Spectroscopic and Thermogravimetric Analysis of PANI/PPy Composite Polymer Electrode: Its Application to Electrochemical Investigation of Pharmaceutical Formulation

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ABSTRACT: The electrochemical preparation of polyaniline/polypyrrole (PANI/PPy) conducting polymer composite film on Tin oxide glass electrode from an aqueous solution containing a pyrrole monomer, *p*-toluenesulphonate electrolyte on to a polyaniline polymer doped with sulfuric acid, and sodium perchlorate is reported. The prepared PANI/PPy composite films were characterized by FTIR spectroscopy, UV–vis spectroscopy, and thermogravimetric analysis and scanning electron microscopy. Optical band gaps of these films were evaluated from UV–vis absorption studies. The optical band gap measurements of both direct and indirect allowed transition, showed a dual band gap for composite film. This type of dual band gaps for a composite polymer film was reported for the first time. The FTIR and UV–vis study showed the composite of PANI/PPy formed through the bond formation between PANI-PPY and dopant anions. Scanning electron microscopic studies confirmed the formation of composite with increased particle size. The TGA results showed that PANI/PPy polymer composite film was thermally stable than either PANI or PPy films. This PANI/PPy composite polymer electrode was used for cyclic voltammetric investigation of cefpodoxime proxetil drug in pharmaceutical formulation. The cyclic voltammetric data of composite electrode for cefpodoxime proxetil drug are compared with glassy carbon electrode. The current obtained on polymer electrode was around three time than that of glassy carbon electrode. The voltagramm also showed two reduction peaks C_1 ($\sim$ 57 µA) and C_2 ($\sim$ 70.0 µA) at potentials 1.2 and 1.6 V, respectively, at concentration 1 mM, which are absent for glassy carbon electrode. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2328–2336, 2008

Key words: composites; electrochemistry; conducting polymers; polypyrrole; electrochemistry; FTIR

INTRODUCTION

The formation of composites is one of the most useful tools in polymer science in which the physical and mechanical properties of a polymer can be controlled and enhanced.[1] PANI and PPy films show good electrical conductivity and are relatively stable over long period of time under ambient conditions. However these polymers are brittle and highly conjugated and they therefore, cannot be molded into the desired shape. These properties severely restrict their application. The mechanical properties can be enhanced by appropriate choice of anion, electrode material, or by composite formation.

Improved mechanical properties were observed in composites and doped conjugated polymer due to the increase in molecular weight.[1–4] The PANI/PPy composites[5] had conductivity in the range of 10^{-2} to 10^{-3} S/cm depending on preparation experimental conditions. Karakisla and Sacak[6] prepared the free standing polymer film of polyaniline and polypyrrole on insulating polycarbonate electrode. PANI/PPy film composite with high electrical conductivity and good mechanical properties were reported by Yang et al.[7] The composite films were flexible and strong enough and have electrical conductivity as high as 5–6 S/cm. Polyaniline-polypyrrole composite coating were electrochemically synthesized by Rajagopalan and Jude[8] on low carbon steel for corrosion protection.

The UV–vis spectra provided information about the existence of π-conjugation in conducting polymers and the optical band gap. With the help of these band gaps it is easy to find whether the polymer is conducting, semiconducting, or insulating. The UV–vis spectra of chemically synthesized hydrochloric acid-doped polyaniline was recorded by Mishra and Chandra[9] and found that the band gap of doped polyaniline was 2.14 eV.

The activity in new electrode materials has been growing over the last 20 years and is motivated by

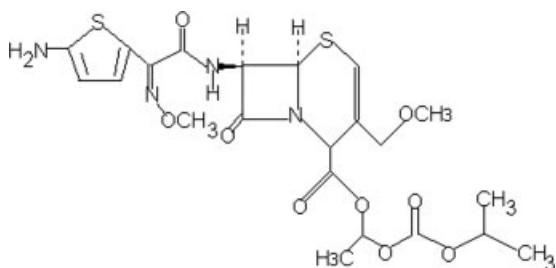*Correspondence to:* D. C. Tiwari (dctiwari2001@yahoo. com).

Figure 1 Cefpodoxime Proxetil.

the need to develop well-defined surfaces for studying electron exchange processes for controlling electrochemical reactions. In recent years chemically modified electrodes have found wide applications in rechargeable batteries,[10] electrochemical devices,[11] electrosynthesis,[12] protective films for prevention of corrosion,[13] electrochemical sensors,[14] and in electrocatalysis.[15] Many papers on the study of drug delivery system on modified electrode are also available,[16-18] however the present papers report the preparation and systematic study on the stability of PANI/PPy composite film. UV–vis studies were carried out to determine the optical band gap of the composite film. The FTIR studies were carried out to elucidate the structure of PANI/PPy composite film. The thermal stabilities of these polymers were studied using thermogravimetric analysis and it was observed that the PANI/PPy composite was more stable than its constituents. Surface morphology is studied by scanning electron microscopy. This electrochemically deposited PANI/PPy composite polymer film was then used as working electrode in cyclic voltammetry for the investigation of cefpodoxime proxetil (CP) drug.

