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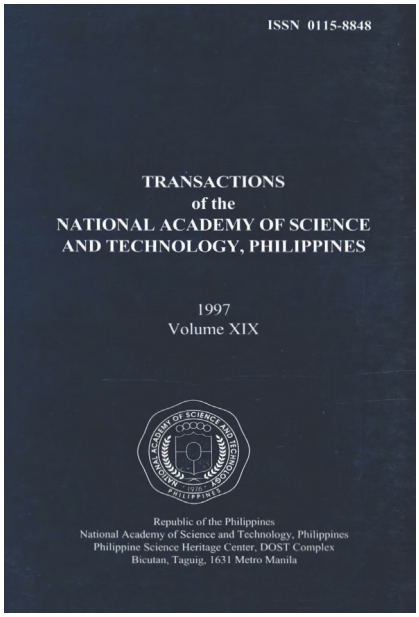

Preparation and Photoelectrochemical Characterization of a Conducting Polymer (Polyaniline) Doped with a Dye (Copper Phthaloccyanine Tetrasulfonate)

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PREPARATION AND PHOTOELECTROCHEMICAL CHARACTERIZATION OF A CONDUCTING POLYMER (POLYANILINE) DOPED WITH A DYE (COPPER PHTHALOCYANINE TETRASULFONATE)

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ABSTRACT

Photoelectrochemistry of polyaniline (PAni), a conducting polymer deposited on an indium-doped tin oxide (ITO)-coated glass substrate, was studied in aqueous medium consisting of 2mM $Fe(CN)6^{3-/4-}$ in 1M KCl. On illumination of the polymer-modified electrode and application of negative potential, cathodic photocurrent densities greater than $20nA/cm^2$ were detected. Doping of the conducting polymer with a dye, copper phtahlocyanine tetrasulfonate (CuPcTS) doubled the photoelectrochemical response to about $40mA/cm^2$. The polymer was prepared by electropolymerization of aniline in 0.1M H_2SO_4 via repeated cycling between 0.0 to 0.7v vs. Ag/AgCl. Copper phthalocyanine tetrasulfonate (Na salt) was incorporated by polymerizing the aniline monomer in the presence of the dye. The conducting polymer-dye composite was characterized by IR, UV-Vis, scanning electron microscopy and cyclic voltammetry.

Keywords: Polyaniline (PAni), copper phthalocyanine tetrasulfonate (CuPcTs), photoelectrochemical cell, photosensitizer dye, conducting polymer, electropolymerization

INTRODUCTION

Interest in conducting polymers has grown steadily in the last two decades commencing with the accidental discovery of polyacetylene possessing high conductivity by Shirikawa et al. In 1977 (1). Polyaniline (PAni), in particular, has been intensively studied due to its inherent chemical stability and the ease at which it can be prepared. It has been used in a wide variety of applications ranging from electronic (2) to electrochemical devices (3). Chemical sensors (4) and batteries (5) have also been fabricated utilizing its special electrochemical properties.

Functionalization of the polymer has also been achieved through incorporation of various molecules including enzymes, redox species and chromophores (6).

Very few however were done on photoelectrochemical characterization of conducting polymers (7, 8, 9) and their photosensitization with dyes like phthalocyanines (10) which are good spectral sensitizer of large band gap semiconductors.

This research, therefore was done to study the photoelectrochemistry of polyaniline and its composite with copper phthalocyanine tetrasulfonate (CuPcTS) (Fig. 1) electrochemically deposited over indium-doped tin oxide (ITO).

METHODOLOGY

Illumination was done using the light coming from a 150-W tungsten lamp (Hanimex) of a slide projector passed through a 5.5 cm water-filter and a camera UV filter (Astron) to remove the unwanted IR and UV radiation. Potential control and current measurement was done using Bioanalytical Systems CV27 voltammograph coupled to a Hewlett-Packard XYt recorder.

PAni was synthesized by oxidative electropolymerization of aniline in acidic medium using repeated potential cycling. CuPcTS was purchased fom Aldrich Chemical Co. as the sodium salt and used as received. The dye-polymer composite of Pani and CuPcTS was prepared by electropolymerization of aniline in the presence of CuPcTS (Na salt or acid form).

