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SYNTHESIS AND OPTICAL CHARACTERIZATION OF ACID-DOPED POLYANILINE THIN FILMS

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ABSTRACT
Polyaniline has attracted much interest among researchers because of its reasonably good conductivity, stability, ease of preparation, affordability and redox properties compared to other organic compounds. In this work, Polyaniline (PANI) thin films were synthesized by chemical oxidative polymerization of aniline in the presence of Hydrochloric acid using Ammonium peroxydisulfate as an oxidizing agent. The synthesised PANI thin films, doped with Tetraoxosulphate VI acid (H_2SO_4) and Citric acid, were characterised using UV-Vis spectroscopy to investigate the variations in the optical properties. The thin films were found to be of the same thickness (0.2µm) and their absorption spectra revealed two absorption peaks at around 300nm and 650nm for the pure PANI and the sample doped with Citric acid while that doped with H_2SO_4 had its peaks at 300 nm and 880nm. Doping reduced the direct band gap of the PANI from 2.75eV to 2.4eV.

Keywords: *polyaniline thin film, organic compounds, chemical oxidant polymerization, synthesized polyaniline, optical properties*

1. INTRODUCTION
Conducting polymers have been of great interest for their applications in modern technologies and are considered as materials for the next generation of electronic and optical devices. In view of this, a great deal of attention has been given to their mechanical, optical and conducting properties. The conductivity of these polymers can be controlled by the process of doping which involves the transfer of charges from dopant to polymer or from polymer to dopant [1]. They combine the electrical properties of metals with the advantage of polymers such as smaller weight, greater workability, resistance to corrosion and lower cost [1] hence can be regarded as suitable candidates for the replacement of metals [2]. Polyaniline PANI is one of the most useful of these polymers due to its easy synthesis, good environmental stability, reversible electrical properties and low cost of monomer [3,4]. Its high absorption coefficient in the visible part of the electromagnetic spectrum, high mobility of charge carriers and great stability has made it very attractive to scientific researchers [1]. PANI is unique among conductive polymers in that its electrical properties could be reversibly controlled both by charge transfer doping and by protonation, this makes it a potential material for applications such as chemical and biological sensors, actuators, micro electronic devices, etc. It is a good material for applications in photocells, transducers, circuit boards, rechargeable batteries, biosensors, corrosion protection materials, electromagnetic protection, and electro-optic devices. PANI is a phenylene-based polymer having an –NH– group on either side of its phenylene ring. The oxidation and reduction of this polymer takes place on this –NH–group, resulting in various forms due to the number of imine and amine segments on the PANI chain. The polymer may occur in different redox states with emeraldine base being considered as the most useful form of polyaniline due to its high stability at room temperature [5]. It is insulating, and the only form of polyaniline which can be doped by acids [6]. Acid doping converts the insulating emeraldine base to the conductive form, the emeraldine salt [7]. This is the most conducting form of polyaniline with conductivity on a semiconductor level of the order of $100 S \cdot cm^{-1}$, many orders of magnitude higher than that of conventional polymers ($<10^{-9} S \cdot cm^{-1}$) but lower than that of metals ($>10^{4} S \cdot cm^{-1}$) [1].

In this work, we synthesized three samples of Polyaniline (PANI) thin films by chemical oxidative

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polymerization of aniline in the presence of Hydrochloric acid using Ammonium peroxydisulfate (APS) as an oxidizing agent. The Aniline Hydrochloride and Ammonium peroxydisulphate solutions were prepared by mixing 0.25M of Aniline and 1.5M of APS in 1M of HCl respectively. Two samples of the synthesised PANI thin films were each doped with Tetraoxosulphate VI acid (H_2SO_4) and Citric acid while the third sample was left un-doped to serve as a control. The thickness of the films was measured using a profilometer, while the optical properties of the films were investigated.

2. MATERIALS AND METHODS

2.1 Reagents and Apparatus

The chemicals used in the preparation of PANI are Aniline (Merck), Ammonium peroxydisulphate [$(NH_4)_2S_2O_8$] (Qualickems), Hydrochloric Acid (HCl) (Merck), Tetraoxosulphate (VI) acid (H_2SO_4) (BDH), Citric Acid –Biology grade (BDL), precleaned microscope slides (micropoint), Veeco Dektak 150 Surface Profiler, UV-Visible spectrophotometer Shimadzu UV-1601 and Four-point probe with a signatone quad pro resistance mapping V3.7 machine.

2.2 Synthesis of Polyaniline

Polyaniline thin films were synthesized by chemical oxidative polymerization of aniline in the presence of Hydrochloric acid using ammonium peroxydisulfate (APS) as an oxidizing agent. The Aniline Hydrochloride and APS solutions were prepared by mixing 0.25M of Aniline and 1.5M of APS in 1M of HCl respectively. The process involved the dropwise addition of Aniline Hydrochloride and Ammonium peroxydisulphate solutions on a glass substrate, in the ratio of 3:1 at room temperature. The solution was thoroughly mixed by stirring and left for about 1min. 20 seconds, during which the solution started to take on a blue-black colour. The conducting emeraldine salt form of PANI (green colour) was obtained by the addition of about 3 more drops of Aniline hydrochloride solution with continuous stirring for about a minute. This procedure was repeated on two additional substrates to obtain three thin films which were dedoped by dipping each into Ammonium Hydroxide (NH_2OH) to form PANI (emeraldine base) films.

2.3 Doping of Polyaniline

Two of the thin films were re-doped by dipping each into solutions of H_2SO_4 and Citric acids respectively for about 2mins after which they were rinsed with distilled water and allowed to dry.

