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Abstract

Polyaniline (PANI) thin films have been electrochemically synthesized onto conducting glass substrates. The current study demonstrates that the properties of PANI films depend on the concentration of dopant acid. Well-adherent PANI coatings were obtained under potentiodynamic conditions during sequential scanning of the potential region between -0.35 V and $+1.7$ V with respect to silver/silver chloride. The structural, optical, and morphological properties of PANI films were studied with the aid of X-ray diffraction (XRD), Raman spectroscopy, ultraviolet–visible (UV-Vis) absorption spectroscopy, photoluminescence (PL) spectroscopy, and field-emission scanning electron microscopy (FESEM). Current–voltage (I - V) measurements were performed to study the electrical properties of PANI films. The XRD peaks observed at $2\theta = 15.4^\circ$, 24.2° , and 25.1° confirm the synthesis of emeraldine form of PANI. The strong absorption peaks observed in the UV-Vis absorption spectra at 317 nm (π - π^* interband transition), 371–427 nm (polaron band transition), and 750 nm (bipolaron band transition) confirm the formation of emeraldine oxidation state of PANI. A broad peak attributed in the PL spectra around 395 nm is related to the transition from polaronic band to the π band. All the intense bands attributed in the Raman spectra are associated with the emeraldine oxidation state of PANI. FESEM images reveal the formation of fibers and belts of PANI. Highly conducting thin films of PANI deposited at higher concentrations of dopant acid were confirmed by I - V measurements.

Keywords

Polyaniline, electropolymerization, Raman spectroscopy, emeraldine salt, FESEM

Introduction

Polyaniline (PANI) is one of the widely studied conducting polymers due to its high mobility, good environmental and chemical stability, and its application in various areas like solar cells,¹ sensors,² electrocatalysis,³ supercapacitors,⁴ rechargeable batteries,⁵ electrochromic displays,⁶ light-emitting diodes,⁷ and anticorrosion coating.⁸ The different nanostructures of PANI have been prepared by various techniques, namely electrodeposition,⁹ template synthesis,¹⁰ seeding,¹¹ and interfacial polymerization.¹² However, electrodeposition is the most attractive technique because of its simplicity and ability to tailor the morphological and electrical properties of materials either by varying the condition of bath or growth potential and/or the dopant acid.⁹

PANI basically exhibits three allowed oxidation states characterized by the ratio of imine to amine nitrogens. Their fully reduced state is leucoemeraldine, and fully oxidized state is pernigraniline. The emeraldine form is associated with partially oxidized or reduced state. The

emeraldine base (EB) form of polymer is generally an insulator. Among these, the protonated emeraldine has higher conductivity. The EB form of PANI can be protonated (doped) to form emeraldine salt (ES) by an acid, and the EB form can be dedoped back using a base. The doping process causes a conductivity variation approximately from 10^{-10} to $10 \Omega^{-1} \text{cm}^{-1}$.¹³ The conductivity of PANI films mainly depends on the oxidation state, pH of the electrolyte, and the type of dopant used for protonation.¹⁴

