

Electrochemical Preparation and Characterization of Conducting Copolymer/Silica Composite

Al-Nakib Chowdhury,¹ Mohammad Rezaur Rahman,² Dewan Sadequ Islam,¹
Farhana Sultana Saleh¹

¹Department of Chemistry, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

²Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

Received 7 August 2007; accepted 5 April 2008

DOI 10.1002/app.28506

Published online 10 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A composite based on organic copolymer and inorganic oxide, polyaniline/poly *o*-toluidine/silica (PANI/POT/SiO₂), has been synthesized successfully by a simple electrochemical method. The composite film was found to be deposited on a Pt substrate by sweeping the potential between -0.2 and $+1.0$ V versus a saturated calomel electrode with a scan rate of 100 mV/s. The polymeric composite film thus obtained was characterized by scanning electron microscopy, infrared spectroscopy, conductance measurement, and cyclic voltammetry techniques. Incorporation of silica in the copolymer results a clear difference in surface morphology compared with the bulk homo- and copolymers. Further evidence of silica in the composite was achieved by infrared spectral analysis.

Indeed, a chemical analysis of the composite matrix showed a content of as high as 25% SiO₂ in the composite thus prepared. Based on the results of cyclic voltammetric analysis, the composite electrode as prepared was found to show good electrochemical stability even at high positive potentials. It also exhibited excellent electroactivity even after incorporation of silica in the matrix. The electroactive composite film was thus examined as electrode modifier to study the redox behavior of ferrous/ferric (Fe²⁺/Fe³⁺) and hydroquinone/benzoquinone (H₂Q/Q) couples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 808–816, 2008

Key words: composites; conducting polymers; matrix

INTRODUCTION

The application area of polymers is already wide, and it has a visible tendency to grow wider. As an outcome of the developments in polymer technology, conductive polymers can form substitutes for naturally conductive materials. Conductive polymers are being used commonly for various purposes including rechargeable batteries, electronic devices, functional electrodes, electrochromic devices, optical switching devices, sensors, and so on.^{1–7} Polyaniline (PANI) is one of the conducting polymers that have been preferably used in many practical applications as indicated earlier. The large-scale application of PANI is sometimes limited by the difficulty of its processing by conventional methods, less stability, and electroactivity in the ambient and extreme environmental and electrochemical conditions. These shortcomings have usually been overcome by the synthesis of new conjugated polymers whose structures have been suitably modified to introduce processibility and better material properties without compromising the electrical conductivity of the system.^{8–11}

Besides, multicomponent matrices, such as copolymer, bilayer, and composites, are also known to be synthesized to achieve desired properties of a material. In view of this, copolymer of aniline and *o*-toluidine seems to be interesting to be studied as the individual homo polymers have already been addressed for their wide technological application. Moreover, in a copolymer of aniline and *o*-toluidine, it is expected to combine and modify the electrical, chemical, and physical properties of the poly *o*-toluidine (POT) and PANI and thus combine the advantages of POT with PANI^{12–16} in the single copolymer matrix.

Indeed, preparation of composites of conducting polymers has already been considered to provide a potential solution to the processibility problem as well as to enhance the material properties with desirable physical and mechanical characteristics.³ Composite made of PANI and silica (SiO₂) is worth mentioning and previously prepared by both chemical and electrochemical methods.^{17–21} It is expected that the presence of SiO₂ in the polymer composite could develop surface property (e.g., luminescence, effective surface area, surface hardness, etc.) of that composite.^{22–24} To our knowledge, no attempt has yet been made to prepare copolymer/silica composite either by chemical or electrochemical means.

In this article, we report synthesis of a copolymer/silica composite, i.e., PANI/POT/SiO₂ by anodic

Correspondence to: A. N. Chowdhury (nakib@chem.buet.ac.bd).

oxidation of monomers onto a Pt electrode in an aqueous solution containing colloidal SiO_2 and its characterization by cyclic voltammetry (CV), scanning electron microscopy (SEM), infrared (IR) spectroscopy, and conductivity measurements. In addition, stability, i.e., the extent of degradation on overoxidation, and the redox response of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{H}_2\text{Q}/\text{Q}$ systems on this copolymer/silica composite are also examined.