Cefpodoxime proxetil (CP) (Fig. 1) belongs to the third generation cephalosporins. Nowadays CP is extensively used in clinical practice and therapy. Cephalosporin is generally electroactive and gives a Faradaic response on an electrode immersed in their solution. Most of the new cephalosporin possesses a reducible methoxyimino group in the side chain at Position 7. One of them is the third generation cephalosporin-cefpodoxime proxetil. A literature search related to the reduction mechanism of this methoxyimino group showed that most of the investigations were performed at mercury and HDME electrodes and some of them were at Pt, Au, and carbon paste electrodes.[19-21] Good results were observed using differential pulse polarography (DPP) at mercury electrode and cyclic voltammetry (CV) at hanging dropping mercury electrode (HDME).[20] Most of the papers reported on the reduction of cephalosporins and only a few reports their oxidation at solid electrodes.[22,23]

The current obtained in cyclic voltammetry at polymer electrode was around three times higher than glassy carbon electrode. We are for the first time reporting that the composite polymer has a dual band gap nature. This electrode could be successfully used for drug investigation and is thus useful for pharmaceutical industries.

EXPERIMENTAL

Materials

Both pyrrole (99%) and aniline (99.8%) were procured from Aldrich chemicals and redistilled before use. All solutions and supporting electrolyte were of Analytical Grade and prepared using ultra pure water. Tin oxide was deposited on glass slide using chemical vapor deposition technique. The Cefpodoxime proxetil solutions were prepared immediately before use and were purged by passing nitrogen gas. The pH was adjusted with phosphate buffer solutions. The ionic strength was kept constant with aqueous $1M$ KCl.

Instrumentation

Voltammetric measurements were performed using Eg and G Princeton applied research model 273; the potentiostat was controlled by the electrochemistry software 4.30A. Three-electrode set up was equipped with composite PANI/PPy as working electrode, an Ag/AgCl reference electrode and a platinum-wire counter-electrode. The pH of the solutions was measured by using pH meter Systronic Decibel Instrument (DB-1011). All measurements were carried out at the laboratory temperature (27°C + 0.1°C). Scanning electron microscopy (SEM) images of the modified electrodes were obtained with a electron microscope JEOL JSM 840 after coating with gold at 5 Kv and 6×10^{-10} A. Thermal stability of the modified electrodes was studied by thermogravimetric method using TA instrument US in air at heat rate of 20°C from 25 to 800°C.

Preparation and activation of the PANI/PPy working electrode

Polyaniline films were deposited on tin oxide coated glass slide using cyclic voltammetric technique in H type cell. For electrochemical deposition of polymer tin oxide coated glass slide was used as working electrode, Ag/AgCl reference electrode and graphite rod as counter electrode were used. Sulfuric acid (H_2SO_4 $10^{-1}M$) and sodium perchlorate ($NaClO_4$ $10^{-2}M$) were used as doping agents for polyaniline formation. The voltage applied was varied from (−0.3) V to (+1.0) V and the concentration of aniline

Assignments of FTIR Bands of PANI, PPy, and PANI/PPy composite Films

Assignment PANI	PANI (wavenumber cm^{-1})	PANI/PPycomposite (wavenumber cm^{-1})	PPy (wavenumber cm^{-1})	Assignment PPy
N—H stretching	3331.07	3342.64	3444.87	N—H stretching
Aromatic C—H Stretching	3226.91	3226.91	–	–
Aromatic C—H stretching	3057.17	3057.17	–	–
C—H stretching	2926.01	2924.09	2924.09	C—H stretching
C—H stretching	2854.65	2854.65	2854.65	C—H stretching
C= C Ring stretching	1591.27	1591.27	1543.05	C=C ring stretching
C=N Stretching	1496.76	1494.83	1456.26	C=C ring stretching
–	–	1176.35	1168.86	N—H in plane bending
Benzenoid ring stretching	1448.54	1450.47	–	–
C—N radical cation Stretching	1303.88	1301.95	–	–
C—N benzene diamine unit stretching	1249.7	1246.02	–	–
In plane C—H bending	1149.57	1155.36	1116.78	In plane C—H bending
C—H out of plane Deformation	754.17	752.24	777.31	C—H out of plane deformation
C—H out of plane deformation	694.37	692.44	673.16	C—H out of plane deformation
–	–	565.14	536.21	N—H out of plane bending
Asymmetric S (=O)$_2$ Stretching	1400.32	1352.2	1379.10	Asymmetric S(=O)$_2$ stretching
Symmetric S (=O)$_2$ Stretching	1120.64	1120.64	1116.78	Symmetric S(=O)$_2$ stretching
C—CI absorption of perchlorate ion	624.94	623.01	–	–