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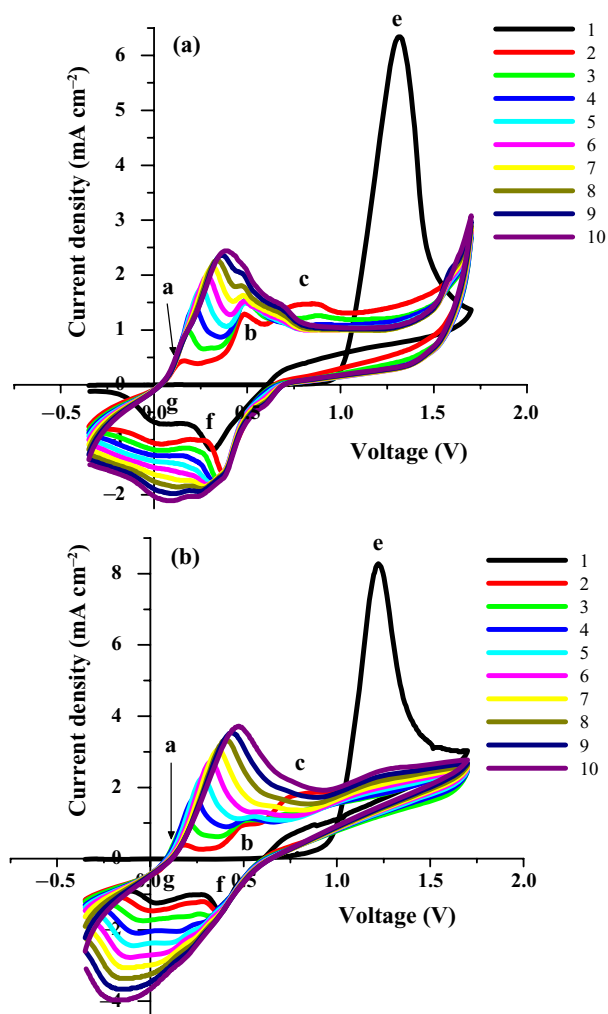


Figure 1. CVs (10 scans) recorded for polyaniline thin films in the presence of (a) 1 M and (b) 2 M concentrations of HClO_4 with respect to Ag/AgCl reference electrode. HClO_4 : perchloric acid; CV: cyclic voltammogram; Ag: silver; AgCl: silver chloride.

Here, we report the effect of dopant acid concentration (pH) on the structural, optical, morphological, and electrical properties of PANI thin films prepared by electropolymerization.

Experimental details

Analytical reagent grade aniline and perchloric acid (HClO_4) were used for the electropolymerization of PANI in an aqueous (double-distilled deionized water) bath. Three-necked electrochemical cell was employed for the deposition of PANI thin films. Fluorine-doped tin oxide-coated glass substrates, silver (Ag)/silver chloride (AgCl), and platinum were used as working, reference, and counter electrodes, respectively. The electrolyte used for electropolymerization was composed of aqueous solution of 0.05 M aniline and different concentrations of dopant

acid. The protonation process in the benzoid rings was controlled by HClO_4 . PANI thin films were electropolymerized by sweeping the potential between -0.35 V and $+1.70$ V versus Ag/AgCl reference for 10 numbers of scans. All the experiments were performed at room temperature without stirring. Well-adherent, greenish-colored thin films of PANI were deposited for 1 M and 2 M HClO_4 . The samples were dried in open air, and subsequently, various properties were studied. Cyclic voltammetry was carried out using potentiostat/galvanostat AUTOLAB, $\mu 3\text{AUT} 70762$ (Metrohm, USA). The prepared thin films were characterized by means of X-ray diffraction (XRD), using a Bruker D8 advance diffractometer (Bruker, Billerica, Massachusetts, USA). Optical absorption measurements were carried using a JASCO ultraviolet-visible (UV-Vis) spectrophotometer (Tokyo, Japan). Photoluminescence (PL) spectra were recorded using a JASCO photometer. The surface morphology was studied using HITACHI, S 4800 field-emission scanning electron microscope (FESEM; Tokyo, Japan). Raman spectra were obtained with Invia Renishaw Raman microscope (Renishaw Plc, Gloucestershire, UK) coupled with Philips charge-coupled device camera (Philips, Amsterdam, The Netherlands) with 785 nm excitation laser. The electrical measurements, that is, current-voltage (I - V) characteristics, were performed by two-point probe measurement with Ag wires attached to the Ag contacts made on PANI film by thermal evaporation.

Results and discussion

The PANI films electropolymerized in the presence of 1 M and 2 M concentration of HClO_4 were characterized using a range of characterization techniques to study the structural, optical, morphological, and electrical properties.