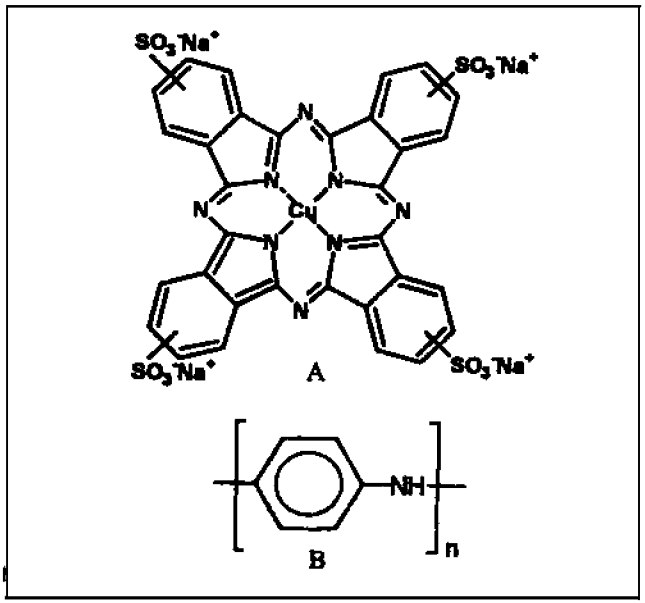

Figure 1. Structures of (A) copper phthalocyanine tetrasulfonate (Na salt) and (B) polyaniline.

All photoelectrochemical experiments were done in aqueous solution of 1M KCl in conventional three-electrode cell fitted with a flat quartz window. Redox couple used was $FeCn_6^{3-/4-}$(potassium salt, J.T. Baker). The reference electrode was positioned close to the working electrode by a Luggin capillary tip. Substrate material was indium-tin oxide (ITO) optically transparent electrode ($40W/_{\square}$, Delta Technologies). All potentials are referred against a Ag/AgCl reference electrode.

UV-Vis spectroscopic characterization of thin films were performed using an LKB Biochrom Ultrospec II spectrophotometer using ITO as blank. Infrared spectroscopy for polymer thin films was obtained from Bio Rad FTS 40 FTIR directly as diffuse reflectance using the DRIFT accesory (Bio-Rad PN 099-0931) and reported as average of 16 scans at $2cm^{-1}$ resolution.

Electron micrographs were obtained using a JEOL JSM 5200 Scanning Electron Microscope.

RESULTS AND DISCUSSION

Our preliminary studies have indicated that a film of polyaniline (PAni) on indium-doped tin oxide (ITO) glass substrate yielded current response on illumination with white light. Shown in Fig. 2 is the photocurrent response of PAni in contact with the redox solution consisting of the $Fe(CN)_6^{3-/4-}$ couple in 1M KCl on slow potential cycling at 20 mV/s and illuminated intermittently. At potentiostatic condition, the photocurrent response was found to be fast in comparison with an ion-conducting polymer-CuPcTS system (11) but rather low at $3mA/cm_2$ (Fig. 3).

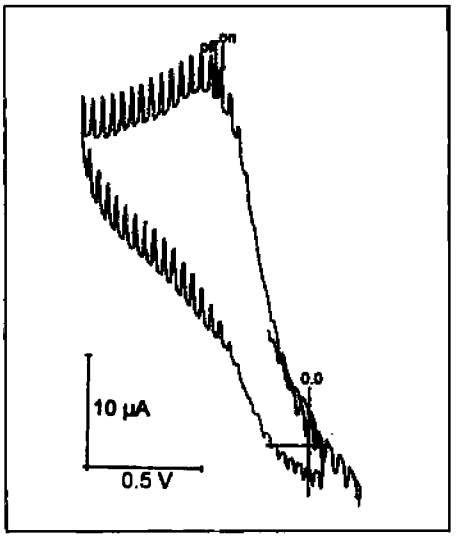

Figure 2. Cyclic voltammogram of PAni in contact with the redox solution and illuminated by a light source chopped at 0.5 Hz.

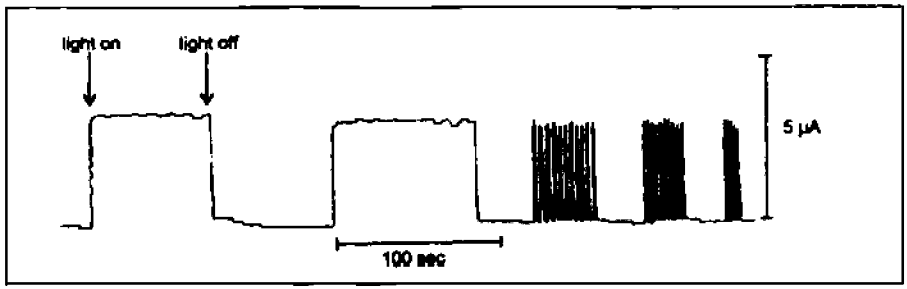

Figure 3."Square wave" anodic photocurrent response of PAni biased at +0.40 V.

Further studies have shown that the $Fe(CN)_6^{3-/4-}$ couple has a supersensitizing effect (12) resulting in an increase of photocurrent response. The cathodic response, in particular, was found to increase rapidly on addition of small amounts of the oxidizing $Fe(CN)_6^{3-}$ (Fig. 4).