EXPERIMENTAL

Aniline and *o*-toluidine were supplied from E. Merk (Darmstadt, Germany) and were distilled twice under nitrogen atmosphere before use. SiO_2 was acquired from BDH (Poole, UK). Sulfuric acid (H_2SO_4), also from E. Merk (Darmstadt, Germany), was of A. R. grade and used as received. Thin films of PANI, POT, copolymer PANI-POT, and copolymer/composite PANI/POT/ SiO_2 were synthesized electrochemically on the platinum (Pt) substrates under cyclic voltammetric conditions in a single compartment glass cell. A three electrode cell geometry was employed during the electrochemical polymerization in which Pt foil as working (0.25 cm^2) and counter electrode (1 cm^2), and a saturated calomel electrode (SCE) as the reference electrode were used. The films were electrodeposited from a solution containing monomers (0.5M each) and 0.8M supporting electrolyte (H_2SO_4) by applying sequential linear potential at a scan rate of 100 mV/s between -0.2 and $+1.0 \text{ V}$ versus SCE. Aqueous colloidal suspension of SiO_2 used for the copolymer/silica composite synthesis was prepared as described elsewhere.¹⁸ In this study, aqueous colloidal suspension of SiO_2 was prepared by adding 2.0 g of SiO_2 powder (mesh size = 100) to water followed by beating the mixture for 2 h . The resulted dispersion was then allowed to settle for 2 h . During this span of time, relatively bigger SiO_2 particles were found to sediment at the bottom of the container. The smaller SiO_2 particles remain in the supernatant water as colloidal particles. The colloidal solution was then decanted and used for PANI/POT/ SiO_2 composite preparation. After deposition, the films were washed with distilled water to remove any unbounded supporting electrolyte and SiO_2 . The surface morphologies of the solids were examined using a scanning electron microscope (Philips XL 30, Eindhoven, Holland). An IR spectrophotometer (IR-470, Shimadzu, Tokyo, Japan) was used for IR measurements in the region $4000\text{--}400 \text{ cm}^{-1}$. A conventional two point-probe method was employed to measure the compressed pellet d.c. conductivity of the solids at room temperature. Chemical analysis of the composite was done by the Hydrofluorization method.²⁵ For this purpose, 1 g of the composite sample was

treated with 10 mL of HF and 1.0 mL of H_2SO_4 . The cyclic voltammetric measurements were performed using a potentiostat/galvanostat (HABF 151, Hokuto Denko, Tokyo, Japan) coupled with an X-Y recorder (Riken Denshi, Tokyo, Japan). Throughout the electrochemical studies, anaerobic conditions were maintained with nitrogen gas atmosphere.

RESULTS AND DISCUSSION

Typical CVs of electrochemical preparations of (a) PANI/POT copolymer and (b) PANI/POT/ SiO_2 composite films are given in Figure 1. The copolymer PANI/POT was deposited by sweeping the