Figure 1(a) and (b) shows the cyclic voltammograms (CVs) of electrolyte containing aniline monomer with 1 M and 2 M concentrations of HClO_4 . The CVs were recorded for 10 successive cycles at a scan rate of 5 mV s^{-1} for potential range from -0.35 to 1.70 V. The redox peak attributed around -1.30 V and -1.20 V for the first cycle of CV in the presence of 1 M and 2 M HClO_4 are associated with the oxidation of aniline oligomers.¹⁵ The decrease in growth rate upon repeating the potential cycle is explained by the poor electrochemical activity of the PANI film formed on the electrode surface due to the difficulty in maintaining the protonated and doped structures of the polymers.¹⁶ The successive anodic scan shows the presence of three distinct peaks marked as “a”, “b”, and “c” are assigned to the oxidation of fully reduced form of PANI (leucoemeraldine) to its polaron form, oxidation of intermediate species, and final transition from delocalized polaronic state to bipolaron or quinoid form, respectively.¹⁵ The peak potential of peak a is shifted toward higher anodic side with successive scanning could be due to the

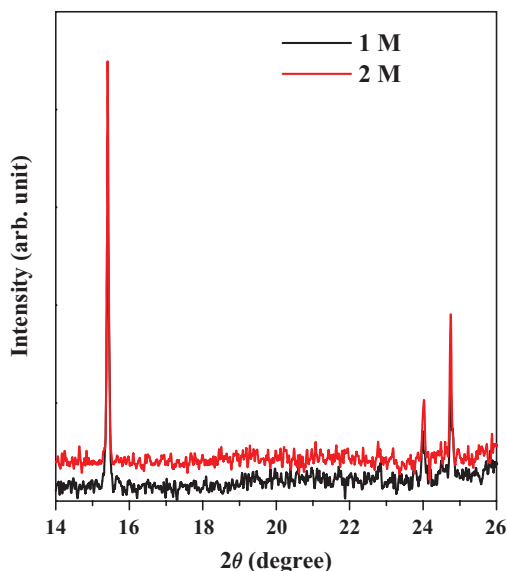


Figure 2. XRD pattern for polyaniline thin film electropolymerized in the presence of 1 M and 2 M concentrations of HClO_4 . XRD: X-ray diffraction; HClO_4 : perchloric acid.

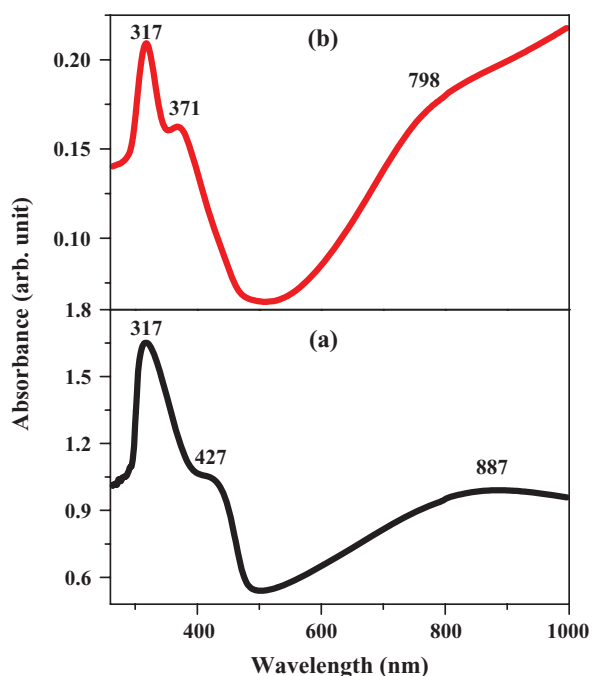


Figure 3. Optical absorption spectra of polyaniline thin films recorded in the presence of (a) 1 M and (b) 2 M concentrations of HClO_4 . HClO_4 : perchloric acid.

degradation of PANI deposited in the previous scan. After completing 10 cycles, greenish-colored thin films were deposited which confirms the formation of ES of PANI.