was taken 0.2M. On this preexisting polyaniline film, polypyrrole film was deposited electrochemically by constant potential coulometry at constant potential 0.8 V. The deposition was allowed till the accumulated charge reaches 15 coulombs. The concentration of pyrrole was 0.2M and the amount of supporting electrolyte p-toluene sulfonate was taken 0.1M. All the films were prepared in aqueous media and stored in air at room temperature. To obtain a more sensitive and stable voltammetric response the working electrodes were cyclically scanned 20 times in the potential range from ($-$1.6) V to ($+$1.2) V to get a stable background current.

Preparation and analysis of drug sample

Five tablets of CP (Cipla, India), each containing 200 mg of CP were powdered in a mortar and the amounts corresponding to $1 \times 10^{-3}M$ of CP were weighted and dissolved in methanol. The contents of the flask were sonicated for 15 min to affect complete dissolution. After the excipients have settled down, an aliquot of the clear supernatant was transferred quantitatively into a calibrated flask and diluted to a final volume of 10 mL with DMF. Determination of CP in working solution was performed by cyclic voltammetric procedure.

RESULTS AND DISCUSSION

FTIR spectrum

The FTIR spectrum of PANI film doped with H_2SO_4 + $NaClO_4$, PPy doped with P-toluene sulfo-

nate, and PANI/PPy composite film were recorded using IR Prestige-21-FTIR (200 VCE) Shimadzu (Japan) and assignment of various molecular groups are given in Table I. The absorption band in the spectrum near 3400 cm^{-1} corresponds to N—H stretching vibration. It is clear from the table that in the PANI/PPy composite film N—H stretching band (3342.64 cm^{-1}) shifts towards lower wave number, where as for PANI it is at 3331.07 cm^{-1} and for PPy it is at 3444.87 cm^{-1}. The bands corresponding to in plane and out of plane N—H bending in polypyrrole (1168.86 and 536.21 cm^{-1}) are shifted to higher wave number in PANI/PPy composite films. The shifting observed in N—H banding indicates that atoms might be getting attached to the amine nitrogen sites in the composite film. The spectrum of composite resembles the individual spectra of polyaniline and polypyrrole with the following main bands: the key bands corresponding to the aromatic ring in PANI (1591.27 cm^{-1} for C=C stretching and 1496.76 cm^{-1} for C=N stretching) and PPy (1543.05 and 1456.26 cm^{-1} for C=C stretching) are clearly visible (1494.83 and 1591.27 cm^{-1}), in PANI/PPy composite film. The benzenoid ring stretching is seen at $\sim$ 1450.47 cm^{-1} in composite and this is also seen at 1448.54 cm^{-1} for PANI. The formation of composite makes an effective change in the molecular structure. From the Table I it is clear that almost all the molecular groups seen in either PANI or PPy are also present in the composite. The dopent H_2SO_4, p-toluene sulfonate, and $NaClO_4$ show their effective presence at 1352.2, 1120.64, and 623.01 cm^{-1} in the composite.
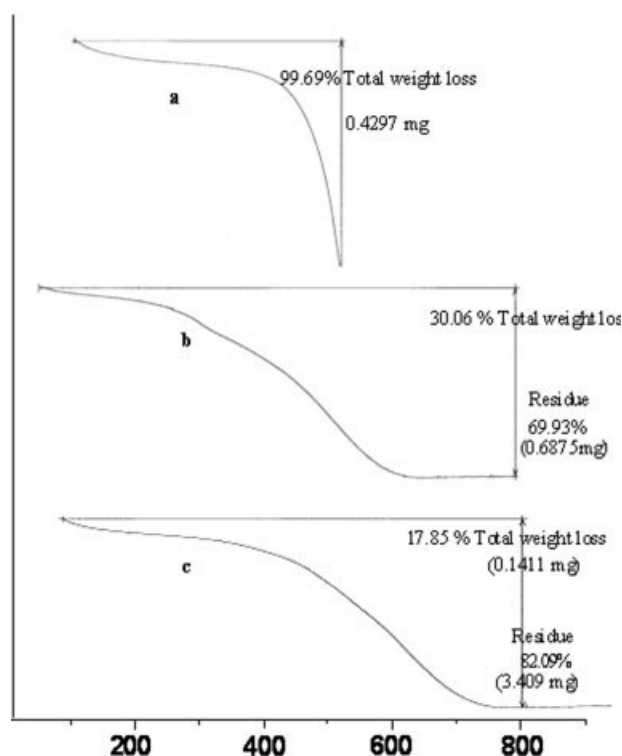
Figure 2 TGA graphs for different polymer films modified electrodes (a) PANI film doped with H_2SO_4 + $NaClO_4$. (b) PPy film doped with *p*-toluensulphonate. (c) PANI/PPy composite film.