Also, increasing the amount of PAni deposited (monitored by Absorbance at 370 nm) increased the cathodic photocurrent yield as shown on Fig. 5.

On the other hand, the photocurrent response is also pH dependent as demonstrated by Fig. 6. While large photocurrent response was observed at high pH, the polymer (PAni) was unstable and easily peeled from the electrode. The condition at lower pH (pH 4) was therefore more preferred in this study because of the greater stability of the PAni film.

Fig. 7 below shows the doubling effect of the dopant, copper phthalocyanine tetrasulfonate (CuPcTS) on the photocurrent response of PAni (from 0 to --0.3 v). CuPcTS was incorporated in polyaniline by anodic electropolymerization of aniline (0.1M) in the presence of H_2SO_4 and CuPcTS via potential cycling.

Spectrochemical characterization of the polymer and composite shown in series of figures 8a, 8b, 8c, reveale electrochemic spectral change which could primarily be attributed to the incorporation of CuPcTS in the polymer. The 610 nm absorption of CuPcTS is shown (Fig.8b) present in the composite UV-Vis spectra as the electrode potential is varied. Additional data on CuPcTS incorporation in PAni could be inferred from the DRIFT Spectrum of CuPcTS, PAni, and composite, shown in Fig. 9. The prominent features in the composite spectra are the characteristic bands of PAni (the major component) with additional band at 1026 cm-1 which could be attributed to shift S=O stretch in CuPcTS.

Figures 10a and 10b below are the electron micrographs of PAni and PAni/ CuPcTS composite. While the polymer morphology is fibrillar, that of the composite is granular. The morphological change is probably due to aggregation of CuPcTS which is known to occur in dye solution of high concentration. Figure 10c is the micrograph of composite prepared from CuPcTS acid and which also shows granular morphology.

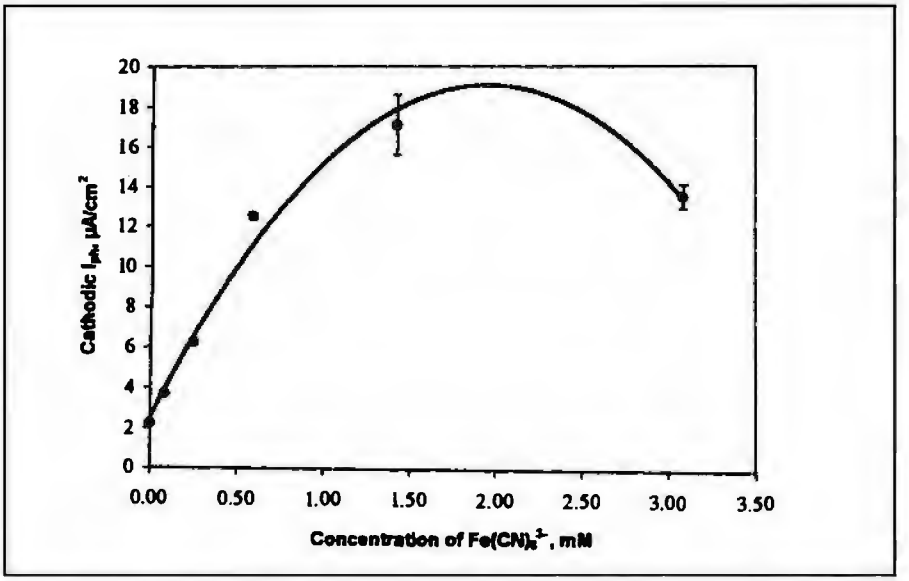

Figure 4. Dependence of photocurrent response of PAni on ITO with increasing concentration of $Fe(CN)_6^{3-}$.

