OPTICAL AND ELECTRICAL CHARACTERISTICS OF ACID-DOPED THIN POLYANILINE FILMS

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(Received August 10, 2017)

Abstract

Conjugated conducting polymers, such as polypyrrole (PPY), polyaniline (PANI), and polythiophene (PT), are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. In this work, three samples of thin PANI 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 synthesized thin PANI films were doped with tetraoxosulphate(VI) acid (H_2SO_4) and citric acid, while the third sample was left undoped to serve as a control. We used a VeecoDektak 150 profiler to measure the film thickness; a UV-Visible spectrometer Shimadzu UV-1601 was used to determine the optical absorption spectra of the films. The measurement of DC conductivities was accomplished through the four-point probe technique with a Signatone V3.7 QuadPro resistance mapping system using a Keithley 2400 source meter. The thin films were found to be of the same thickness (0.2 μm); their absorption spectra revealed two absorption peaks at around 300 and 650 nm for the pure and citric acid-doped samples, while the H_2SO_4-doped PANI exhibited peaks at 300 and 880 nm. Doping reduced the direct band gap of the PANI from 2.75 to 2.4 eV. In addition, the results obtained from electrical characterization revealed that the H_2SO_4-doped PANI has the best conductivity among the doped samples, while the pure sample showed no value for electrical conductivity.

1. Introduction

Conjugated polymers, most notably polypyrrole (PPY), polythiophene (PT), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(*p*-phenylene vinylene) (PPV), have been synthesized in the form of free-standing films and bulky powders using electrochemical or chemical polymerization methods [1, 2]. PPY and PANI can be formed chemically or electrochemically through oxidative polymerization of pyrrole and aniline monomers; the final form of PPY and PANI is that of a long conjugated backbone, as shown in Fig. 1 [1, 3]. These polymers have resonance structures that resemble the aromatic or quinoid forms [1]. Some polymers can become conductive after certain modifications [4–6]. Conducting polymers are a new class of sensing materials, which can be prepared by simple oxidative polymerization method. These polymers provide a suitable structure for the immobilization of ligands, enzymes, and antibodies; therefore, their use in the development of novel chemical and biological sensors has received considerable attention [3].

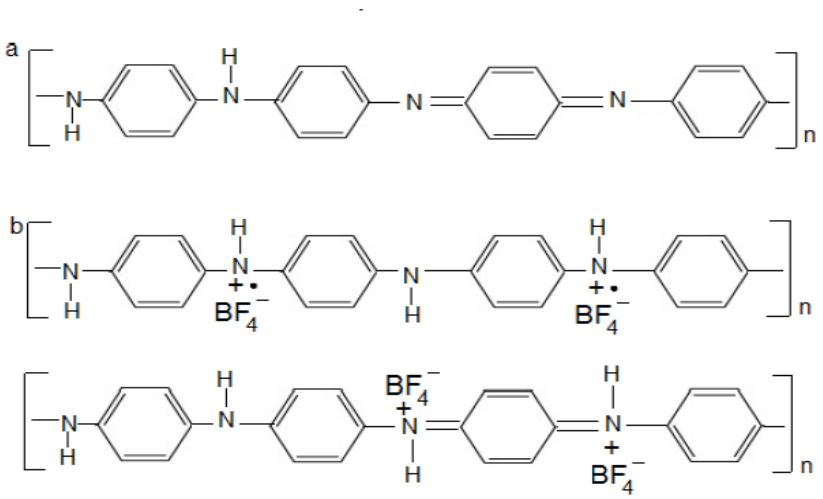

Fig. 1. (a) Emeraldine form of PANI (b) with polarons states and (c) with bipolaron states [1].

