

Optical Properties of Conducting Polyaniline Doped by H₂SO₄

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Abstract Semiconductors materials have a conducting property in between conductors and insulators. They have wide range of applications in the field of optical and electronic devices. An organic semiconductor 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 conductivity. It is a cheap, easily synthesizable and environmentally stability compound, with exciting electrochemical, optical and electrical properties. The synthesis was done by oxidation of aniline using ammonium peroxide Sulphate (APS) and doped by Sulphuric acid H₂SO₄ which forms an emeraldine salt (PANi-ES) as a conductive polymer. It was characterized by UV-Vis Spectrophotometer, FT-IR spectrum, FESEM analysis.

Keywords PANi, Semiconductors, environmentally stability, UV-Vis, FT-IR.

Introduction

An organic semiconductor material has attracted much interest during the past decade in both fundamental reaches and technical applications due to their unique size, optical and electrical properties [1]. Polymer based semiconductor materials are in the great of development because of their easy and cheap preparation procedures. The optical, chemical and electrical properties have provided a large scope in the field electrical conductivity compared to metallic counter parts. Conductive polymers like polyaniline and polypropylene have been subjected to numerous investigations in the past decades [2, 3]. Polyaniline is an excellent example of a conjugate polymers. The compound of polyaniline can be specifically synthesized for the application like rechargeable batteries [4], biosensors [5], corrosion protection [6], and for molecular electronic materials. It is a cheap, easily preparation and environmentally stable compounds, with exciting electrochemical, and optical properties. Several of methods like seeding [7], electrochemical synthesis [8] have been reported. We synthesized the polyaniline by oxidation of aniline using ammonium persulphate (APS), which forms an emeraldine salt ES which shows excellent optical and electronic properties. These properties were characterized by UV-Vis Spectrum, FT-IR, and FESEM.

Materials and Methods

Reagents

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

Synthesis of conductive polyaniline (PANi-ES)

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



stirring and kept for overnight undisturbed. The obtained green polyaniline was washed several times with 100ml 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 80°C for 6 hours and stored in air tight container.

Instruments and Characterization

The synthesized polymer PANi was used to study the morphology through FESEM. The Morphological by FESEM study the thin films of PANi was carried out using by field effect scanning electron microscopy FESEM (Model: FEI Nova Nano SEM 450) operating at 20 kV. UV-Visible the spectrophotometer of the samples which were dispersed in demonized water under ultrasonic action, which were recorded on a used for the analysis band gap of energy using the instrument Shimadzu -1800 UV-vis spectrophotometer. To confirm the analysis UV Visible spectrophotometer FTIR spectra of the polymer was recorded. The Fourier Transfer Infrared spectrum was used for the analysis of functional groups of the polymer, with the help of Perkin Elmer (Model: Perkin Elmer Spectrum Gx) was studied in the frequency range of 400–4000 cm^{-1} .

Results and Discussion

Ultra violet and visible spectra were recorded from the synthesized Polyaniline using Shimadzu-1800 UV-Vis spectrophotometer. Figure 1 shows the UV-Visible pattern of Polyaniline with thickness ($t=285\text{nm}$). The spectrum has 3 peaks, one at 340 nm, 450nm and other one at 803 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 $\pi-\pi^*$ interactions of the molecule and this shows that it is a conducting polymer. The principal peak is credited to $\pi-\pi^*$ transition and it affected with the thickness of the films. The second peak at 450nm might be identified with a shift toward short wavelength while the third peak at 803nm makes relatively few changes. The shoulder showing up in the spectrum of PANi-ES (H_2SO_4), can be assigned to the excitation of transition coming about because of the electron exchange from benzenoid rings to quinoid rings [9]. Based on the antecedent reports, the doping can be generally evaluated from the absorption spectra of the polyaniline in which the proportion of absorbance peaks at 750-800nm demonstrate the doping concentration of polymer.