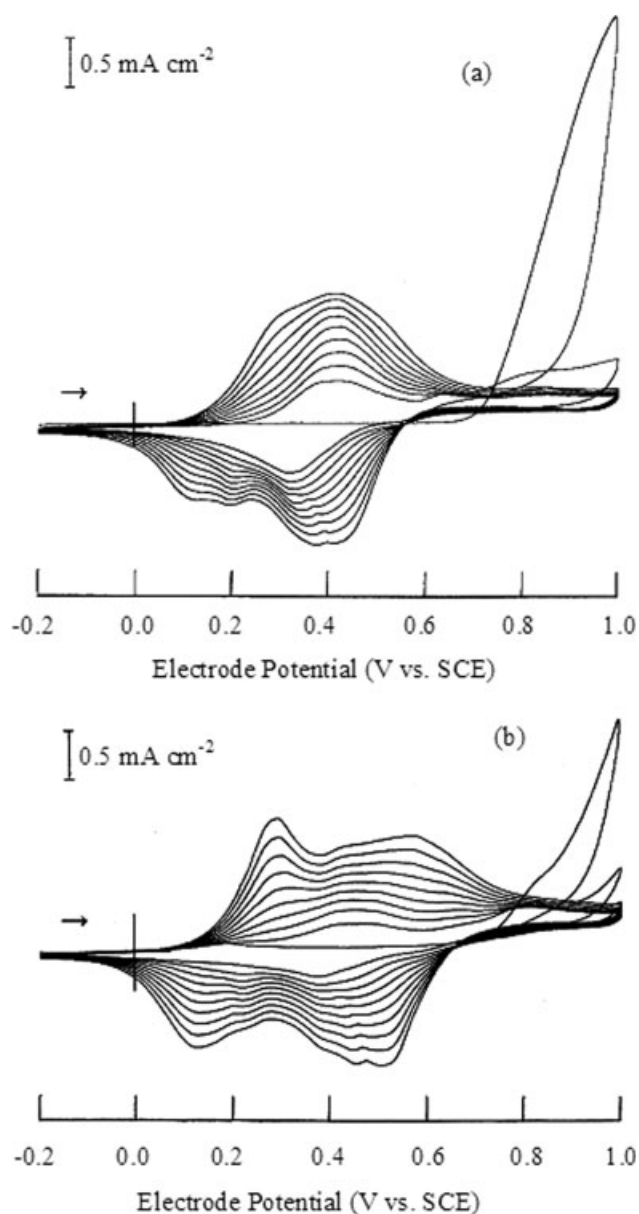


Figure 1 CV during electrochemical synthesis of (a) PANI/POT and (b) PANI/POT/ SiO_2 composite on a Pt electrode.

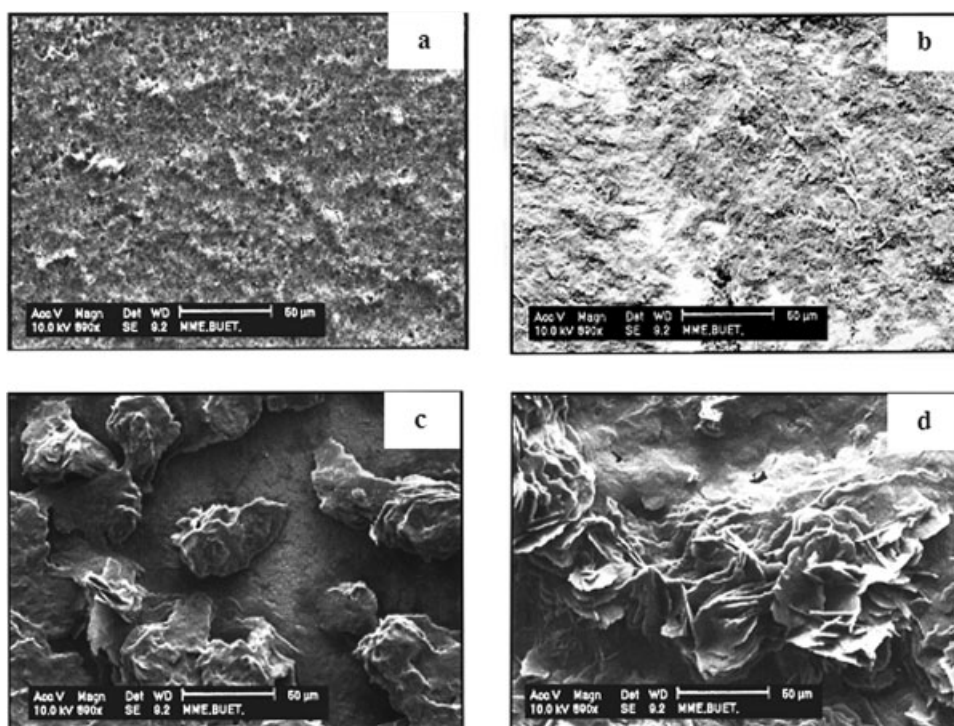


Figure 2 SEM Micrographs of (a) PANI, (b) POT, (c) PANI/POT, and (d) PANI/POT/SiO₂.