Thermogravimetric analysis

Thermogram for PANI doped with H_2SO_4 + $NaClO_4$ is recorded in Figure 2(a). Here it is observed that the film looses 10% weight at 250°C. The temperature for 50% weight loss is 325°C. Weight loss of 99.69% was observed at 350°C which is attributed to complete degradation of the polymers which shows instability with rise in temperature.[24,25]

The TGA curve corresponding to PPy film doped with *p*-toluene sulfonate is shown in Figure 2(b).

Here the initial weight up to 100°C is due to the moisture content. A 10% weight loss was seen at 390°C. The TGA curve corresponding to doped PPy film shows a partial decomposition at 600°C weight loss of 30.06% only.

The TGA corresponding to PANI/PPy composite is recorded in Figure 2(c). The composite is more stable as it looses initially the moisture and weight of 10% was seen at 475°C. The composite remains stable up to 650°C with a weight loss of only 17.85%, and the composite polymer film remains up to a temperature 800°C having 82.09% residue. It is concluded here that the composite of PANI/PPy is thermally more stable than either of the constituents which is supported by previous literature.[26] It is evident that in the process of composite formation some realignment of molecular groups has definitely occurred.

Scanning electron microscopic study

SEM images of PANI/PPy (Fig. 3) composite films, clearly indicates the growth of the polypyrrole membrane along the polyaniline chain in a granular pattern. The average particle size for polypyrrole was about ~ 6–10 μm with Globular structure. The size of the grain varied due to the variation in polyaniline and polypyrrole chains observed in IR spectra of composite film. SEM studies show a rough surface for providing large area for the electrode activity.[27]

UV–visible spectral studies

UV–vis absorption spectra recorded on (190–800 nm) on Systronics Double beam UV–vis spectrophotometer 2101 of PANI, PPy and PANI/PPy composite films are shown in Figure 4(a-c), respectively. The spectrum of PANI shows characteristic band at ~ 263, ~ 286.4, and 559.5 nm corresponding to π–π*, polaron–π*, and π–polaron transitions, respec-
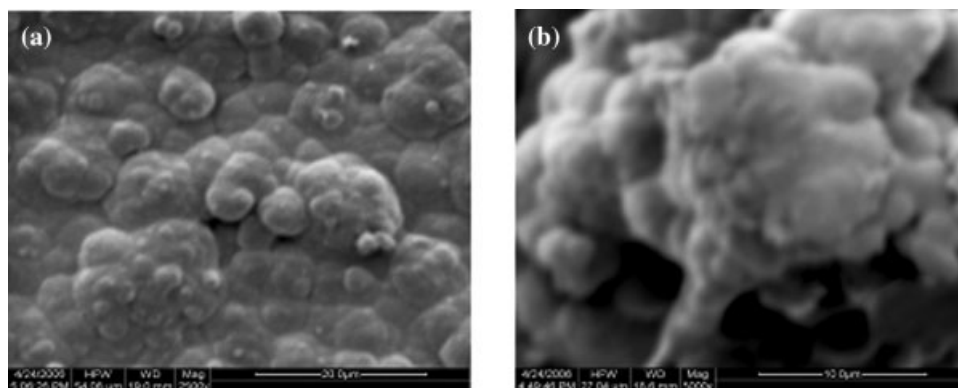
Figure 3 SEM image of PANI/PPy composit film successively deposited polypyrrole (constant potential at 0.8 V for 15 min, containing 0.2*M* pyrrole) on polyaniline film (by cyclic voltammetry at −0.3 V ± 1 V from an aqueous solution containing 0.2*M* aniline) by electrochemical technique (a) ×2500 magnification, (b) ×5000 magnification.
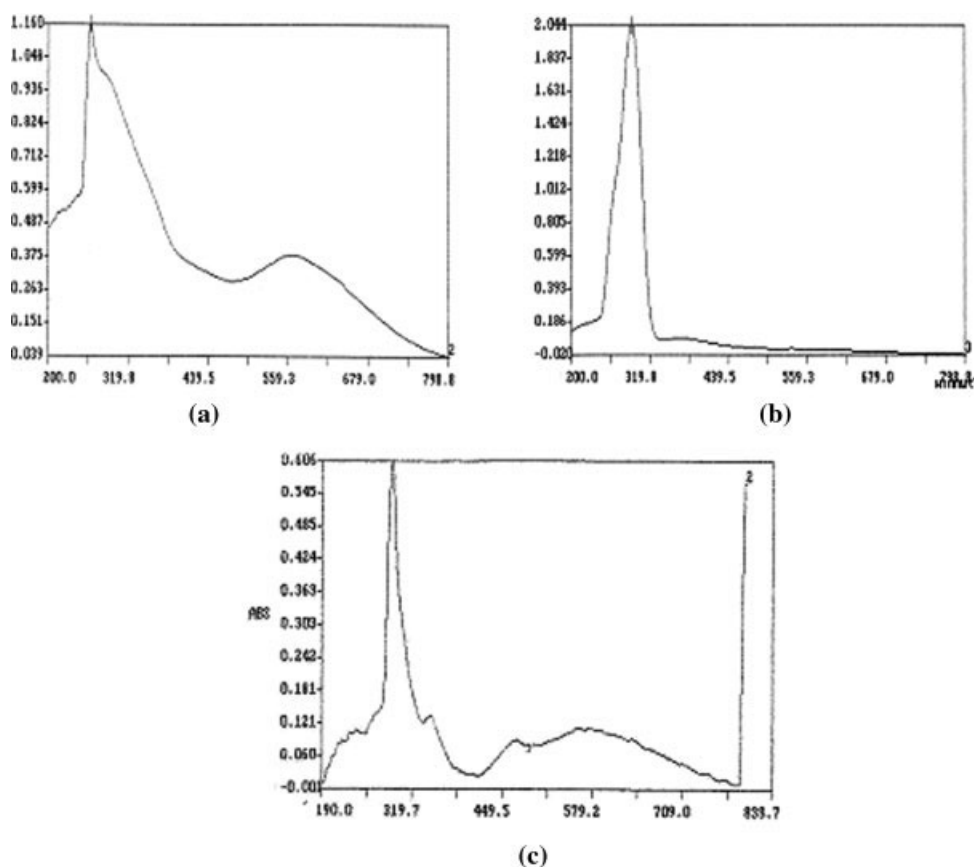
Figure 4 UV–vis spectra of (a) PANI deposited by CV (−0.3 V ± 1.4 V) at tin oxide coated glass electrode doped with H_2SO_4 + $NaClO_4$, (b) PPy film deposited at tin oxide coated glass slide electrode at constant potential 0.8 V doped with P-toluene sulfonate, (c) PANI/PPy polymer film successively deposited each other by electrochemical deposition.

