobalt doping

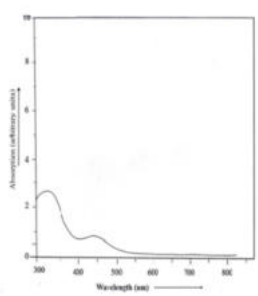

Fig. (c) UV-Visible absorption spectra of PANI film (vacuum deposited) with cobalt doping

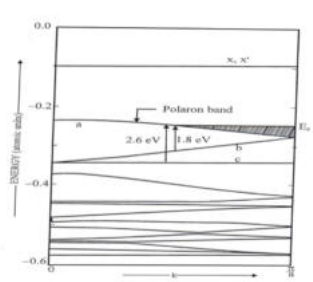

Fig. (d) Band Structure for polaron lattice of 50% proton doped polyemeraldine

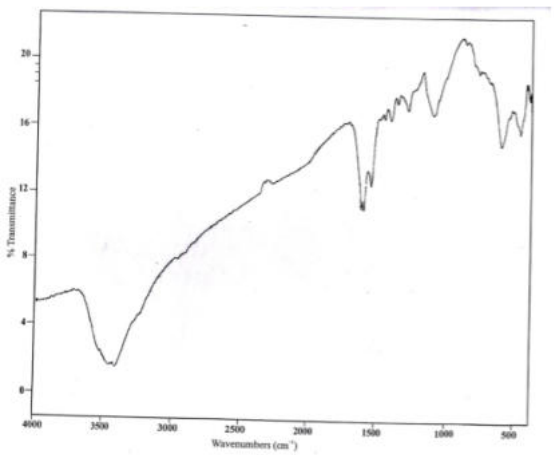

Fig. (e) FITR spectra of PANI with cobalt doping

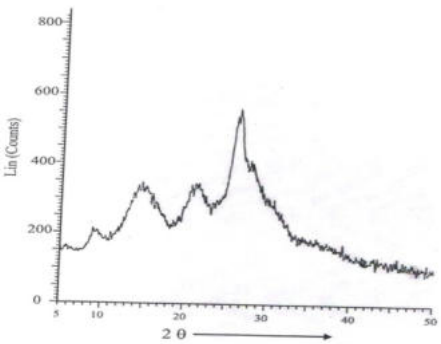

Fig. (f) X-ray diffractogram for PANI with cobalt doping

1.1 **Conclusions**

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

1.2 **UV- Visible absorption**

The UV-Visible absorption (UV-Vis-NIR V670JASCO) spectra obtained, after dissolving the sample 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 cobalt metal-doped. The optical absorption spectra obtained however, for the film varieties of PANI support the theoretical predictions of Stafstrom et al [13].

1.2.1 **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.

1.2.2 **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.

Acknowledgements

The authors wish to gratefully acknowledge the financial support from Department of Science & Technology (Govt. of India) , New Delhi as inspire fellow (IF140869) & library facility provided by National Physical Laboratory (NPL), New Delhi.

REFERENCES

1. Arslan, A., & Hur, E. (2014). Electrochemical storage properties of polyaniline, Chemical Papers, 68, 504–515. 2. Dubal, D. P., Patil, S. V., Gund, G. S., & Lokhande, C. D. (2013). Polyaniline-polypyrrole nanograined composite via electrostatic adsorption for high performance electrochemical supercapacitors. Journal of Alloys and Compounds, 552, 240–247. 3. Genies, E. M., & Tsintavis, C. (1985). Redox mechanism and electrochemical-behaviour of polyaniline deposits. Journal of Electroanalytical Chemistry, 195, 109–128. 4. Electrochemical study of polyaniline in aqueous and organic medium. Redox and kinetic properties. Molecular Crystals and Liquid Crystals, 121, 181–186. 5. J. Prokes, I. Krivka, E. Tobolkova & j. Stejskal, Polym. Degrad. Stab. 68, 261 (2000). 6. G. K. Elyashevich, L. Terlemoezyan, I. S. Kurisdyn V. K. Levretyev, P. Mokreva, E. Yu. Rosava & Yu. M. Sazanov, thermochim. Acta 374, 23 (2001). 7. M. A. el-Serif, J. Yuan & A. G. MacDiamond, J. Intelligent Mater. Synth. Struct. 11, 407 (2000). 8. S. Pruneanu, E. Veress, I. Marian & L. Oniciu, J. Mat. Sci. 34, 2733 (1999). 9. P. S. Rao, J. Anand, S. Palaniappan and D.N. Satyanarayana, Eur. Polym. J. 36, 415 (2000). 10. C.N. R. Rao "Ultra-Violet & Visible spectroscopy, 2nd Ed. (Butterworth, 1967). 11. J.L. Bredas and R. Silbey Eds., " Conjugated Polymers", Kluwer Academic Publishers, Dordrecht, The Netherlands (1991). 12. D. Chinn, J. Li, J. Janata & M. Jorowicz, chem.., Mater. 7, 1510 (1995). 13. S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, A. F. Ritecher, W. S. Huang & A. G. MacDiamond, Synth. Met. 118 203 (1987). 14. J. Tang, X. Jing, B. Wang & F. Wang. Synth. Met. 24, 231 (1988).