potential between -0.2 to $+1.0$ V versus SCE with scan rate of 100 mV s^{-1} from the $0.8\text{M H}_2\text{SO}_4$ electrolytic solution containing 0.5M of each monomer whereas the PANI/POT/SiO₂ composite film was deposited in the same way from the colloidal SiO₂ suspension containing $0.8\text{M H}_2\text{SO}_4$ and 0.5M of each monomer. The CV (a) shows a sharp rise in current at a potential *ca.* $+0.75$ V versus SCE where a deep blue deposits were observed to be formed on the Pt substrate. As the sweeping repeated, i.e., in the second and subsequent cycles, the formation of more deposits on the substrate took place. Similar observation can also be seen in the CV for the PANI/POT/SiO₂ composite (b) and also during electropolymerization of aniline and *o*-toluidine in the absence of silica reported earlier.^{26–28} The anodic peak at *ca.* $+0.75$ V may indicate the oxidation of aniline and *o*-toluidine monomers to yield the polymers as blue deposit. The other anodic peak at *ca.* $+0.40$ V can be assigned to the oxidation of the polymeric segment as deposited on the electrode whereas the cathodic peak at *ca.* $+0.35$ V may be due to the reduction of the polymer matrix. The deep blue color of the deposits turned to greenish-yellow when potential sweeping approached to the cathodic direction at *ca.* $+0.35$ V or below. It is expected that during polymerization of the monomers from the electrolytic medium containing SiO₂ suspension, SiO₂ particles could be incorporated to the polymer matrix and thus formed the composite PANI/POT/SiO₂. As

SiO₂ particles have negative surface charge²⁹ and both the PANI and POT chains are polycations,^{30,31} so it is reasonable to expect that the electrostatic force of attraction may play dominant role in anchoring the SiO₂ particles in the polymer matrices to form the PANI/POT/SiO₂ composite.

Although, the CVs for the synthesis of PANI/POT [Fig. 1(a)] and PANI/POT/SiO₂ [Fig. 1(b)] seem to be identical, experimentally it has been evidenced that the composite contains fairly good amount of silica in it, indicating the formation of PANI/POT/SiO₂ composite under the experimental condition employed. The composite thus synthesized was analyzed for its silica content. The result indicated a silica content of approximately 25% in the sample. SEM observations clearly revealed differences between the surface morphologies of the matrices with and without SiO₂. Figure 2 shows the SEM microphotographs of the polymers and the composite matrices. It can be seen that a grain-like morphology appears when PANI is prepared electrochemically from the electrolytic solution containing H₂SO₄ and the surface looks to be uniformly covered with the PANI grains (a). Similar morphology for PANI synthesized electrochemically was also reported previously.³² In case of POT (b), the surface morphology seems to be composed of fibrils having short-length and aggregated compactly over the substrate. The surface uniformity and homogeneity of POT seem to be different than that observed for PANI. On the