Figure 2 shows XRD pattern of doped PANI thin film obtained from different concentrations of dopant acid. Intense bands observed approximately at 2θ of 15.4° ,

24.2° , and 25.1° confirm the synthesis of ES of PANI.¹⁷ The crystallinity of PANI thin film deposited in the presence of 2 M HClO_4 was found to be improved due to the change in surface morphology and compactness. The values of full width half maximum, 0.06° and 0.04° , were calculated for PANI thin film deposited with 1 M and 2 M HClO_4 . Indeed, we observed the change in the morphology as well as compactness for the film grown at 1 M and 2 M concentration of HClO_4 . The optical absorption spectra are useful in order to investigate the oxidation state of PANI. Figure 3 depicts the optical absorption spectra of PANI films obtained during the electropolymerization at (a) 1 M and (b) 2 M concentrations of HClO_4 at a fixed scan speed of 5 mV s^{-1} . Three strong absorption peaks attributed at 317, 371–427, and $>750 \text{ nm}$ correspond to the formation of PANI in ES form.

The peak observed at 317 nm is attributed to the transition of electrons from the highest occupied molecular orbital to the lowest unoccupied molecular orbital which is related to the π - π^* electronic transition.¹⁸ The other two absorption peaks observed at about 371–427 nm and above 798–887 nm are associated with the polaron and bipolaron band transitions of PANI, respectively.¹⁸ Basically the polaron and bipolaron are the charge carriers in conducting PANI. In our study, it is observed that at 1 M and 2 M concentration of the dopant acid features related to both the polaron and the bipolaron are attributed, while at 2 M dopant concentration the formation of bipolaron increases due to availability of more hydrogen ions required for the protonation. This indicates that the optical properties of PANI are affected by dopant ions. Figure 4 demonstrates the PL spectra of PANI thin films electropolymerized for (a) 1 M and (b) 2 M concentration of HClO_4 . The samples were excited at 270 nm wavelength. In both PL spectra, four peaks are attributed with slight variation in wavelength. The peak centered around 395–397 nm and 463–466 nm originated due to π^* - π transition of the benzoid units and de-excitation from polaron band, respectively.¹⁹ The origin of the peak attributed at 607–613 nm is unknown. The weak peak appeared at 722 nm is associated with the bipolaron de-excitation. As the concentration of dopant acid increases, the relative intensity of the peak originated due to the de-excitation from polaron band also increases.

The resonance Raman spectra of PANI at different dopant acid concentrations were recorded using 785 nm excitation are shown in Figure 5. The bands that appeared in the wave number range of 1100 – 1700 cm^{-1} correspond to the stretching modes of different bonds. Raman band at 1600 cm^{-1} is assigned to the C–C stretching vibration of benzene ring. The band at 1510 cm^{-1} is assigned to N–H deformation vibrations. The band at 1341 – 1352 cm^{-1} yields information about carrier vibrations in PANI in C–N⁺ polaronic structure. The band at 1245 cm^{-1} can be assigned to the C–N stretching mode of polaronic unit. The intense band observed at 1170 cm^{-1} is related to C–H

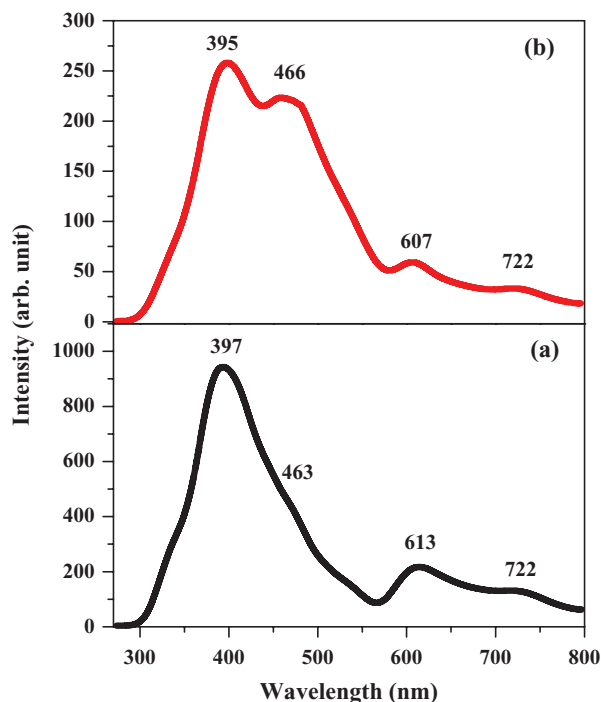


Figure 4. PL spectra of polyaniline thin films electropolymerized in presence of (a) 1 M and (b) 2 M dopant acid concentrations. PL: photoluminescence.