Among all conducting polymers, PANI and derivatives thereof have attracted much interest worldwide because of their chemical stability, simple polymerization, and high conductivity [2, 7, 8]. PANI is a good material for various applications, such as chemical and biological sensors, actuators, photocells, circuit boards, corrosion protection, electromagnetic protection, optoelectronic devices, gas sensors, and microelectronics [2, 9–13]. Several methods of preparation of PANI film, such as spin coating, drop coating, electrochemical deposition, thermal evaporation, emulsion polymerization, and Langmuir–Blodgett (L–B) technique [2, 14–19] have been reported by various authors. Conducting polymers have other advantages, such as smaller weight, greater workability, resistance to corrosion, and lower cost [20]; therefore, they can be regarded as suitable candidates for the replacement of metals [21]. PANI is unique among conductive polymers because the electrical properties of this material can be reversibly controlled both by charge transfer doping and by protonation.

PANI is a phenylene-based polymer having an –NH– group on either side of the 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. Among conducting polymers, PANI has the highest number of revealed and characterized forms with different properties. Due to interaction with acids, each of three protonated forms has a corresponding deprotonated form with low conductivity. Thus, the polymer can exist in at least six forms differing in both the degree of oxidation and the protonation state. These are both salt and base versions of leucoemeraldine, pernigraniline, and emeraldine. The polymer can occur in different redox states with an emeraldine base being considered as the most useful form of PANI due to high stability at room temperature [22]. It is insulating and the only form of PANI which can be doped with acids [23]. Acid doping converts the insulating emeraldine base to the conductive form, the emeraldine salt [24]. This is the most conducting form of PANI with conductivity on a semiconductor level on the order of 100 S cm^{-1}, which is many orders of magnitude higher than that of conventional polymers (<10^{-9} S cm^{-1}), yet lower than that of metals (>10^{4} S cm^{-1}) [1, 20].

In this work, three samples of PANI thin films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using ammonium peroxydisulfate

(APS) as an oxidizing agent. Aniline hydrochloride and APS solutions were prepared by mixing 0.25 M of aniline and 1.5 M of APS, respectively, in 1 M of HCl. Two samples of the synthesized thin PANI films were doped with tetraoxosulphate(VI) acid (H_2SO_4) and citric acid, while the third sample was left undoped to serve as a control. The film thickness was measured using a profilometer, while the optical and electrical properties of the films were investigated.

2. Materials and Methods

2.1 Reagents and apparatus

The chemicals used in the preparation of PANI were aniline (Merck), APS [$(NH_4)_2S_2O_8$] (Qualickems), hydrochloric acid (HCl) (Merck), tetraoxosulphate(VI) acid (H_2SO_4) (BDH), and citric acid (biology grade, BDL). Precleaned microscope slides (micropoint), a Veeco Dektak 150 Surface Profiler, a Shimadzu UV-1601 UV-Visible spectrophotometer, and Four-point probe with a Signatone V3.7 QuadPro resistance mapping system were used.

2.2 Synthesis of PANI

Thin PANI films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using APS as an oxidizing agent. Aniline hydrochloride and APS solutions were prepared by mixing 0.25 M of aniline and 1.5 M of APS, respectively, in 1 M of HCl. The process involved the dropwise addition of aniline hydrochloride and APS 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 80 s, within which the solution started to take on a blue-black color. The conducting emeraldine salt form of PANI (green color) was obtained by the addition of about 3 more drops of aniline hydrochloride solution under continuous stirring for about 1 min. This procedure was repeated on two additional substrates to obtain three thin films which were redoped by dipping each into ammonium hydroxide (NH_2OH) to form PANI (emeraldine base) films.

2.3 Doping of PANI

Two of the thin films were redoped by dipping each into solutions of H_2SO_4 and Citric acids, respectively, for about 2 min and then they were rinsed with distilled water and allowed to dry.

2.4 Measurement of thickness

The thickness of the synthesized samples (both doped and pure) was measured with a Veeco Dektak 150 profiler. This machine was computerized; therefore, measurements were taken with the help of experts. The major precaution taken was to measure the thickness of each sample many times and calculate the average value.