tively.[28,29] The band at ∼ 292 nm present in UV–vis spectrum of PPy film is attributed to the presence of π−π* transition. The spectra of PANI/PPy composite film shows all characteristic bands of PANI (∼ 263, ∼ 380, and ∼ 559 nm) and PPy (291 nm). With additional bands at ∼ 344.7 and ∼ 460 nm. These additional bands conform to the structural changes as shown by IR of PANI/PPy composite film.

The information recorded from UV–vis spectra for various polymer films can help us to find direct and indirect band transition band gap at ultraviolet frequency range. The photon absorption in many amorphous materials is found to obey the Tauc relation,[30] which is given by:

$$\alpha h\nu = B(h\nu - E^{opt})^n$$

where α is the absorption coefficient, hν is the photon energy and B is the temperature dependent parameter describing the degree of materials randomness, and the index n is with the distribution of the density of states. The index $n = 1/2$ corresponds to the direct allowed transition and $n = 2$ represents the indirect allowed transition energy gap.[17]

To determine the direct transition energy gaps, $(\alpha h\nu)^2$ as a function of photon energy (hν) are plotted and are shown in Figure 5(a-c) for PANI, PPy, and composites, respectively. The intercept of these curves on the photon energy axis gives the value of direct transition band gap for these materials. To determine indirect band gap $(\alpha h\nu)^{1/2}$ versus hν (photon energy) are plotted in Figure 6(a-c), respectively. The band gaps are noted from the intercepts of tangent on x-axis to the curve. The direct and indirect transition energies graphs for the PANI, PPy, and PANI/PPy composite films are listed in Table II.

