

Characterization of Polyaniline for Optical and Electrical Properties

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Abstract: Semiconductors have the conducting properties in between conductors and insulators. They have wide range of applications in the field of electronics and communications. Silicon compounds are mainly used as semiconducting materials, but the method of production is costly. Hence, the organic semiconductors can be considered, because of cheap raw materials for synthesis and their mode of construction or design. The organic semiconductors like polyaniline (Pani) can be considered because of its aromatic ring and lone pair of electrons on nitrogen for conducting electricity. It is a cheap, easily synthesizable and environmentally stable compound, with exciting electrochemical, optical and electrical properties. The synthesis was done by oxidation of aniline using hydrochloric acid and ammonium persulphate (APS), which forms an emeraldine salt. It was characterized by FT-IR, XRD, SEM NIR and UV-Vis Spectrophotometer.

Keywords: Semiconductors, Silicon, Pani, environmentally stable, FT-IR XRD

I. Introduction

Semiconductor nano particles have attracted much interest during the past decade in both fundamental reaches and technical applications due to their unique size and optical and electrical properties¹.

Polymer based semiconductors are in the ocre of development because of their easy and cheap synthetic procedures. The optical, chemical and electrical properties have provided a tremendous scope in the field electrical conductivity compared to metallic counter parts. Conductive polymers like polyacetylene and polyaniline have been subjected to numerous investigations in the past two decades^{2,3}.

Polyaniline is an excellent example of a conjugate polymer. The nanofibers of polyaniline can be specifically synthesized for the application like rechargeable batteries⁴, biosensors⁵, corrosion protection layers⁶, separation membranes⁷ and for molecular electronic materials. It is a cheap, easily synthesizable and environmentally stable compound, with exciting electrochemical, optical and electrical properties.

Several methods like hard templates⁸, soft templates⁹, seeding¹⁰, electrochemical synthesis¹¹ have been reported. We synthesized the polyaniline by oxidation of aniline using hydrochloric acid and ammonium persulphate (APS), which forms an emeraldine salt which shows excellent optical and electrical properties. These properties were characterized by FT-IR, XRD, SEM NIR and UV-Vis Spectrophotometer.

II. Materials And Methods

2.1 Reagents:

The reagents required were procured from Merck chemicals. Aniline was first distilled before the use. The catalyst, hydrochloric acid and oxidant ammonium persulphate (APS) were used as they were. The water used was double distilled and demineralised.

2.2 Synthesis of polyaniline nanofibers:

First aniline was distilled and stored in a clean bottle. 2ml of distilled aniline was dissolved in 1N 100ml hydrochloric acid. Exactly weighed 6g of ammonium persulphate (APS), the oxidant was dissolved in 100ml 1N hydrochloric acid. About 20ml of APS solution was added to the aniline solution drop wise with constant stirring and kept for 24 hours undisturbed.

The obtained green polyaniline was washed with 1N hydrochloric acid to remove unreacted aniline, then with distilled water to remove APS in the material, then with acetone to remove any organic impurities. The filtered material was dried at 60⁰C for 5 hours and stored in air tight container.

III. Characterization

The synthesized polymer was used to study the morphology through XRD. The XRD pattern was recorded with the help of Rigaku miniflex II desktop X-Ray diffractometer using Cu -K α X-ray of wave length 1.54Å. UV visible spectrophotometer was used for the analysis of band gap using the instrument Beckman Coulter DU730 LSUV/Vis Spectrophotometer. To confirm the analysis UV Visible spectrophotometer NIR spectra of the polymer was recorded. The Fourier Transfer Infrared spectrum was used for the analysis of

functional groups of the polymer, by dissolving Polyaniline in dimethyl sulphoxide (DMSO) with the help of Perkin Elmer Spectrum Version 10.03.09.

IV. Results And Discussion

Polyaniline was characterized for various parameters for knowing the required properties. During these experiments at most care was taken to reduce the error while analysis.

4.1. XRD analysis

In the Fig. 1, shows the X-ray diffraction pattern of Polyaniline at room temperature with four diffraction peaks at 9.27° , 15.16° , 20.65° and 25.19° respectively.