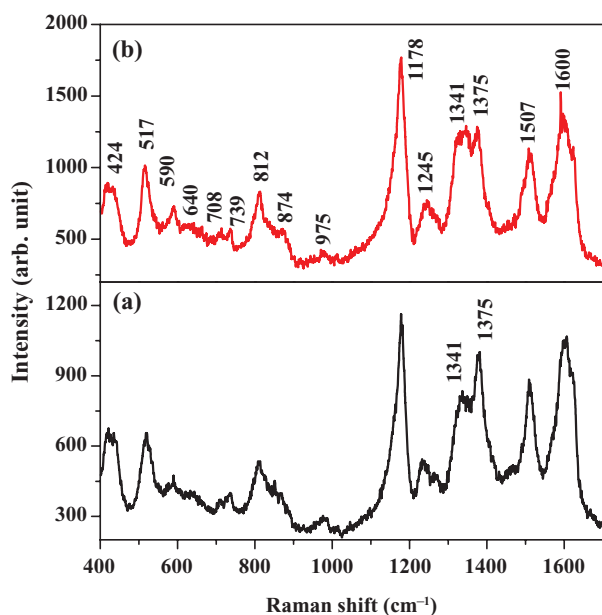


Figure 5. Raman spectra of polyaniline thin films electropolymerized in the presence of (a) 1 M and (b) 2 M dopant acid concentrations.

vibrations of aromatic rings. The band from 1000 to 400 cm^{-1} gives information about deformation vibrations of the benzene rings. The bands at 874, 812, and 424 cm^{-1} are in plane and out of plane vibrations of ring of

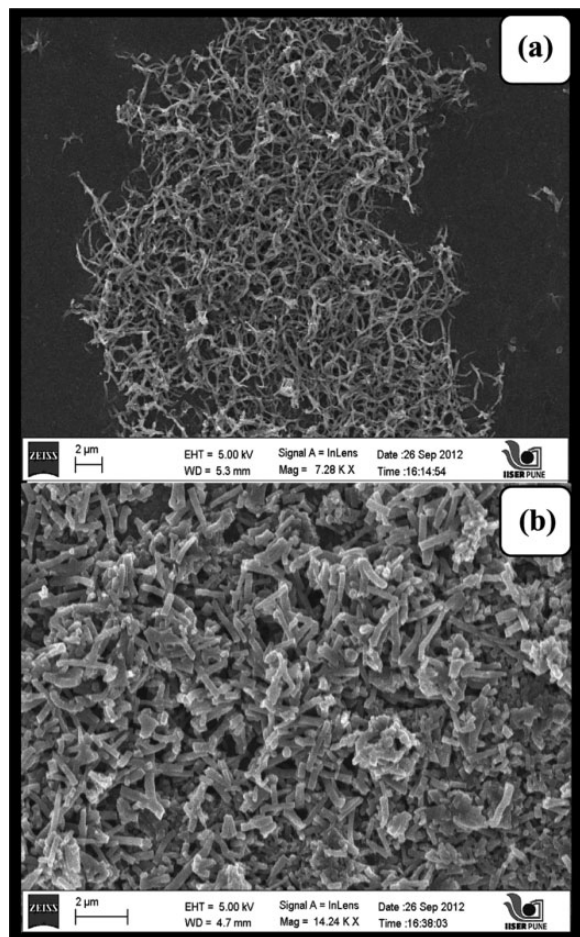


Figure 6. SEM images of polyaniline thin films deposited in the presence of (a) 1 M and (b) 2 M HClO_4 . HClO_4 : perchloric acid; SEM: scanning electron microscopy.