The optical band gap of PANI film in both direct and indirect transition is low 3.25 and 2.75 eV, respectively. PPy film shows high optical band gap 4.01 and 3.94 eV corresponding to direct and indirect allowed transitions. Whereas PANI/PPy composite film sample exhibits the duel band gap character. Figures 5 and 6 clearly show two band gap corresponding to PANI/PPy composite film in both direct (2.9 and 3.0 eV) and indirect allowed transitions (3.85 and 3.4 eV). On the basis of these results, we can say that in the composite formation there is
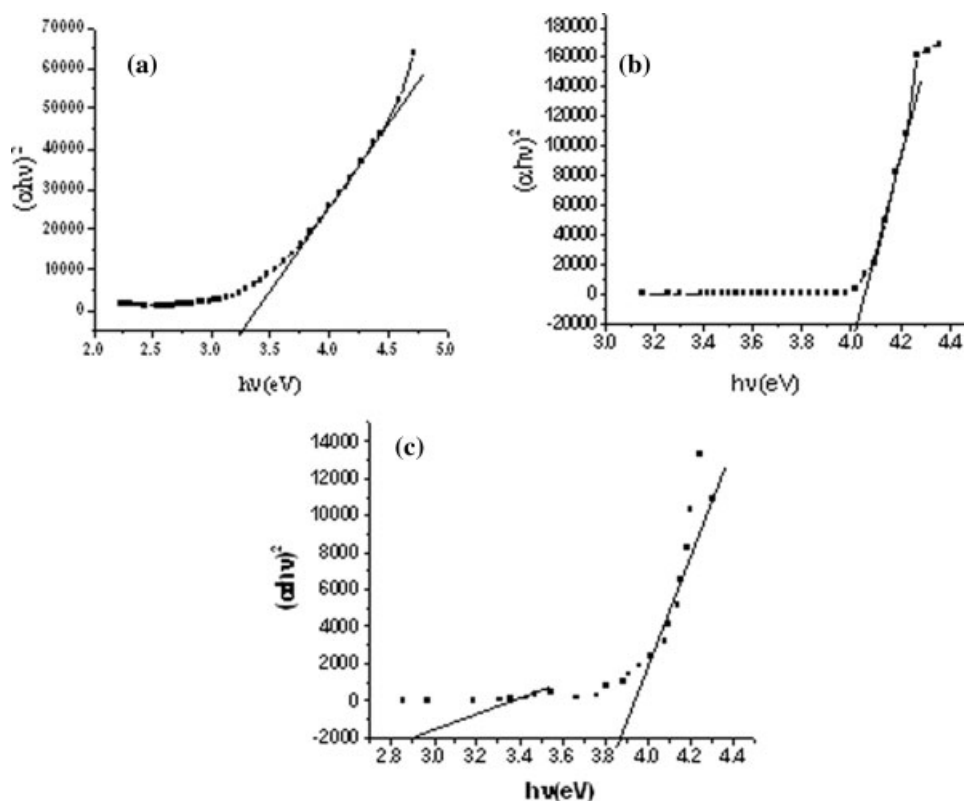
Figure 5 Direct allowed transition band gap of (a) PANI film doped with H_2SO_4 + $NaClO_4$, (b) PPy film doped with p-toluene sulfonate, (c) PANI/PPy composite film.
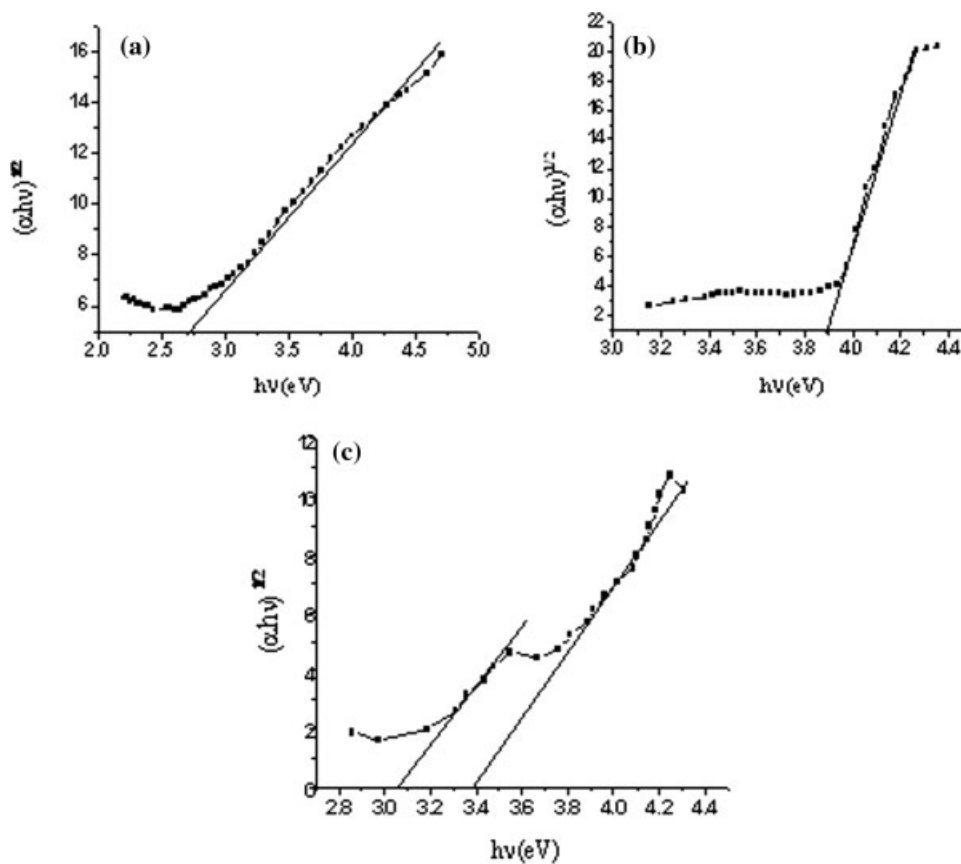
Figure 6 Indirect allowed transition band gap of (a) PANI film doped with H_2SO_4 + $NaClO_4$, (b) PPy film doped with p-toluene sulfonate, (c) PANI/PPy composite film.

