Preparation and Characterization of PAni Films by Electrochemical Polymerization

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In this paper, a thin film of H_2SO_4 doped polyaniline (PAni) has been electrochemically polymerized on conducting indium tin oxide (ITO) substrate. Electrochemical synthesis was carried out by potentiostatic method at 0.7V. The structural and chemical characteristics of the prepared film were investigated by using x-ray photoelectron spectroscopy (XPS), scanning electron microscopy SEM, energy dispersive spectroscopy EDS, and Fourier transformation infrared spectroscopy FT-IR. The direct optical band gap of PAni was estimated from the optical properties and found to be 2.6 eV. The optical properties confirmed that the synthesized film has two broad absorption bands. The surface conductivity measurement was conducted with a four point probe.

Keywords: PAni films; Electrochemical polymerization; Thin films; ITO substrate
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1. Introduction

Polyaniline is one of the most promising organic polymers due to its potential technological applications such as gas sensors, storage batteries, light emitting diodes (LEDs), corrosion control, electrodes for redox supercapacitors, protection coating, electrochromic displays biosensors, photovoltaic devices, etc. Polyaniline is environmental stable, well-behaved electrochemistry, and has high electrical conductivity "upon doping". PAni films were prepared by different techniques such as; precipitation polymerization, dispersion polymerization, flash dry deposition, pulsed-plasma polymerization, and electrochemical polymerization [1].The electrochemical polymerization has many advantages over the other methods, these advantages are: simplicity, rapidity, good control on electrical resistivity, and deposition of doped and undoped PAni films directly on the electrode [2]. Gaikwad et.al reported on synthesized of H_2SO_4 doped PAni film on platinum substrate, they have showed that doping of PAni film with 0.5 M concentration sulfuric increase its electrical conductivity [3]. In the present study, we have synthesized sulfuric acid doped PAni thin films deposited on ITO synthesized by electrochemical polymerization. The structural, chemical transformation, cross-linking assignments, optical, and electrical properties of sulfuric acid doped PAni films are characterized extensively by SEM, EDX, XPS, FT-IR, UV, and four point probe, respectively.

2. Experimental

PAni doped with H_2SO_4 thin films were deposited by electrochemical polymerization of aniline (Sigma-Aldrich Co.) on cleaned indium tin oxide (ITO) glass substrate (Sigma-Aldrich Co.) having a sheet resistance of 8 Ω/sq. The electrochemical synthesis of PAni films was carried out in AR grade 0.1M H_2SO_4 and 0.5M aniline aqueous solution at room temperature. The electrolyte cell consists of ITO as working electrode, platinum as counter electrode, and Ag/AgCl as the reference electrode. SEM equipped EDS was used to examine the surface morphology and composition of PAni film. FT-IR spectrum analysis of the films was recorded by Shimadzu IR Affinity-1 instrument in the region of 500 cm^{-1} to 1800 cm^{-1}. The optical properties of the synthesized PAni films were measured using a spectrophotometer (SP 8001 Metertech Inc) in the range of (350-900nm). XPS analysis of PAni the films were conducted. The conductivity of the synthesized films was obtained using four point probe system (Veeco FPP 5000). The film thickness of PAni film was measured by ellipsometer .Current-voltage characteristics of PAni films deposited on ITO substrate were measured at room temperature.

3. Results and discussion

Surface morphology of PAni films obtained from SEM is given in Fig. (1). It is evident from Fig.1 that the morphology of a film doped with H_2SO_4 is uniform fibrous structure; the sizes of these fibers ranged from sub-microns to microns. EDX analysis identifies the elemental composition of the film. Only 18.2%N, 43% C, and 38.5%O were observed

in EDX spectrum of the PAni films as shown in Fig. (2) which confirms the occurrence of polymerization in aniline.