2.5 Optical measurements

The absorption spectra of the as synthesized PANI thin films were recorded over a wavelength range of 300–1000 nm in the ultraviolet (UV) region, the visible light (VIS) region and, the near infrared (NIR) region. A UV–Visible spectrophotometer (Shimadzu UV-1601) was

used for the optical measurements; with the help of professional machine experts, we constructed graphs of optical absorbance versus wavelength.

To have a quantitative estimate of the optical band gap of the film, the Tauc relation was employed [25–28]:

$$\alpha h\nu = A(h\nu - E_g), \quad (1)$$

where α is the absorption coefficient, $h\nu$ 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, $\gamma = 3$ [29, 30]. In this work, the direct transition band gap of the films was determined by plotting a graph of $(\alpha h\nu)^2$ versus $h\nu$, where the band gap values were obtained by extrapolating the linear part of the graph to the axis of abscissa.

2.6 Electrical characterization

The measurement of DC conductivities was accomplished through the four-point probe technique with a Signatone V3.7 QuadPro resistance mapping system using a Keithley 2400 source meter. The four-point probe apparatus has four probes in a straight line with an equal inter-probing spacing of 1.27 mm; the radius of the probe needle is 125 μm. In order to take the measurements, the user lowers the four-point probe head onto the sample and then selects the test button in the software.

4. Results and Discussion

4.1 Absorbance spectra for pure and doped samples

The UV–VIS absorbance spectra in the region of 300–1080 nm for pure and doped PANI are shown in Fig. 2. The figure shows two absorption peaks at around 300 and 650 nm 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 [31]. The absorption spectra for PANI doped with H_2SO_4 and citric acid also exhibit two peaks around 300 and 880 nm assigned to π→π* electronic transitions and polaron–π* transitions, respectively [32]. Generally, the H_2SO_4 doped PANI exhibited the best optical absorbance in the UV, visible, and NIR regions among the three PANI samples.

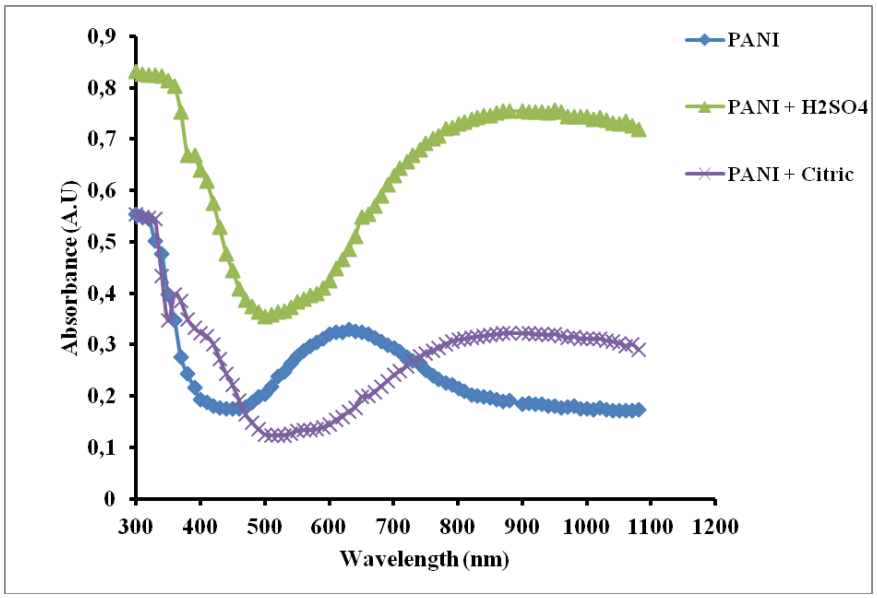

Fig. 2. Plot of absorbance versus wavelength (nm) for the thin PANI films.

4.2 Optical band gap

Considering the Tauc's relation in Eq. (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 *h*υ axis at $\alpha h\upsilon = 0$ [33, 34].