TABLE II
**Direct and Indirect Allowed Transition Band gap of PANI, PPy, and PANI/PPy Composite Films**

Sample name	Direct allowed transition band gap (eV)	Indirect allowed transition band gap (eV)
PANI	3.25	2.75
PPy	4.01	3.94
PANI/PPy Composite (1)	2.9	3.0
PANI/PPy Composite (2)	3.85	3.4

reduction in band gap of the composite. The composite behaves as an intermediate band gap material.

Polyaniline is inherently conducting polymer and its conductivity lies in the close ranges to graphite level.[31,32] The reduction in the band gap is due to the dopent $NaClO_4/H_2SO_4$ groups which are incorporated in the polymer chain and there by entering the density of states in band structure. That is why the optical band for aniline is low for direct as well as indirect transition.

Voltammetric behavior of CP at PANI/PPy composite polymer electrode

To understand the electrochemical activity of PANI/PPY composite polymer electrode, the cyclic voltammetry of cefpodoxime proxetil drug in pharmaceutical formulation was carried out. CP was studied systematically in the pH range 1.8 to 12.0 in Britton-Robinson (BR) buffers. At pH 1.8, CP was found to give two peaks (Fig. 7) and these peaks are attributed to the reduction of azomethine group by two electron processes in two steps.[20]
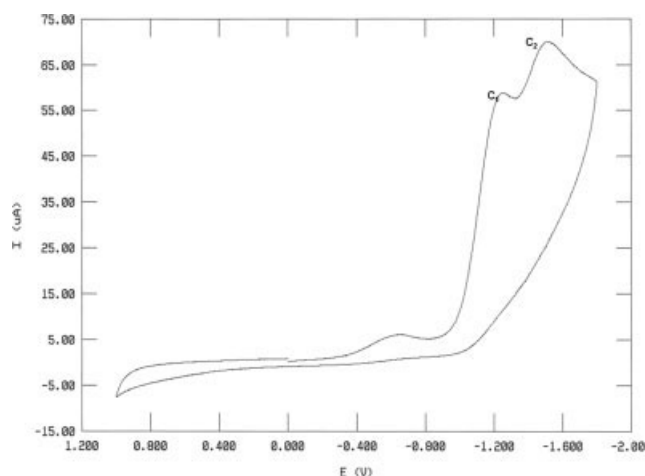
Figure 7 Cyclic voltamogram of cefpodoxime proxetil at PANI/PPy composite polymer electrode in BR buffer at pH 1.8 and scan rate 20 mV/S and concentration 1 mM.

The effect of different scan rate on the electrode process was studied by recording cyclic voltammograms at various sweep rates from 10 to 300 mV/S in 1 mM solution of CP. No evidence of reversibility was observed for the peak in the range 10–300 mV/S. The reduction peak shifted to more negative potential with increase in scan rate as shown in Figure 8(a). The peak current i_p (μA) was found to increase proportionally with square root of scan rate $v^{1/2}$ (mV/S) [Fig. 8(b)], which confirmed the diffusion controlled behavior of the electrode process. The equation noted below refers to BR buffer at 1.8 pH:
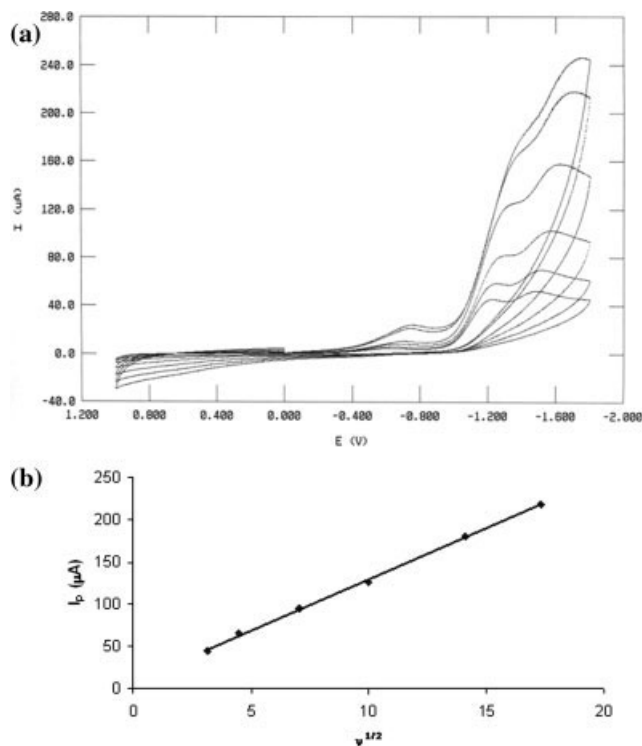
$$i_p(\mu A) = 8.48101 + 12.07342 \; v^{1/2} \; (mV/S)$$

where $r = 0.99952$.