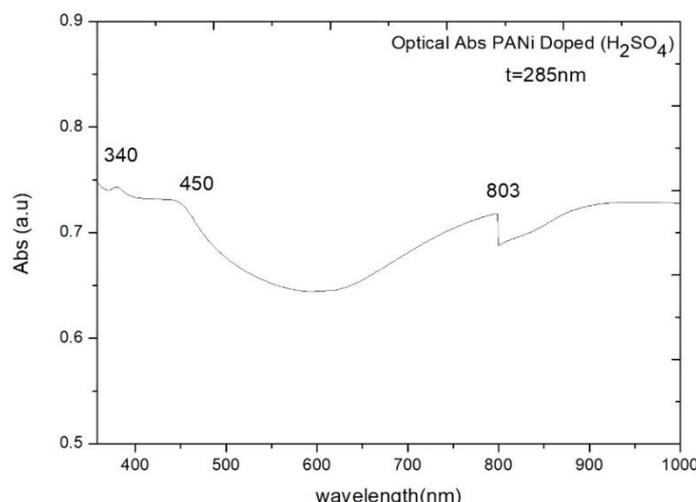


Figure 1: The absorption spectra of PANi-ES doped H_2SO_4

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are separated by band gap of energy which are fundamentally important, which it determines the electrical conductivity and optical absorbance of polyaniline. The band gap has been calculated by absorbance coefficient data as a function wave length using Tauc relation:

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

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) corresponding wavelength was calculated by using Beer Lambert's eq:

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

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 optical energy band gap defined from the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) appears in Figures. 2 for PANi doped state of polymer at thickness 285nm. The estimation of energy gap is acquired by extrapolating the linear district of the plot $(\alpha h\nu)^2 = 0$. The allowed direct transition optical band gap is found. The estimations of band gap energy E_g of PANi- H_2SO_4 , with the thickness at 285nm are 4.14 eV. Additionally, the correlation with the band gap energy of PANi doped polymer expansive is somewhere around 4.1 and 4.25 eV [10]. The distinction is ascribed to the presence of $(-CH_3)$ bonds in PANi and its doping state.

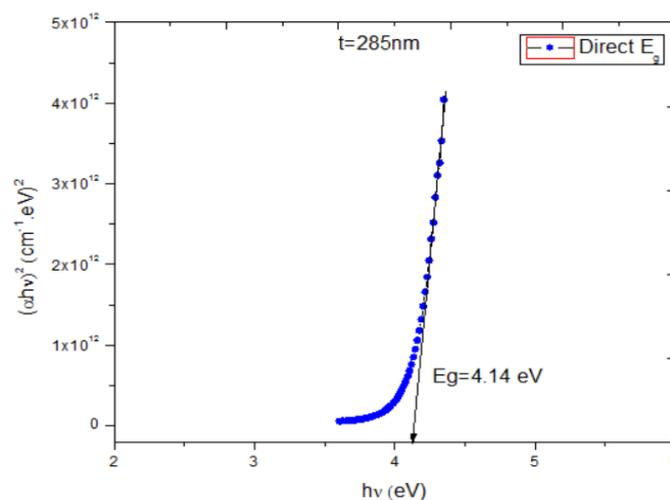


Figure 2: Relation between $(\alpha h\nu)^{1/2}$ and $h\nu$ for the polyaniline

According to Figure. 3, in the analysis of Fourier Transfer Infrared spectra, the observed peak for the prepared Polyaniline doped at room temperature with the same concentration of Sulphuric acid H_2SO_4 , listed in Table 1 demonstrates the fundamental transmission groups of the PANi. The watched peak at $750, 801\text{cm}^{-1}$ is a measure of the amount of chlorine which came back to the utilized monomer aniline hydrochloric [11]. The peak at $1290\text{-}1350\text{ cm}^{-1}$ could be related to the sulphate compounds and amine which is produced by dopant acid. The most important property bands groups for prepared PANi are the bands watched at 1650 cm^{-1} and 1961cm^{-1} , which represent the benzenoid rings and quinoid rings respectively. Alternative groups which showed existence of vibration bonds of water molecules in the generality of the spectra presented in Figure.3 demonstrated a high-level humidity during estimations that were made [11].