protonated emeraldine form of PANI.²⁰ The band observed at 1375 cm^{-1} , is generally present in the less conducting form of PANI, which disappeared for the PANI films deposited with higher (2 M) concentration of HClO_4 . The morphology of the PANI electropolymerized in the presence of 1 M and 2 M concentrations of dopant acid is shown in Figure 6(a) and (b), respectively. Long fibers with few microns length and approximately 50–100 nm diameter are observed in SEM micrographs of PANI films electropolymerized in the presence of 1 M dopant acid, whereas the microbelts and microrods of diameter approximately 300 nm are formed in the presence of 2 M dopant acid concentration. Both films were compact; however, the only film grown at 2 M dopant acid concentration fully deposited all over the substrate could be due to the high current flow from electrolyte to the electrode.

Figure 7 shows the current density–voltage (J - V) curves of PANI films electropolymerized in 1 M and 2 M concentrations of dopant acid. The J - V characteristics of the PANI

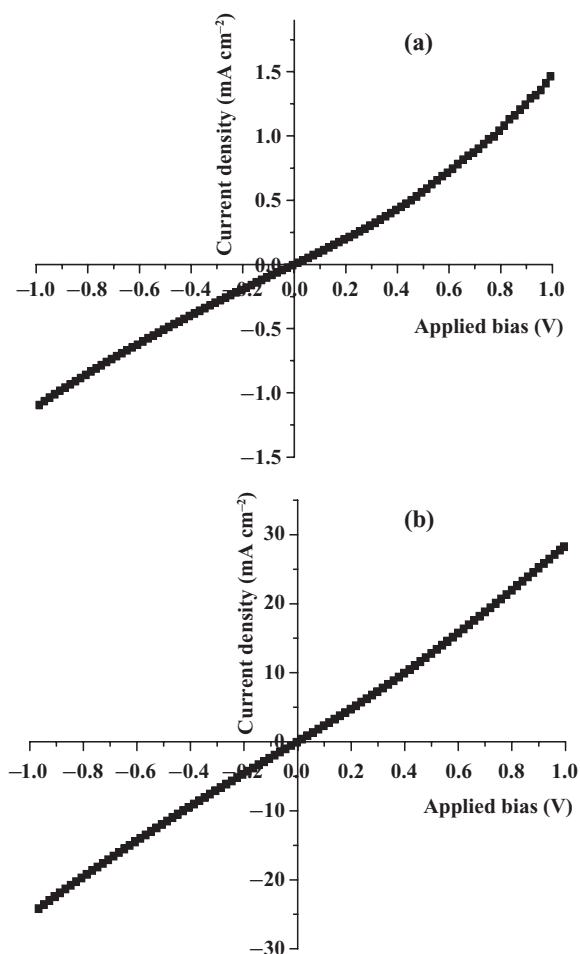


Figure 7. *J-V* characteristics of polyaniline thin films deposited in the presence of (a) 1 M and (b) 2 M concentration of HClO_4 . *J-V*: current density–voltage; HClO_4 : perchloric acid.

films recorded at room temperature were shown to be ohmic in nature. The values of conductivity calculated for PANI film electropolymerized with 1 M and 2 M HClO_4 were 1.89×10^{-5} and $2.11 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, respectively.

Conclusion

PANI nanofibers and belts were successfully electropolymerized in the presence of HClO_4 . The effect of concentration of HClO_4 on various properties of PANI was extensively studied. The XRD peaks observed at approximately 15.4° , 24.2° , and 25.1° confirm the formation of ES PANI. Highly crystalline PANI films were electropolymerized in the presence of 2 M dopant acid. Optical absorption spectra showed absorption peak for $\pi-\pi^*$, polaron, and bipolaron transitions. A broad peak attributed in the PL spectra around 395 nm is related to the transition from polaronic band to the π band. All the intense bands attributed in the Raman spectra are associated with the emeraldine oxidation state of PANI. FESEM images reveal that the formation of two distinct morphology long

fibers and belts of PANI depend on the dopant acid concentration. Highly conducting thin films of PANI are obtained at higher concentration of dopant acid.