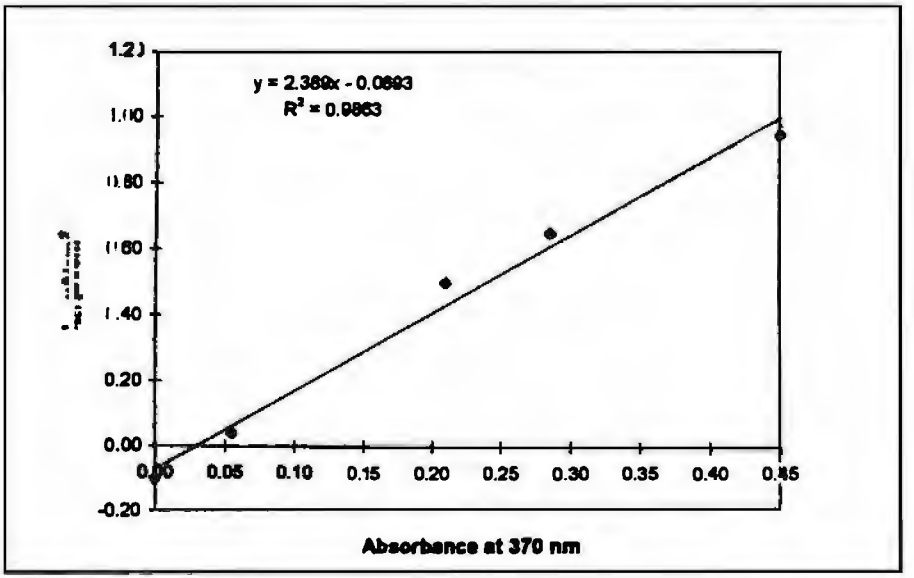

Figure 5. Dependence of short-circuit photocurrent response on film absorbance at 370 nm.

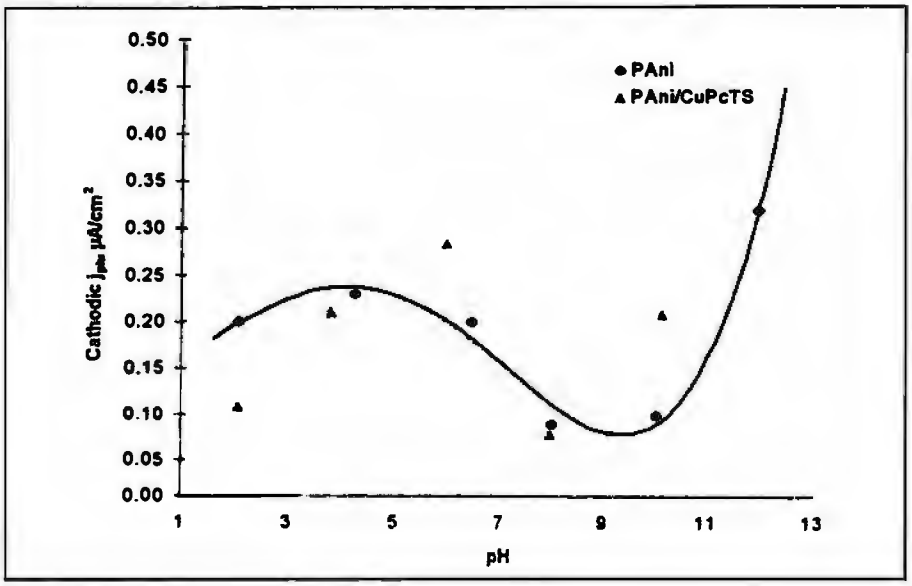

Figure 6. Dependence of the photocurrent on the pH of the electrolyte consisting of 2mM Fe $(CN)_6^{3-/4-}$ in 1 MKCl; pH was adjusted with HCl and KOH.

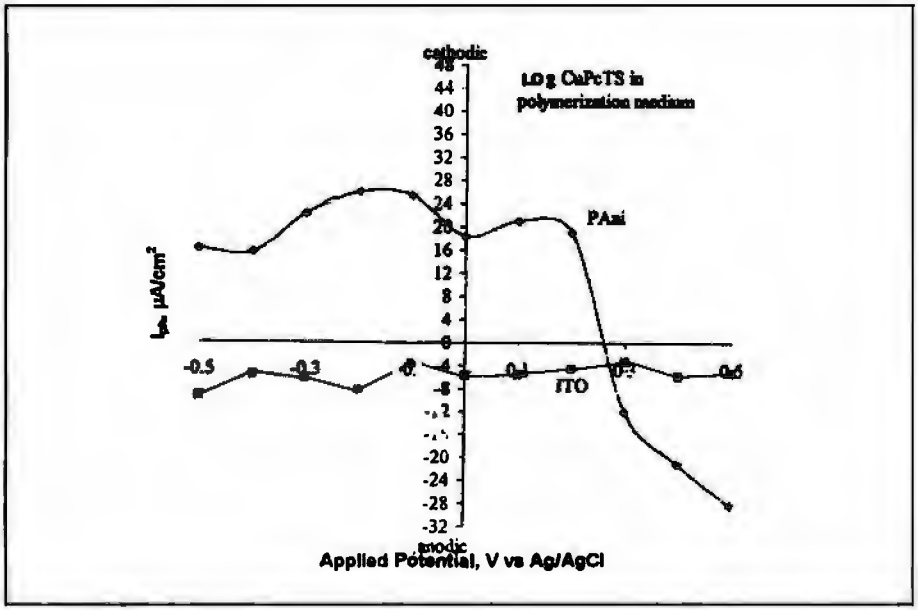

Figure 7. Photocurrent-potential plot of ITO, PAni and PAni/CuPcTS inn contact with the redox couple at Ph 4.0.