The presence of S traces in EDX spectrum is due to the presence of $H_2SO_4^-$ which is in good agreement with results published by Molina et al. [4]. The selected - area EDS of the elemental map microanalysis of carbon, nitrogen, sulphur and oxygen elements in PAni film is demonstrated in the inset of Fig. (2).

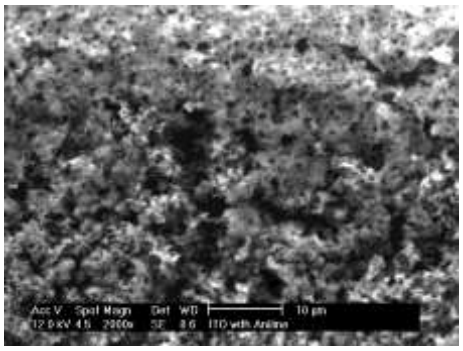

Fig. (1) SEM image of PAni film

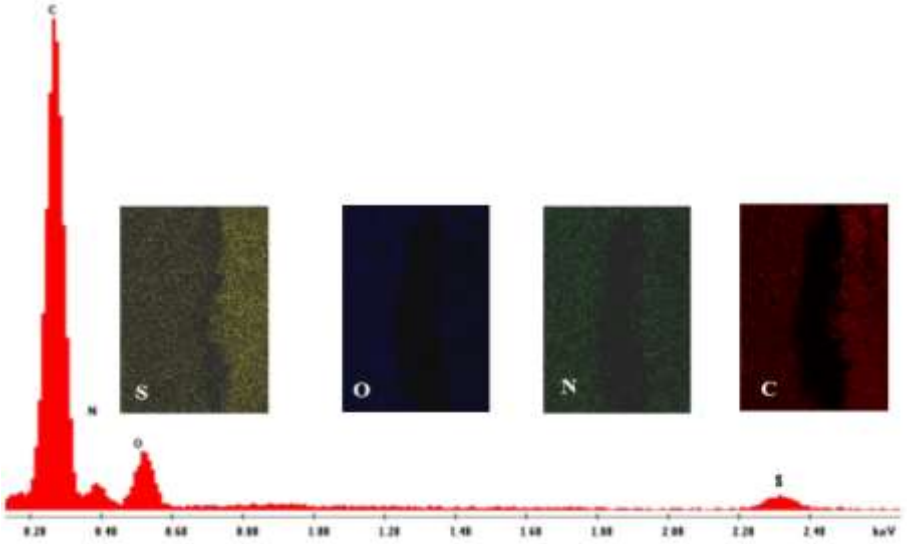

Fig. (2) EDS spectrum of PAni film. Inset is the elemental mapping in PAni film

The XPS spectrum of PAni films, given in Fig. (3), reveals two peaks corresponding to N1s and C1s core level spectra located at binding energies of 397 eV and 282 eV respectively. The peak of N 1s is assigned to =N- bond and the C 1s peak is assigned to sp^2 C=C bond [5]. The C/N ratio of PAni films was found to be close to 5. The XPS spectrum showed also a peak of O1s located at 530 cm^{-1} which is assigned to HSO_4^- bond [6].

Visual inspection revealed that the color of the synthesized PAni films was green and has good uniformity and transparency as shown in Fig.4. The film exhibited good adhesion to ITO substrate. Optical microscopic study revealed that no cracks were found on the surface of PAni film. The UV-Vis absorption spectrum of a PAni film deposited on ITO substrate is shown in Fig.5. In Fig.5, there are two absorption bands located at (348-420nm) and (750-830 nm) which originate from π→polaron, polaron →π* and π→π* transitions in PAni [7]. The optical band gap E_g is determined from Tauc law:

$$\alpha h\nu = A\left(h\nu - E_g\right)^{0.5} \qquad (1)$$

where α is the absorption coefficient, A is a constant, $h\nu$ is the photon energy. The direct optical band gap of PAni film is calculated by extrapolating the linear part of $(\alpha h\nu)^2$ versus $h\nu$ plot (given in Fig. 6) at α=0 which indicates direct transition at E_g=2.6 eV.

