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Synthesis and characterization of conducting polymer Polyaniline doped with Salicylic Acid

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Abstract: Conducting Polymers have attracted considerable attention in the recent years due to their unique thermal, electrical, optical and magnetic properties. These polymers have been used for optoelectronic devices. Among these polymers polyaniline (PANI) possesses exceptional properties to be considerable for application in diodes, Field effect transistors, Solar cells and Gas sensors. In this work PANI was synthesized in the form of emeraldine salt by the chemical oxidation method using Ammonium peroxydisulphate as an oxidizing agent adding Salicylic acid as dopant. The synthesized PANI was subjected to the physico-chemical characterization by X-ray diffraction, photoluminescence and FTIR Spectroscopic study. From the XRD pattern it was observed that interfacial polymerization offers a peak at a 2θ value of 22.9° with d spacing value 3.88Å. Photo luminescence spectrum of the synthesized PANI shows an emission peak at 421 nm with band gap value 2.95 eV. FTIR absorption peaks representing the surface bondings of PANI and their vibrational modes were also observed.

Keywords: Polyaniline Chemical Polymerization, XRD, Photoluminescence, FTIR.

1. Introduction

Over 30 years conjugated polymers were considered as a futuristic new material that would lead to the next generation of electronic and optical devices. The development of plastic electronics devices based on conjugated polymers has evolved the states of these materials from academic curiosity to the rapidly growing new electronic industry.

Among all conducting polymers, polyaniline (PANI) and its derivatives have attracted much interest in worldwide. Because of chemical stability, simple polymerization, high conductivity, PANI has been used in various application, like, optoelectronics, bio-sensors, gas sensors, microelectronics etc[1-2].

Among different methods to synthesize of PANI, the chemical oxidation and electrochemical synthesis are prominent [3]. The chemical oxidation polymerization is practically viable due to feasibility of synthesis mechanism for producing large scale PANI powder. Generally PANI exists in three forms namely Leucoemaraldine, Pernigraniline and Emaraldine. In the Emaraldine form, it exists in insulating state [Emaraldine base (EB)] and conducting state [Emaraldine salt (ES)] with conductivity (σ) around 10^{-10} S/cm and 10^{-1} S/cm respectively. Emaraldine salt form is obtained upon protonation of Emaraldine Base with protonic acids i.e., oxidative doping. In this work synthesis of PANI in emeraldine salt form by chemical

oxidation method using Ammonium peroxydisulphate as an oxidizing agent and doping with Salicylic acid was carried out and its characterization was done by X-ray diffraction, photoluminescence and FTIR spectroscopic studies.

2. Experimental

Polymerization process

In the synthesis process, 0.268 g of salicylic acid and 0.93 g of aniline were dissolved in deionized water (190mL) with magnetic stirring at room temperature for 30 minute. After that 10mL aqueous solution of APS (1 mol/L) was added to the above mixture in one portion. The resulting solution was stirred for another 10 minute to ensure complete mixing. The reaction was then allowed to proceed without agitation for 24 hour at room temperature. Finally, the products were washed with deionized water and ethanol until the filtrate became colorless, and then dried in air at room temperature. The XRD pattern is recorded with help of Phillips XPERT diffractometer by using CuKα X-rays of wave length 1.54Å. Photoluminescence (PL) spectra were recorded on a RF-5301 spectrometer excitation wavelength 421nm at room temperature. Fourier transform infrared (FTIR) spectrum was recorded by FTIR spectrometer (Perkin Elmer spectrum 100).

3. Results and discussions

3.1 XRD analysis

The X-ray diffraction pattern of PANI emeraldine salt form (Figure 1) shows a sharp peak at $2\theta=22.9^0$.The interplanar distance value obtained is 3.88 Å. The average crystallite size is calculated by Debye Scherer equation,

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, K is the shape factor (0.89); D is the average crystallite size; λ is the wavelength of X ray radiation used (1.54Å); β is the full width at half maximum; θ is the diffraction angle.

Table 1: The XRD data of PANI emeraldine salt:

Pos. [°2Th.]	Heigh t [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
22.9	22	1	3.88109	100.00

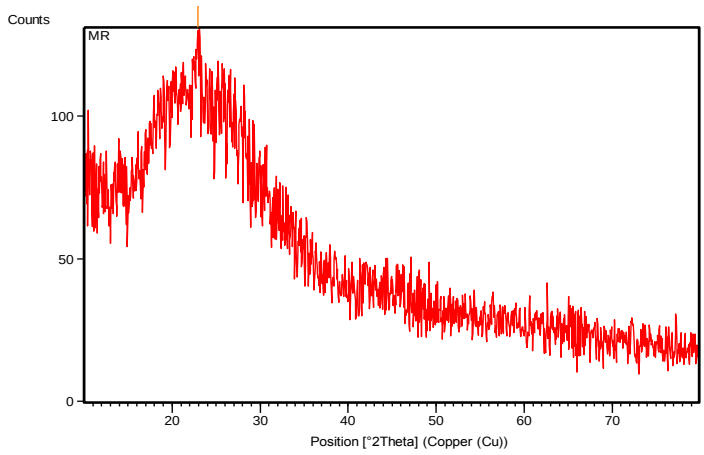

Figure.1 XRD Pattern of PANI emeraldine salt

Average crystallite size value obtained is 1.398nm [4, 5] .The XRD data are given in Table 1. Generally polymers are considered to be amorphous, but here the synthesized polymer showing crystalline structure due to its fiber nature and planar nature of benzenoid and quinoid functional groups.