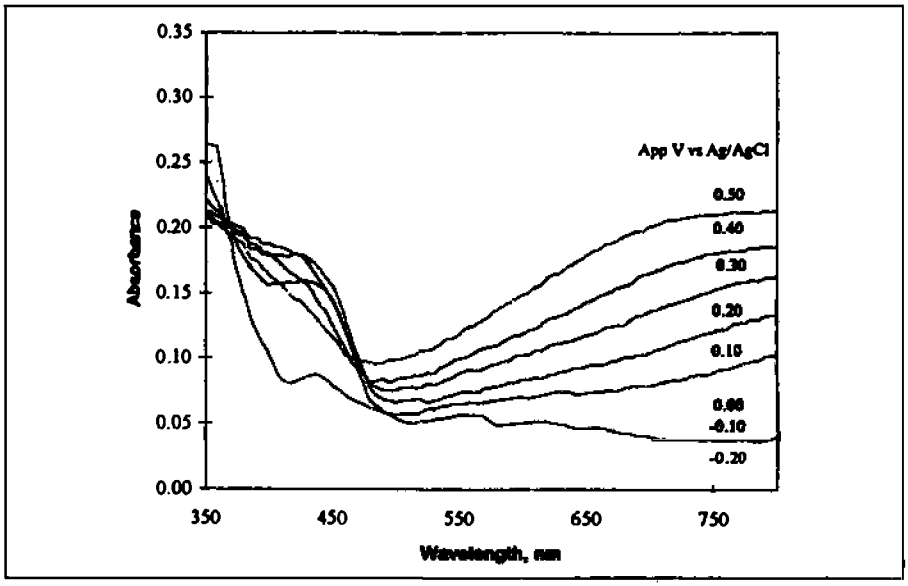

Figure 8.a Spectroelectrochemistry of PAni.

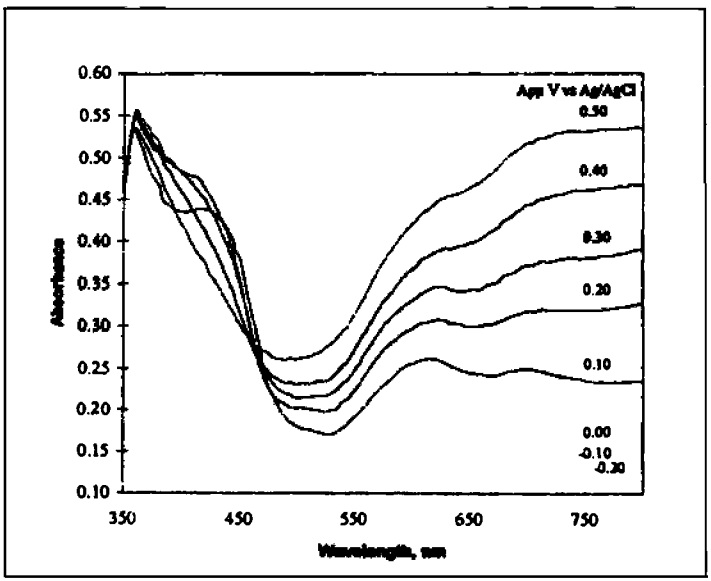

Figure 8.b Spectroelectrochemistry of PAni/CuPcTS in 0.1 M HCl

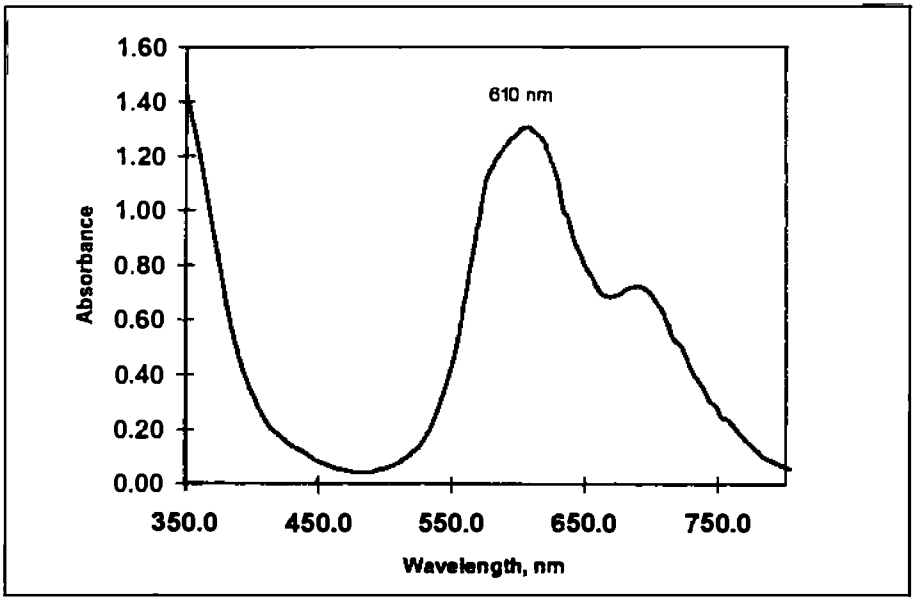

Figure 8.c Spectroelectrochemistry of visible absorbance of a dilute aqueous solution of CuPcTS

Two models to explain the charge generation in PAni and PAni/CuPcTS are being proposed and are shown in Fig. 11a and Fig. 11b, respectively.

