EFFECT OF PH ON THE OPTICAL - ABSORPTION OF POLYANILINE THIN FILMS PREPARED BY ELECTROCHEMICAL POLYMERIZATION ON ITO GLASS

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ABSTRACT

This paper reports the experimental attempt toward deposition of Polyaniline (PANI) using electrochemical deposition technique to study the optical absorption of PANI thin films deposited at different pH values of aniline solution. The optical absorption measurements were carried out in order to estimate the energy band gap of the electrodeposited PANI layers on ITO glass slides. It was observed that as the pH of aniline solution decreases from 5 to 2, the optical band gap values decreases from 3.92 to 2.2 eV. This confirms the polaron band transition in Polyaniline synthesized using the aniline solution of pH = 2.

Key words: Polyaniline; Conducting Polymer; Electrochemical; Absorbance


1. INTRODUCTION

Polyaniline (PANI) was originally known as “aniline black” [1, 2]. It is now one of the known and widely reviewed conducting polymers [2 - 6] followed by polypyrrole [7]. It was later found to be electrically conductive in nature. Polyaniline has been studied for use in a wide range of applications [8-14]. Polyaniline can be mad electrically conductive by doping However, its conductivity is influenced by various factors including temperature, humidity, pH of aniline solution and the type of anions in the solution [15]. The properties of PANI are very sensitive to fabrication
conditions and to the type of preparation technique used. Therefore, the study of the properties of PANI with respect to different growing as well as ambient conditions is of high significance. In view of this, thin films of conducting polymers including PANI have been studied by several researchers, because of their special electrical properties, their considerable thermal stability and oxidation resistance. These properties are somehow very favorable in various applications such as optoelectronic, biosensors, electrode materials in electro-catalysis in solar energy conversion etc. [16-21]. Depending on the synthesis conditions, PANI can be obtained in various forms and different structures. The physical form of polyaniline is usually as a rigid form resulting from chemical polymerization or an insoluble film resulting from electropolymerization [22-24] which has the merit of easy control of optical and electrical properties as well as morphology. We present in this paper our investigation of optical properties (UV-Visible) of polyaniline thin films deposited on ITO for different pH of aniline solution.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of 0.1 M 500 ml aniline Solution

- Added 4.5ml of aniline to 300 ml of distilled water
- Topped it up with 200 ml of distilled water up to 500ml to produce 0.1 M aniline solution.
- The solution was stirred for 15 minutes using a magnetic stirrer.
- Measured the initial pH, which was found to be 6.4 or approximately 6
- Stirred using a magnetic stirrer for 10 minutes to produce a uniform solution.

Preparation of aniline solution (pH=5)

- Took 75 ml of aniline solution.
- Added drop wise sulphuric acid to reduce the pH from 6.4 to 5

Preparation of aniline solution (pH=4)

- Used the same solution with ph of 5 and added drop wise sulphuric acid to reduce the pH from 5 to 4.

Preparation of aniline solution (pH = 3)

- Used the same solution above with a pH of 4 and added drop wise sulphuric acid to reduce the pH from 4 to 3.

Preparation of aniline solution (pH = 2)

- Used the same solution above with a pH of 3 and added drop wise sulphuric acid to reduce the pH from 3 to 2.

2.2. Preparation of PANI thin films on ITO glass slides

Thin films of polyaniline were synthesized using electrochemical oxidative polymerization method. The polymerization was carried out in a cell using the aniline solution of pH values ranging from 5 to 2. Carbon and ITO electrodes were suspended in the cell as counter and working electrodes in the solution and the deposition was done for 20 minutes at a voltage of 1.7 V
3. RESULTS AND DISCUSSION

3.1. Optical properties

The absorption spectra of PANI thin films were recorded over wavelength range 200 to 1100 nm using a UV-Vis spectrophotometer and were shown in Figs. 1, 3, 5 and 7 for pH values ranging from 5 to 2 respectively. Optical absorption was utilized to estimate band gap and type of optical transition. After measuring the optical absorbance (A) of all the samples as a function of wavelength (λ), the absorbance (A) were plotted as a function of wavelength to observe the possible transitions at different wavelengths.

The energy band gaps of PANI thin films were determined by the absorbance spectra using the following relation:

\[ A = \frac{k (h \nu - E_g)^n}{h \nu} \]

Where, \( \nu = \text{frequency} \)
- \( h = \text{Planck’s constant} \)
- \( n = \text{type of transition} \)
- \( k = \text{transition probability constant} \)

\( E_g \) is the energy gap, \( h \nu \) is the photon energy. In order to determine the optical energy band gaps, the graph of \((Ah \nu)^2\) versus \(h \nu\) were plotted by replacing \( n = 1 \) which was allowed for direct transition. The extrapolation of the straight line to \((Ah \nu)^2 = 0\) to the photon energy axis gives \( E_g \). The values of \( E_g \) obtained were found to be decreasing with decrease of pH of aniline solution as shown in Figs 2, 4, 6 and 8.

![Figure 1 Absorbance vs Wavelength for pH of 5](image-url)
Figure 2 \((\alpha h)^2 \text{ vs } h\nu\) plot of pH=5\((E_g=3.92)\)

Figure 3 Absorbance vs Wavelength for pH of 4

Figure 4 \((\alpha h)^2 \text{ vs } h\nu\) of pH=4\((E_g=3.9)\)
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**Figure 5** Absorbance vs Wavelength for pH of 3

**Figure 6** \((A(hv)^2)/(eV)\) vs \(hν\) of pH=3(Eg=3.8)

**Figure 7** Absorbance vs Wavelength for pH of 2
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http://www.iaeme.com/IJARET/index.asp

Figure 8 (Ahu)^2 vs hυ of pH=2(Eg=2.2)

The absorption peaks obtained at around 320 nm and 350 nm for pH values 5 to 3, and 2 respectively are probably attributed to the transition of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which are related to π→π* electronic transition [25, 26]. However, we also observed an absorption peak at about 400 for pH = 2 that may be due to the polaron band transitions for polyaniine [27, 28] causing the change in the optical band gap from 3.92 to 2.2 eV as the pH decreases from 5 to 2.
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