Funding

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References

1. Tan F, Qun S, Wu J, et al. Electrodeposited polyaniline films decorated with nano-islands: characterization and application as anode buffer layers in solar cells. *Sol Energy Mater Sol Cells* 2011; **95**: 440–445.
2. Zeng FW, Liu XX, Diamond D, et al. Humidity sensors based on polyaniline nanofibres. *Sensors Actuat B: Chem* 2010; **143**: 530–534.
3. Mallick K, Witcomb MJ, Dinsmore A, et al. Fabrication of a metal nanoparticles and polymer nanofibers composite material by an in situ chemical synthetic route. *Langmuir* 2005; **21**: 7964–7967.
4. Shaikh SM, Lim JY and Joo OS. Electrochemical supercapacitors of electrodeposited PANI/H-RuO₂ hybrid nanostructure. *Curr Appl Phys* 2013; **13**: 758–761.
5. Grgur BN, Ristic V and Jugovic BZ. Polyaniline as possible anode materials for the lead acid batteries. *J Power Sources* 2008; **180**: 635–640.
6. Mortimer RJ, Dyer AL and Reynolds JR. Electrochromic organic and polymeric materials for display applications. *Displays* 2006; **27**: 2–18.
7. Yu G, Gao J, Hummelen JC, et al. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor–acceptor heterojunctions. *Science* 1995; **270**: 1789–1791.
8. Chaudhari S and Patil PP. Inhibition of nickel coated mild steel corrosion by electrosynthesized polyaniline coatings. *Electrochim Acta* 2011; **56**: 3049–3059.
9. Baba A, Advincula RC and Knoll W. In situ investigations on the electrochemical polymerization and properties of polyaniline thin films by surface plasmon optical techniques. *J Phys Chem B* 2002; **106**: 1581–1587.
10. Wang CW, Wang Z, Li MK, et al. Well-aligned polyaniline nano-fibril array membrane and its field emission property. *Chem Phys Lett* 2001; **341**: 431–434.
11. Zhang X, Goux WJ and Manohar SK. Synthesis of polyaniline nanofibers by nanofiber seeding. *J Am Chem Soc* 2004; **126**: 4502–4503.
12. Huang J and Kaner RB. A general chemical route to polyaniline nanofibers. *J Am Chem Soc* 2004; **126**: 851–855.
13. Salavagione HJ, Sanchis C and Moralln E. Friendly conditions synthesis of platinum nanoparticles supported on a conducting polymer: methanol electrooxidation. *J Phys Chem C* 2007; **111**: 12454–12460.
14. Focke WW, Wnek GE and Wei Y. Influence of oxidation state, pH, and counterion on the conductivity of polyaniline. *J Phys Chem* 1987; **91**: 5813–5818.

15. Hong SY and Park SM. Electrochemistry of conductive polymers. pH dependence of polyaniline conductivities studied by current-sensing atomic force microscopy. *J Phys Chem B* 2005; **109**: 9305–9310.
16. Stilwell DE and Park SMJ. Electrochemistry of conductive polymers II. Electrochemical studies on growth properties of polyaniline. *Electrochem Soc* 1988; **135**: 2254–2262.
17. Chaudhari HK and Kelkar DS. X-ray diffraction study of doped polyaniline. *J Appl Polym Sci* 1996; **62**: 15–18.
18. Abdulla HS and Abbo AI. Optical and electrical properties of thin films of polyaniline and polypyrrole. *Int J Electrochem Sci* 2012; **7**: 10666–10678.
19. Banerjee S, Sarmah S and Kumar A. Photoluminescence studies in HCl-doped polyaniline nanofibres *J Opt* 2009; **38**: 124–130.
20. Nascimento GM and Temperini MA. Studies on the resonance Raman spectra of polyaniline obtained with near-IR excitation. *J Raman Spectroscopy* 2008; **39**: 772–778.