In both models, the reduced form of PAni is the photoactive component since it is the major oxidation state of Pani at potentials in which cathodic photocurrents are observed. ITO in these models is simply regarded as an electrical contact. In Fig. 11b, the same mechanism occurs for Pani except that the acceptor here is the ground state CuPcTS+.

CONCLUSION

The preliminary results presented here merit further studies to elucidate the fundamental photoelectrochemical processes involved. Of special interest is the determination of the energetics at the heterojunctions ITO/PAni and ITO/PAni/CuPcTS which can explain the role of the conducting polymer in the charge generation and transport phenomena. So far, it has been confirmed that the polymer is photoelectroactive and that this property could be improved by electrochemical doping with CuPcTS which enhances the light absorbing property of the polymer.

The study showed the photosensitizing effect of the CuPcTS dye on the polyaniline film acting as semiconductor which is at present being considered as a photoactive material for low cost and large area solar cells (13).

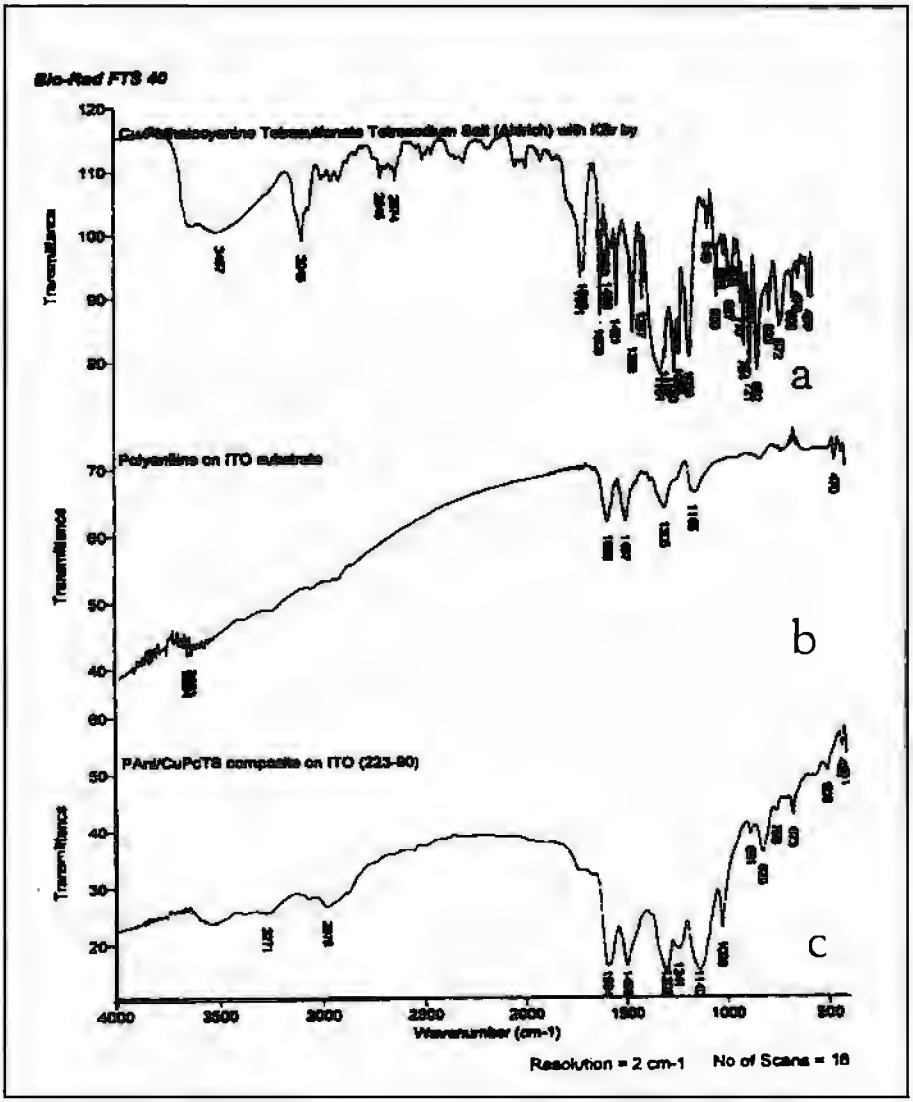

Figure 9. DRIFT spectrum of (a) CuPcTS in KBr, (b) PAni, (c) PAni/CuPcTS between 3500 to 400 cum^{-1}.