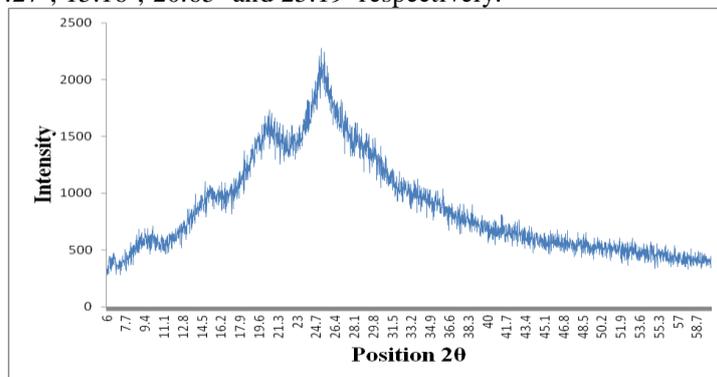


Fig. 1 XRD pattern of emeraldine salt Polyaniline

Polymer is semi crystalline in nature as the patterns show sharp peaks, because of the presence of benzenoid and quinonoid group in the Polyaniline. The interplanar crystallinity distance and crystal size were calculated by Bragg's Law and Debye Scherer equation.

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

where k = Bragg's constant (0.9) and β is the full width half maximum (FWHM)¹².

From the XRD pattern, it was found that the crystallinity of Polyaniline was 36.15% and the crystal size was found to be 2.10nm.

4.2. UV-Visible spectrum Analysis

Ultra violet and visible spectra were recorded from the synthesized Polyaniline using Beckman Coulter DU730 LS UV/Vis Spectrophotometer. Dimethyl sulphoxide(DMSO) was used as solvent during the analysis.

The Fig. 2 shows the UV-Visible pattern of Polyaniline. The spectrum has 2 peaks, one at 272 nm and other one at 400 nm. The first peak represents the presence of aniline moiety. The second peak represents the presence of benzenoid group and lone pair of electrons of nitrogen. This in turn leads to π - π^* interactions of the molecule and this shows that it is a conducting polymer.

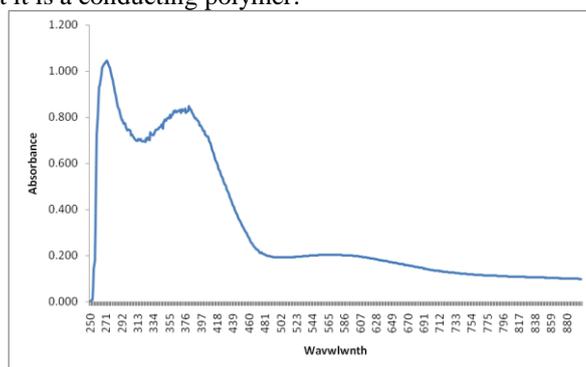


Fig 2 UV-Visible spectrum of Polyaniline

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are separated by band gap which are fundamentally important, which it determines the electrical conductivity and optical absorbance of polyaniline.

The band gap has been calculated by absorbance co-efficient data as a function wave length using Tauc relation

$$\alpha h\nu = B (\nu h - E_g)^n$$

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where α is the absorbance coefficient $h\nu$ is the photon energy, B is the band gap tailing parameter, E_g is a characteristics energy which is termed as optical band gap and n is the transition probability index with discrete value like $1/2$, $3/2$, 2 or more depending on transition of direct or indirect or forbidden band gap. The absorption coefficient (α) at corresponding wavelength was calculated by using Beer Lambert's relation.

$$\alpha = \frac{2.303 A}{l}$$

where l is the path length and A is the absorbance.

The plot $(\alpha h\nu)^{1/2}$ vs $h\nu$ was linear function existence of indirect allowed in transition in Polyaniline. Extrapolation of linear dependence of the relation to yield corresponding band gap E_g . The value of the optical energy of Pani synthesized obtained from Fig 3 is 3.73eV and this is due to π - π^* transition from valance band to conduction band at 381 nm and formation of polar on at 532 nm.