2.4 Measurement of Thickness

The thicknesses of the synthesized samples (both doped and pure) were measured with a Veeco Dektak 150 profiler. The machine was computerized, and our major precaution was to measure the thickness of each sample many times and calculating the average value.

2.5 Optical Measurements

The absorption spectra of the as synthesized PANI thin films were recorded over a wavelength range of 300 to 1000 nm, within an ultraviolet (UV) region, visible light (VIS) region and near infrared (NIR) region. A UV-Visible Spectrophotometer (Shimadzu UV-1601) was used for the optical measurements and with the help of professional machine experts we obtained graphs of optical absorbance versus wavelength. To have a quantitative estimate of the optical band gap of the film, the Tauc relation was employed [8 – 11].

$$ahv = A(bv - Eg)^{y} \quad (1)$$

where α is the absorption coefficient, hv is the photon energy, E_g is the optical band-gap, A is a constant that depends on the properties of the material and γ is a constant that can take different values depending on the type of electronic transition, for a permitted direct transition $\gamma = ½$, a prohibited direct transition $\gamma = 3/2$, a permitted indirect transition $\gamma = 2$ and for a prohibited indirect transition $\gamma = 3$ [12, 13]. In this work, the direct transition band gap of the doped TiO_2 electrode was determined by plotting a graph of $(\alpha hv)^2$ versus hv where the value of the band gap is obtained by extrapolating the linear part of the graphics to the axis of the abscissa.

3. RESULTS AND DISCUSSION

3.1 Absorbance spectra for pure and doped samples

The UV-VIS absorbance spectra in the region 300-1080 nm for pure and doped PANI are shown in Figure 1. This shows two absorption peaks at around 300nm and 650nm for the pure PANI corresponding to π→π* electronic transitions related to the benzenoid form of PANI and electronic transitions in the quinoid rings of PANI respectively [14]. The absorption spectra for PANI doped with H_2SO_4 and Citric acid also showed two peaks around 300nm and 880nm assigned to π→π* electronic transitions and polaron-π* transitions respectively [15]. Generally, the H_2SO_4 doped PANI exhibited the best optical absorbance in the UV, visible and NIR regions among the three PANI samples.

3.2 Optical Band gap

Considering the Tauc's relation in Equation (1) above, the band gap of the thin films were obtained by plotting

graphs of $(\alpha h\nu)^2$ versus hν and extrapolating the straight portion of the graph on hυ axis at αhυ= 0 [10, 11].

The values of the optical band gap obtained for pure PANI, citric acid-doped PANI and H_2SO_4-doped PANI were 2.75, 2.70 and 2.40 eV respectively. The values of optical band gap was found to decrease from 2.75 to 2.4 eV after doping with different acids implying an increase in conductivity [11]. The decrease in the optical band gap may be due to reduction in the disorder of the system [4] and modifications of the polymer [11].

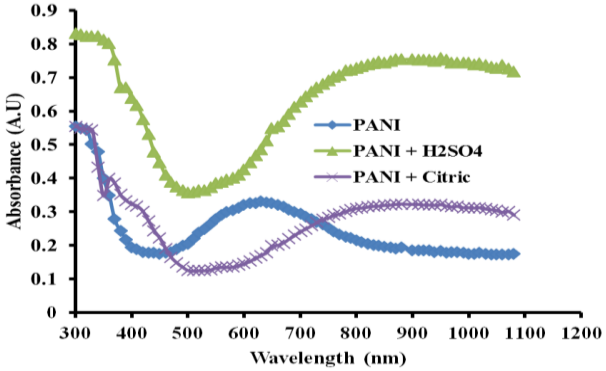

Figure: 1. Plot of Absorbance against wavelength (nm) for Polyaniline thin films

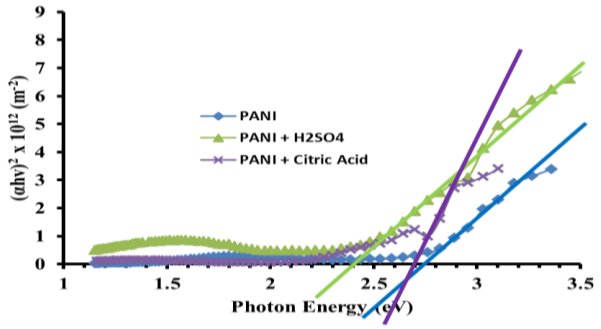

Figure: 2. Plot of $(\alpha h\nu)^2$ versus Photon Energy (eV) for pure PANI, PANI + H_2SO_4 and PANI + Citric acid

4. CONCLUSION

Three samples of Polyaniline (PANI) thin films were synthesized by chemical oxidative polymerization of aniline in the presence of Hydrochloric acid using Ammonium peroxydisulfate as an oxidizing agent. Two samples of the synthesised PANI thin films were each doped with Tetraoxosulphate VI acid (H_2SO_4) and citric acid while the third sample was left un-doped to serve as a control. Their absorption spectra revealed two peaks at 300nm and 650nm for pure and PANI doped with Citric acid with the second peak occurring at about 880nm in PANI doped with H_2SO_4. Among the three samples, we also found out that H_2SO_4-doped PANI has the best optical absorbance both in the ultraviolet, visible and infrared regions. The H_2SO_4-doped PANI has the least optical band gap energy of 2.4eV, while we obtained 2.70 eV and 2.75eV for the citric acid-doped and pure PANI respectively.

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