The cyclic voltammograms were also recorded in the concentration range 1–0.01 mM for CP. The peak current for CP at 20 mV/S increases linearly from 0.5 to 10 mM concentration (Fig. 9). The linear regression equation is:

$$i_p(\mu A) = 70.72975 + 9.40566 \, C \; (mM)$$
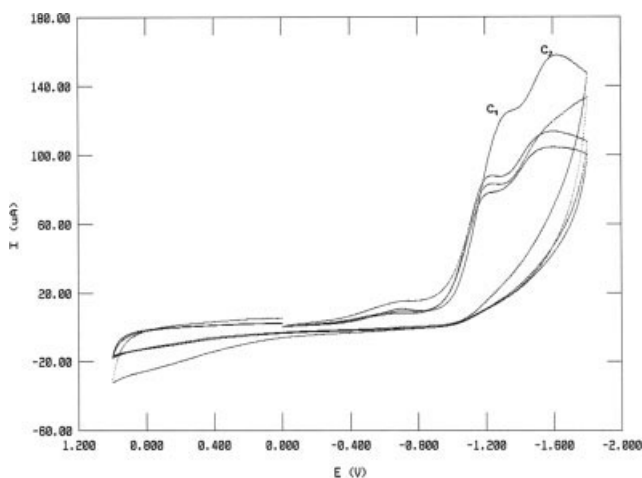
where $r = 0.99957$.

Figure 8 Cefpodoxime proxetil at different scan rates on PANI/PPy compositet polymer electrode (a) cyclic voltammogram from 10 mV/S to 300 mV/S, 0.01 M concentration and pH 1.8, (b) plot of peak current i_p versus square root of scan rate.
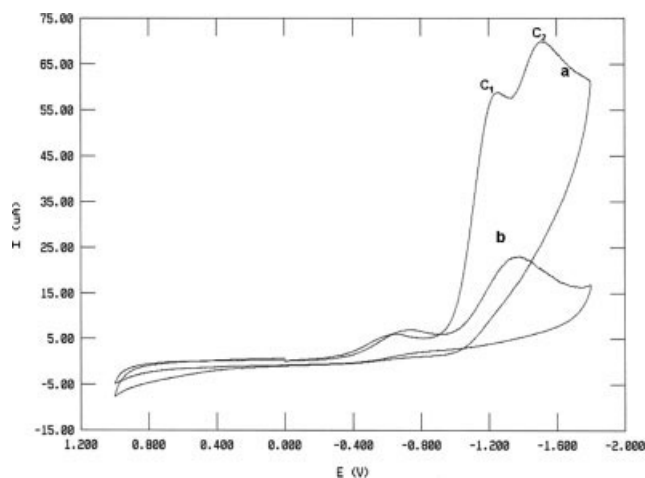
We have compared the results obtained at PANI/PPy electrode for CP with glassy carbon working electrode. Good results were observed at PANI/PPY composite polymer electrode as compared to glassy carbon electrode (Fig. 10). Glassy carbon electrode shows poor current response (23.10 µA) and substantially higher potential with single broad peak at 1.374 V. Whereas PANI/PPy composite polymer electrode shows two reduction peaks with better current response (70.00 µA for C_2). This double peak behavior is due to the reduction of azomethine groups by two electron process in two steps.

Figure 10 Comparative study of cyclic voltammetric response of CP at PANI/PPy composite polymer electrode (a) and at glassy carbon electrode (b).

CONCLUSIONS

PANI/PPy composite polymer film electrode was successfully prepared by electrochemical polymerization on tin oxide coated glass slide. The UV–vis and FTIR studies confirmed the formation PANI and PPy composite. The FTIR and UV–vis and SEM studies showed the existence of certain interaction take place between PANI and PPy. This fact was supported by TGA analysis which showed that the composite possesses higher stability than either PANI or PPy films separately. The unusual dual band gap character of PANI/PPy composite gave intermediate results of band gap corresponding to PANI and PPy films, which indicate that composite film was conducting with better thermal stability. This PANI/PPy composite polymer film showed good electrochemical response towards the cefpodoxime proxetil drug as compared with the glassy carbon electrode. This electrode also showed good adherence to the substrate and provides a sensitive and selective method of CP analysis. The improvement in CP detection indicates good promise for qualitative and quantitative analysis.

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Figure 9 Cyclic Voltammogram of CP at PANI/PPy composite polymer electrode at different concentration from 1 to 10 m*M*.

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