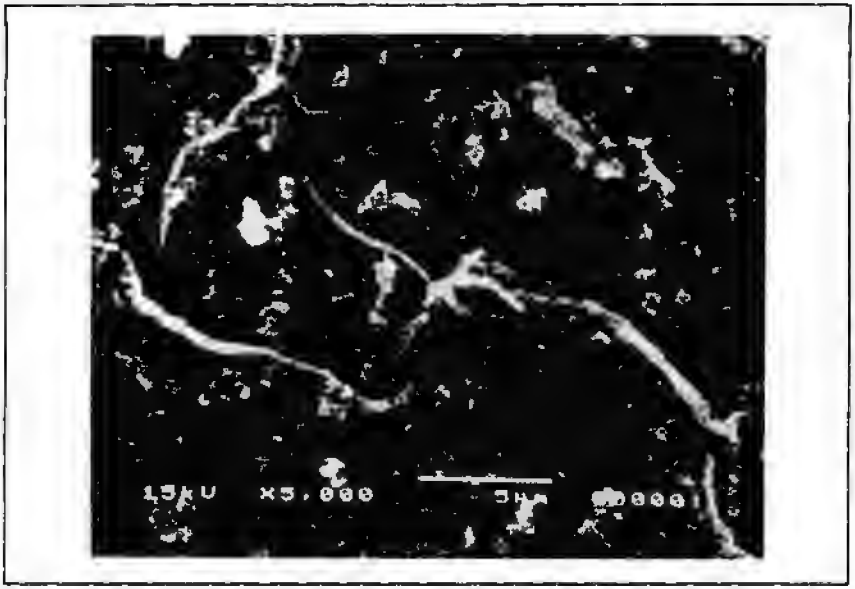

Figure 10.a Scanning electron micrograph of PAni and PAni/CuPcTS on ITO. PAni prepared from a solution of 0.1 M aniline, 0.1 M H_2SO_4.

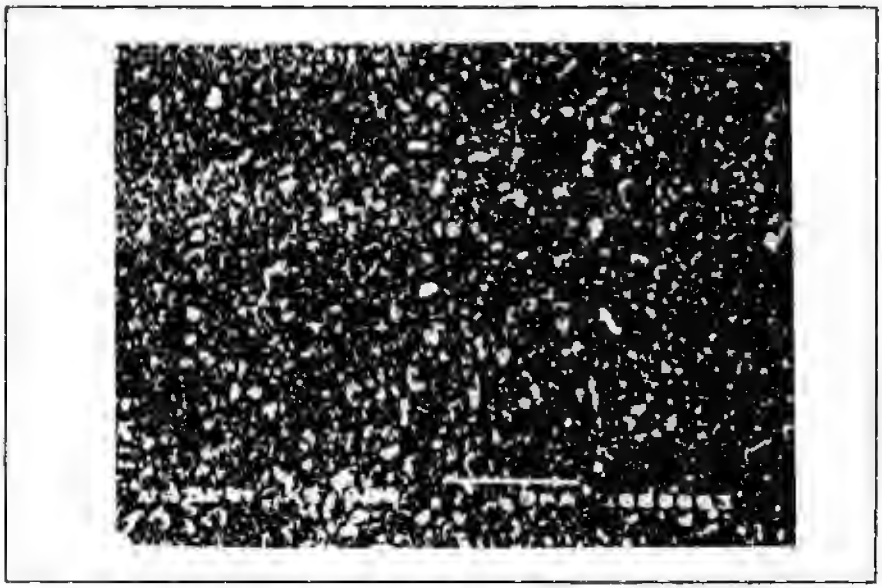

Figure 10.b Scanning electron micrograph of PAni and PAni/CuPcTS on ITO. PAni/CuPcTS prepared from a solution of 0.1 M aniline, 0.1 M H_2SO_4, 0.093 M CuPcTS and scanned -0.2 to + 1.0 V for 30 min at 20 mV/s.