3.2 Photoluminescence analysis

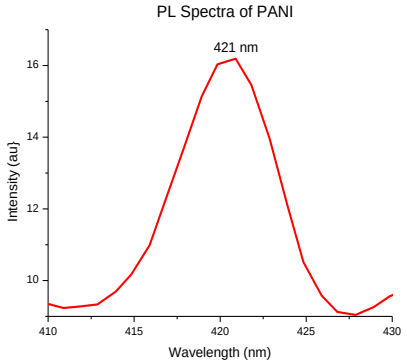

Figure.2 PL Spectrum of PANI emeraldine salt

Photoluminescence is the light emission from any form of matter after the absorption of photons. They undergo emission over a wide range from the violet to the red. They can also be combined in several different forms to produce white light . One category of organic material with PL properties is organic polymers. Photoluminescence emission peak obtained in the present study for polyaniline is 421nm as shown in Figure 2 .This peak arises due to transitions from the polaronic band to the π band structures of PANI (Sharma et al 2006). The direct band gap energy of PANI is found as 2.95eV.

3.3 FTIR analysis

FTIR spectrum of PANI shows all the major peaks of salicylic acid doped PANI. The distinct absorption bands represent the characteristic bands of PANI [6]. The FTIR spectrum of PANI is as shown in Figure 3. In the spectrum the band observed at 3429.43cm^{-1} is due to O-H stretching vibrations. The polymer shows the absorption bands at 2922.16 and 2852.72cm^{-1} were due to asymmetric C-H and symmetric C-H stretching vibrations. The band at 1653cm^{-1} was attributed to C-C stretching mode vibrations. The bands at 1581.63 and 1506.41cm^{-1} were attributed to C-H stretching on aromatic ring. The absorption peak observed at 1301.95cm^{-1}was attributed to C-N stretching of primary aromatic amines. The characteristic peak at 1238.30cm^{-1} is due to C-N stretching mode vibrations. The peak at 1149.57cm^{-1} was attributed to quinonoid unit of PANI. The characteristic peak at 1041.56 cm^{-1} is due to –SO_3H mode. The peak at 829.39 cm^{-1} attributes due to the out of plane hydrogen deformation of aromatic rings in PANI unit sequences [7].The bands at 696.30cm^{-1} and 590.22cm^{-1} were attributed to aromatic ring and also the peak at 507.28cm^{-1} corresponds to C=N amino quinine mode. The above characteristic peaks confirm the formation of PANI.

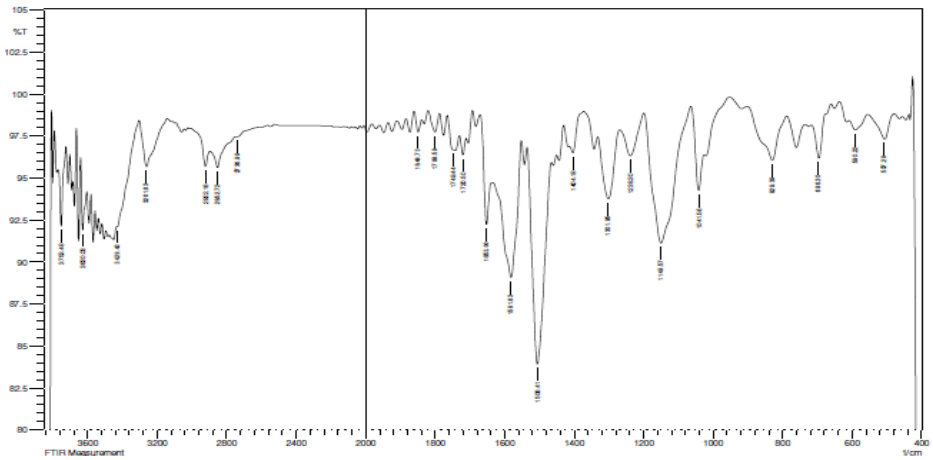

Figure. 3 FTIR Pattern of Polyaniline emeraldine salt

Conclusion

In this work PANI emeraldine salt was synthesized by chemical oxidative polymerization method .The synthesized polymer was characterized by XRD, PL and FTIR spectroscopic techniques. The X ray diffraction pattern of PANI emeraldine salt form shows a sharp peak at $2\theta=22.9^0$ and d-spacing value obtained is 3.88 Å. The PL analysis shows the PANI emission peak at 421nm with direct band gap value obtained is 2.95eV. The FTIR characteristic peaks obtained confirm the formation of PANI.

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