The FTIR spectrum of PAni films shows three absorption characteristics bands at 1440, 1140, 820, and 680 cm^{-1} as shown in Fig.7. The strong absorption peak at 1440 cm^{-1} is assigned to C= C stretching mode [8]. The bands at 1040 cm^{-1} and 830 cm^{-1} are corresponding to –S=O group in PAni-H_2SO_4 and out–of- plane C-H bending modes respectively. The peak at 680 cm^{-1} is attributed to out-of-plane C-H vibration mode [9, 10]. Fig.8 shows the current-voltage (I-V) characteristics of PAni films at room temperature; which obey ohmic law. The film of 300nm thick has room temperature conductivity as high as 0.08 S/cm and this result is in good agreement with results reported by Gaikwad et.al [3].

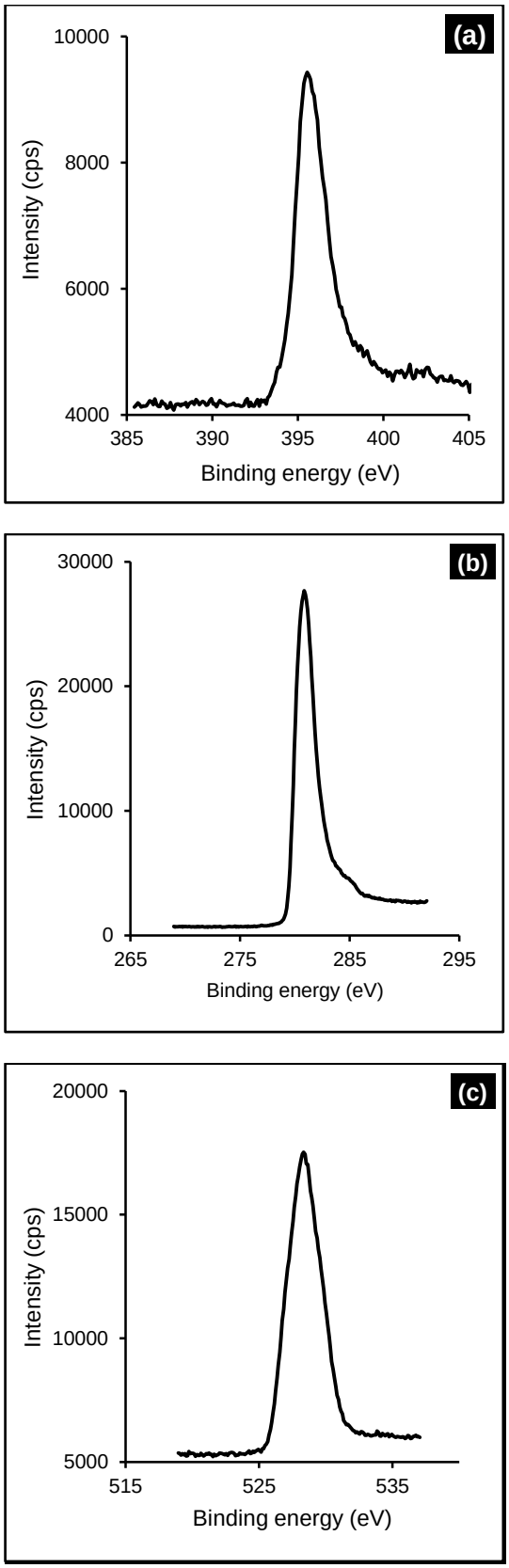

Fig. (3) Nitrogen 1s (a), carbon 1s (b) and oxygen 1s (c) XPS spectra of PAni films