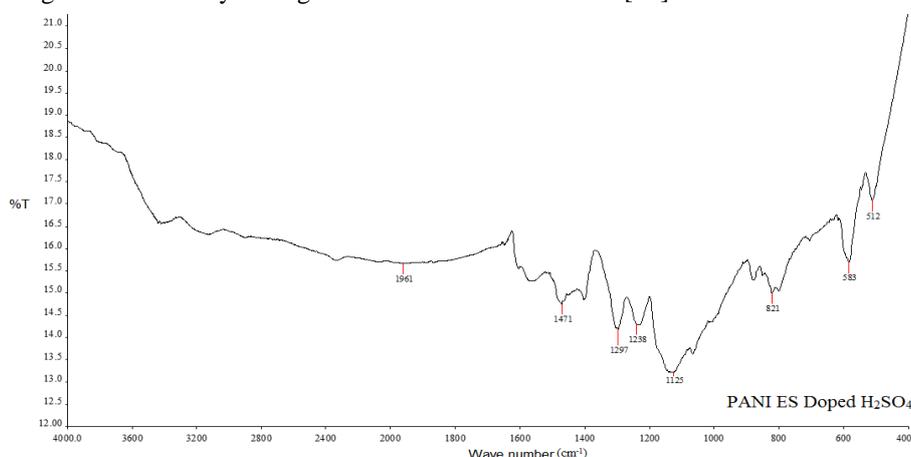


Figure 3: FTIR spectrum of Polyaniline-ES powder doped H_2SO_4



Table 1: List of the FTIR peaks in the PANi-ES (H_2SO_4) sample

Wave number (cm^{-1})	Assigned Functional groups
1650-1961	C=N Benzenoid ring conjugate cycle alkenes band
1380-1475	S=O Sulphur Chloride, stretching band
1299-1350	S=O Sulphur stretching band strong
1200-1297	C-N amine stretching strong band
1020-1125	C-N Benzene derivative amine stretching band
850-500	C-Cl compound stretching band

FESEM images, as shown in the Figures. 4 (a, b), demonstrate the morphology of polyaniline doped polymer emeraldine salt type of powder polyaniline. The image scanning of FESEM samples is taken at profound amplifications at $5\mu m$ and $10\mu m$. Figures .4, exhibits a micro porous pattern of globular microstructures for PANi-ES doped with H_2SO_4 . The exceedingly porosity nature of the material and the bunched circular morphology was confirmed with FESEM study. The orientation of the structures and morphology of samples at the macroscopic scale impact the mobility of charge carriers and affect conductivity of polymer [12].

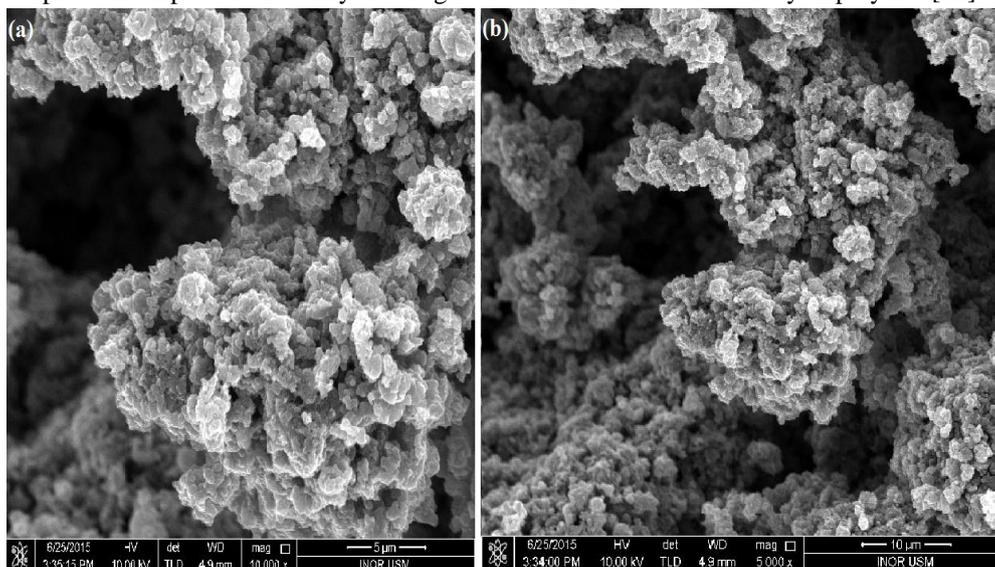


Figure 4: FESEM images of polyaniline (ES) powder synthesized and doped with acid H_2SO_4 (a) magnification to $5\mu m$ (b) magnification $10\mu m$

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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 structure of polymer shows that, semi crystal which is helpful for the π - π^* transition, was studied through UV-Visible spectrophotometer. By this study, the band gap of the conductive polymer was calculated through the Tauc's relation which was found to be 4.14 eV. FT-IR spectroscopy analyzing confirmed the inner structure of the polymer with the existence of Sulphuric acid; the position of the bonds did not more change. Then, optical properties of the polymer films were investigated to determine the optical energy gap E_g . There was an enhancement in the electrical properties of the polyaniline doping by Sulphuric acid. Morphology of polyaniline by FE-SEM analyzing showed that the particle size of polymer is inside the micro scale with the existence of acid. A special characteristic of polyaniline shows that, it is a semiconductor p-type, which could be used in hybrid organic solar cell, where it may be conjugated with any inorganic n-type semiconductor like Titanium Oxide or Zinc Oxide. By this one can expect a good output in the field of photovoltaic.



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