The optical band gap values obtained for pure PANI, citric acid-doped PANI, and H_2SO_4-doped PANI were 2.75, 2.70, and 2.40 eV, respectively (see Fig. 3). The optical band gap value was found to decrease from 2.75 to 2.4 eV after doping with different acids implying an increase in conductivity [34]. The decrease in the optical band gap can be due to a reduction in the disorder of the system [8] and modifications of the polymer [34].

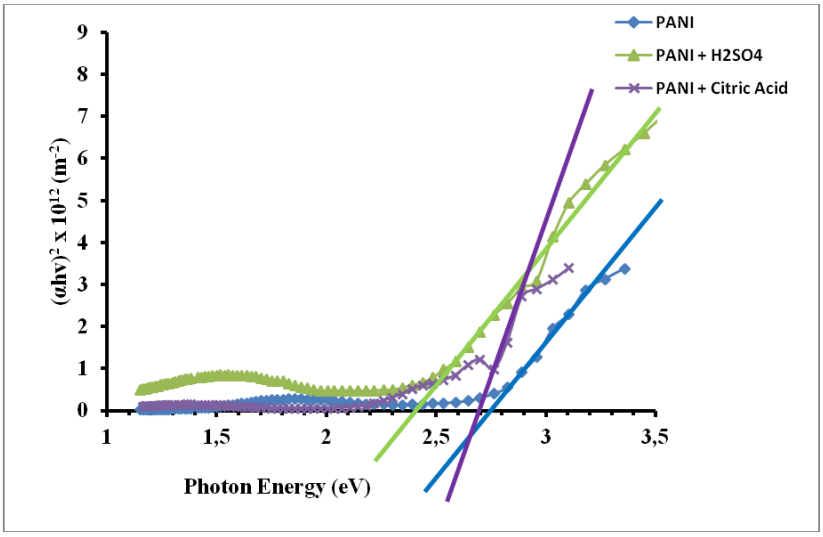

Fig. 3. Plot of $(\alpha h\nu)^2$ versus photon energy (eV) for pure PANI, PANI + H_2SO_4, and PANI + citric acid.

4.3 Electrical properties

The obtained electrical conductivity values were 6.36 and 0.01 S/cm for H_2SO_4-doped PANI and citric acid-doped PANI, respectively. These values can be compared with conductivities on a semiconductor level on the order of 100 S/cm, which is higher than that of conventional polymers ($<10^{-9}$ S/cm), yet lower than that of typical metals ($>10^4$ S/m). These results clearly show that the synthesized samples are conductive polymer films. Moreover, the pure PANI showed no values of electrical conductivity; this phenomenon was verified using a multi-meter. The electrical properties of the films are summarized in the table.

Electrical properties of PANI samples

Samples	**Sheet resistance (Ω/sq)**	**Electrical conductivity (S/cm)**	**Thickness (μm)**
PANI + H_2SO_4	7.85×10^3	6.36	0.2
PANI + Critic Acid	3.83×10^6	0.01	0.2

5. Conclusions

Three samples of thin PANI films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using APS as an oxidizing agent. Two samples of the synthesized thin PANI films were doped with tetraoxosulphate(VI) acid (H_2SO_4) and citric acid, while the third sample was left undoped to serve as a control. Their absorption spectra revealed two peaks at 300 and 650 nm for pure PANI and PANI doped with citric acid with the second peak occurring at about 880 nm for PANI doped with H_2SO_4. It was found that H_2SO_4-doped PANI has the best optical absorbance of the three samples in the ultraviolet, visible, and infrared regions. The H_2SO_4-doped PANI had the least optical band gap energy of 2.4 eV, while we obtained 2.70 and 2.75 eV for the citric acid-doped PANI and pure PANI, respectively. In addition, the results obtained from four-point probe revealed that the H_2SO_4-doped sample has the best electrical conductivity followed by that of the citric acid-doped PANI. Meanwhile, the pure PANI sample was found to be nonconductive

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