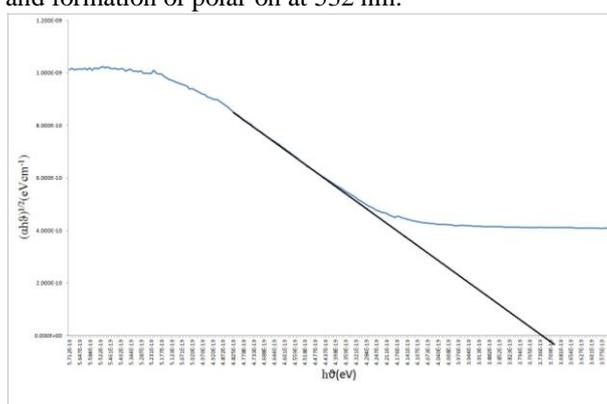


Fig. 3 Relation between $(\alpha h\nu)^{1/2}$ and $h\nu$ for the polyaniline

4.3 FT-IR Spectrum

According to Fig 4, in the analysis of Fourier Transfer Infrared spectra, the main characteristic peaks of PANI appeared at 3436, 2998, 1436, 1311, 1020, 952 and 698 cm^{-1} . The peak at 3436 cm^{-1} is attributed to the stretching mode of N-H band. C-H sp^3 stretch and C=C stretch mode for benzenoid group was which occurred at 2998 cm^{-1} and 1436 cm^{-1} respectively, while the peak at 1020 cm^{-1} was attributed for quinonoid unit of polyaniline. The peaks at 952 cm^{-1} and 698 cm^{-1} represent the C-H and C-C bands of benzenoid group¹³.

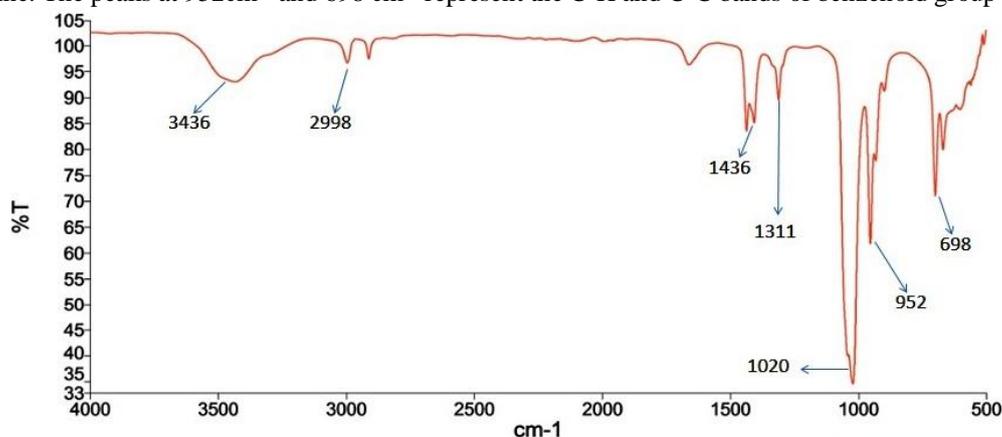


Fig. 4 FT-IR Spectrum of polyaniline

4.4. SEM Analysis

Polyaniline was subjected to Scanning Electron Microscopy to understand the structural make up. This was recorded using Hitachi SEM Insrtument. Polyaniline was fibrous in nature and the length is around 800nm, which shows that the material is in good shape as a nano fiber and can be further processed for needful applications.

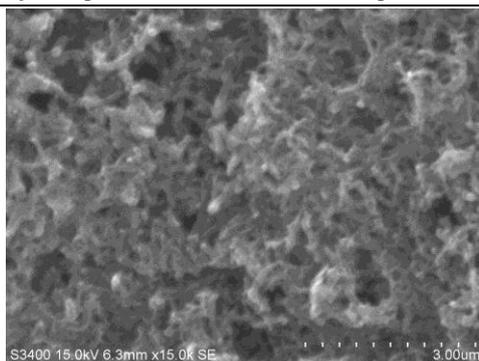


Fig. 5 SEM image of Polyaniline

V. Conclusion

Polyaniline is said to be one of the organic conductor. The optical properties show that it can even acts as an organic semiconductor. The morphology of polymer studied by XRD shows that, crystal size was 2.10nm which is helpful for the π - π^* transition, was studied through UV-Visible spectrophotometer. By this study, the band gap of the polymer was calculated through the Tauc's relation which was found to be 3.73eV.

The properties of polyaniline show that, it is a potent p type semiconductor, which could be used in hybrid solar cell, where it may be conjugated with any inorganic n-type semiconductor like cadmium sulphide or zinc oxide. By this one can expect a good output in the field of photovoltaics.

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