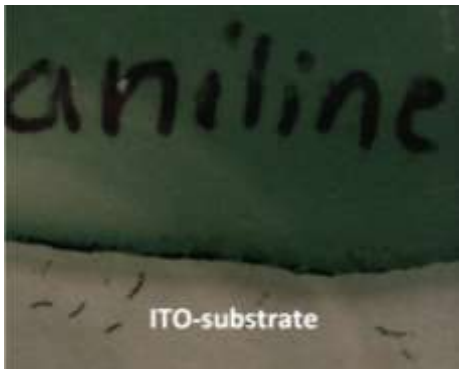

Fig. (4) Photograph of PAni film deposited on ITO

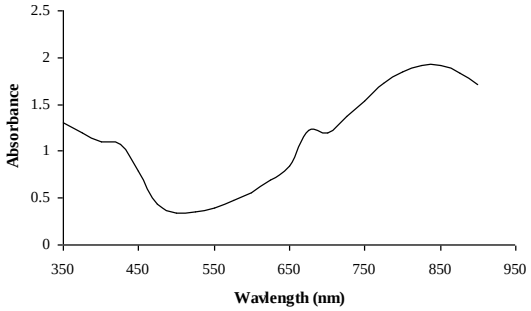

Fig. (5) Absorption spectrum of PAni film

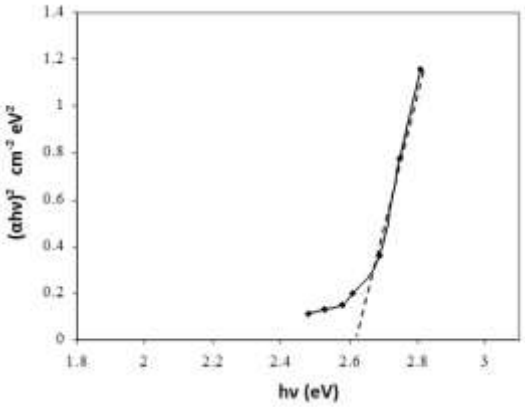

Fig. (6) $(\alpha h\nu)^2$ versus hν plot

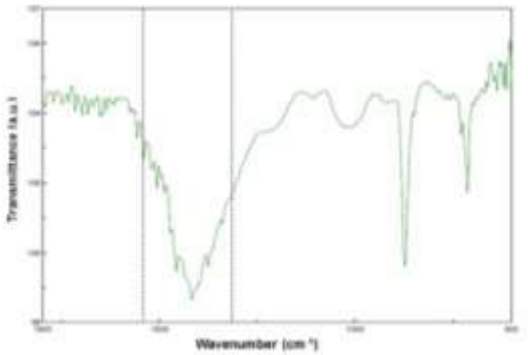

Fig. (7) FT-IR spectrum of PAni film

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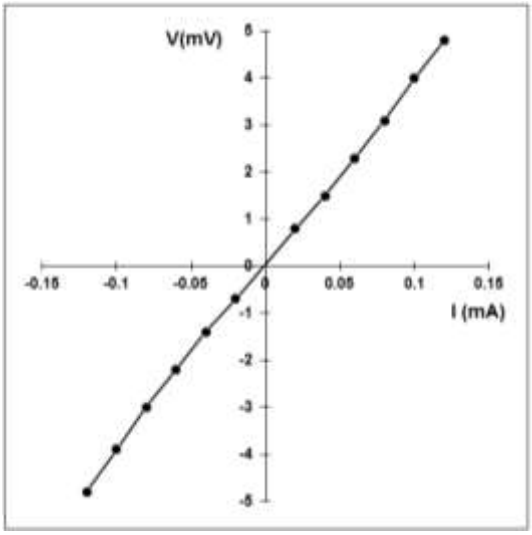

Fig. (8) I-V characteristics of PAni film deposited on ITO

4. Conclusions

Sulfur acid doped PAni films were synthesized on ITO by electropolymerization method. The films were characterized by SEM, EDS, XPS and FT-IR .The electrical investigation results revealed that the synthesized film showed excellent conducting behavior and exhibited good ohmic characteristics. The direct optical band gap of PAni film was around 2.6 eV at room temperature**.**

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