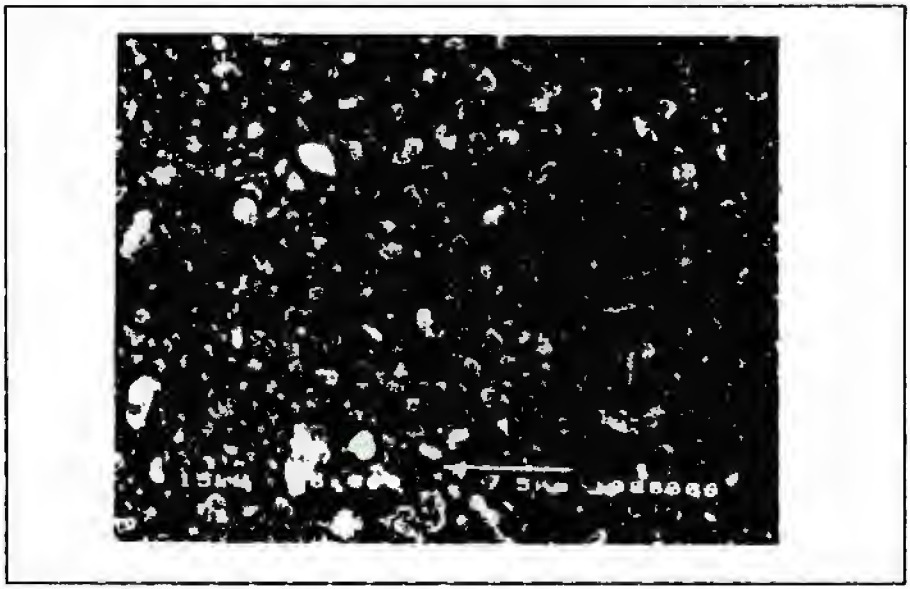

Figure 10.c Scanning electron micrograph of PAni and PAni/CuPcTS on ITO. PAni/CuPcTS prepared from 0.1 M aniline, 0.1 N H_4CuPcTS, 0.05 N aniline and scanned between 0.0 to +1.0 V for 1 hr with initial 4 scans between 0.0 to 1.2 V both at 50 mV/s.

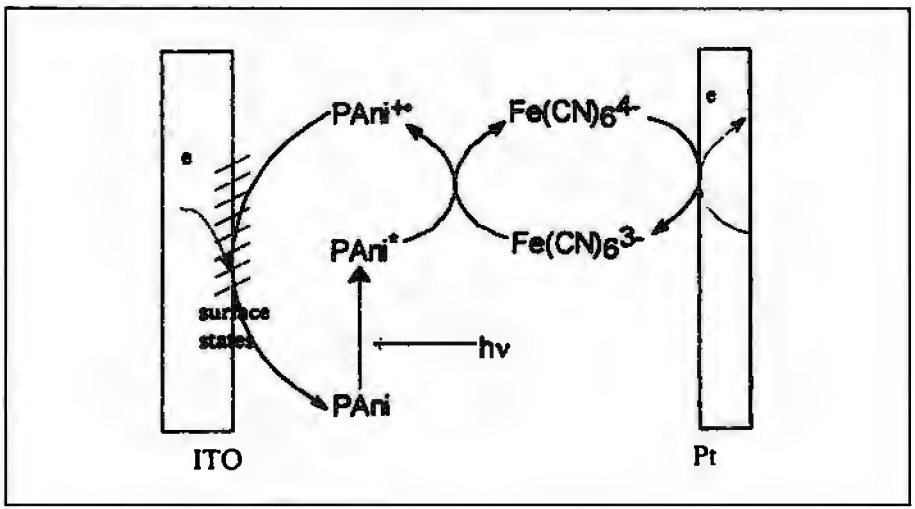

Figure 11.a Schematic diagram to explain the possible photoactivity of PAni.

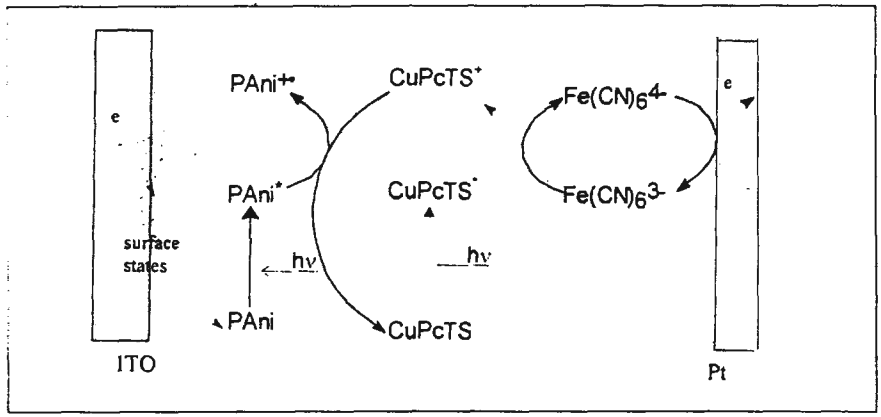

Figure 11.b Schematic diagram showing the possible role of CuPcTS in the charge generation.

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