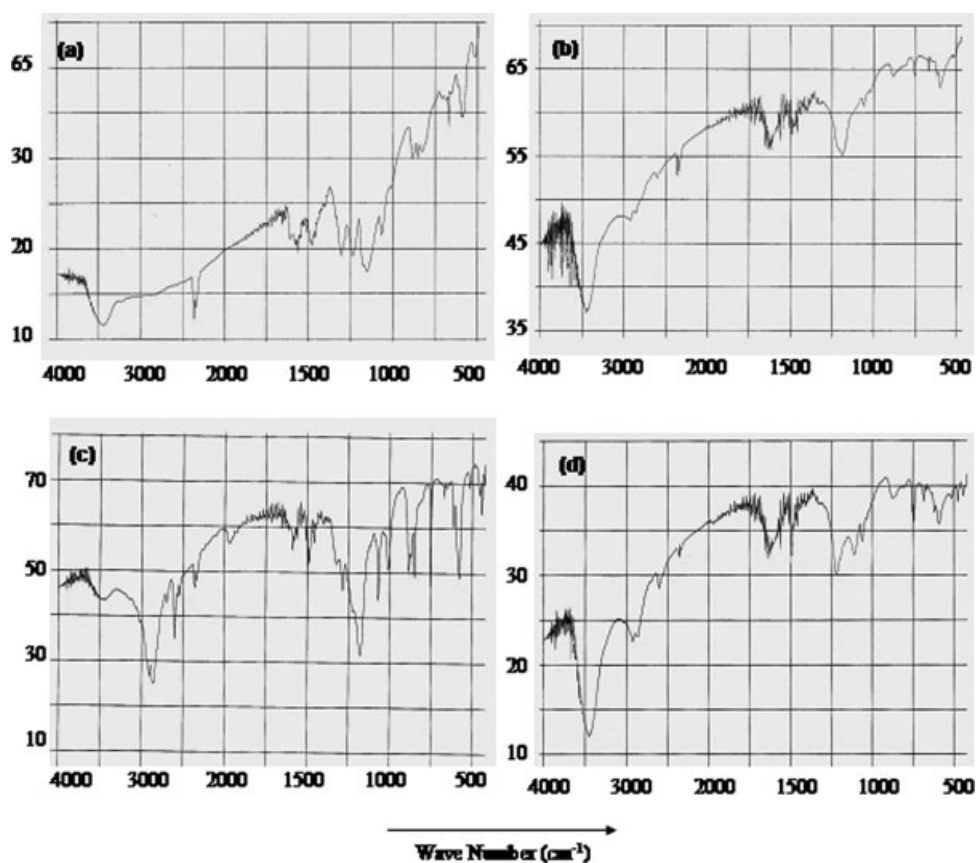


Figure 3 IR spectra of (a) PANI, (b) POT, (c) PANI/POT, and (d) PANI/POT/SiO₂.

other hand, when copolymer PANI/POT (c), as composed of PANI and POT segments, was synthesized, its surface morphology found to be completely different than that of PANI or POT. The morphology of the copolymer seems to be composed of rigid solid particles having irregular shape and size. The resulting surface seems to be rather nonuniform and the particles are randomly dispersed on the substrate. The composite, PANI/POT/SiO₂ (d), on the other hand, formed flake like morphology, packed together, and made the whole surface fully covered with flakes. The SEM observations, thus, predicted quite a dissimilar surface morphologies of the samples studied. The observed dissimilar morphological features of PANI/POT and PANI/POT/SiO₂ may result from the presence of SiO₂ in the composite matrix. However, the observed dissimilar morphological features of the PANI, POT, PANI/POT, and PANI/POT/SiO₂ may also suggest that their electrode behavior for electrochemical processes could be different. The presence of SiO₂ particle in PANI/POT/SiO₂ was further evidenced by the IR study. Figure 3 shows the IR spectra of the PANI (a), POT (b), PANI/POT (c), and PANI/POT/SiO₂ (d) samples. The principal absorptions for PANI and POT are 3438, 2856, 2360, 1655, 1544, 1303, 1218, 1109,

and 850 cm⁻¹. These values are consistent with that of the bulk PANI and POT samples reported elsewhere.^{33–35} The peak appeared in case of bulk POT [Fig. 3(b)] at 2856 cm⁻¹ (C–H stretching) was also present in the spectra of the copolymer without [Fig. 3(c)] and with [Fig. 3(d)] silica and absent in case of bulk PANI [Fig. 3(a)]. A new peak was observed at 1109 cm⁻¹ along with the peaks observed for bulk PANI and POT in the spectrum of PANI/POT/SiO₂ composite [Fig. 3(d)], corresponds to the SiO₂ entity¹⁹ in the sample and thus gives further evidence for the presence of SiO₂ in the PANI/POT/SiO₂ composite. Attempt was also made to evidence SiO₂ further by analyzing the PANI, POT, and PANI/POT/SiO₂ samples by XRD. The XRD patterns of all the samples were found to be identical to each other and thus made it impossible to distinguish between the samples studied by XRD. Typical X-ray diffraction patterns as function of the Bragg angle, 2θ at λ = 1.54 Å for the samples are presented in Figure 4. The result shows that the patterns consist of only diffuse X-ray scattering; the diffuse signals appear in the patterns should correspond amorphous nature of the samples. This observation may suggest that silica particles that incorporated into the matrix have no influence on its structure. Therefore,

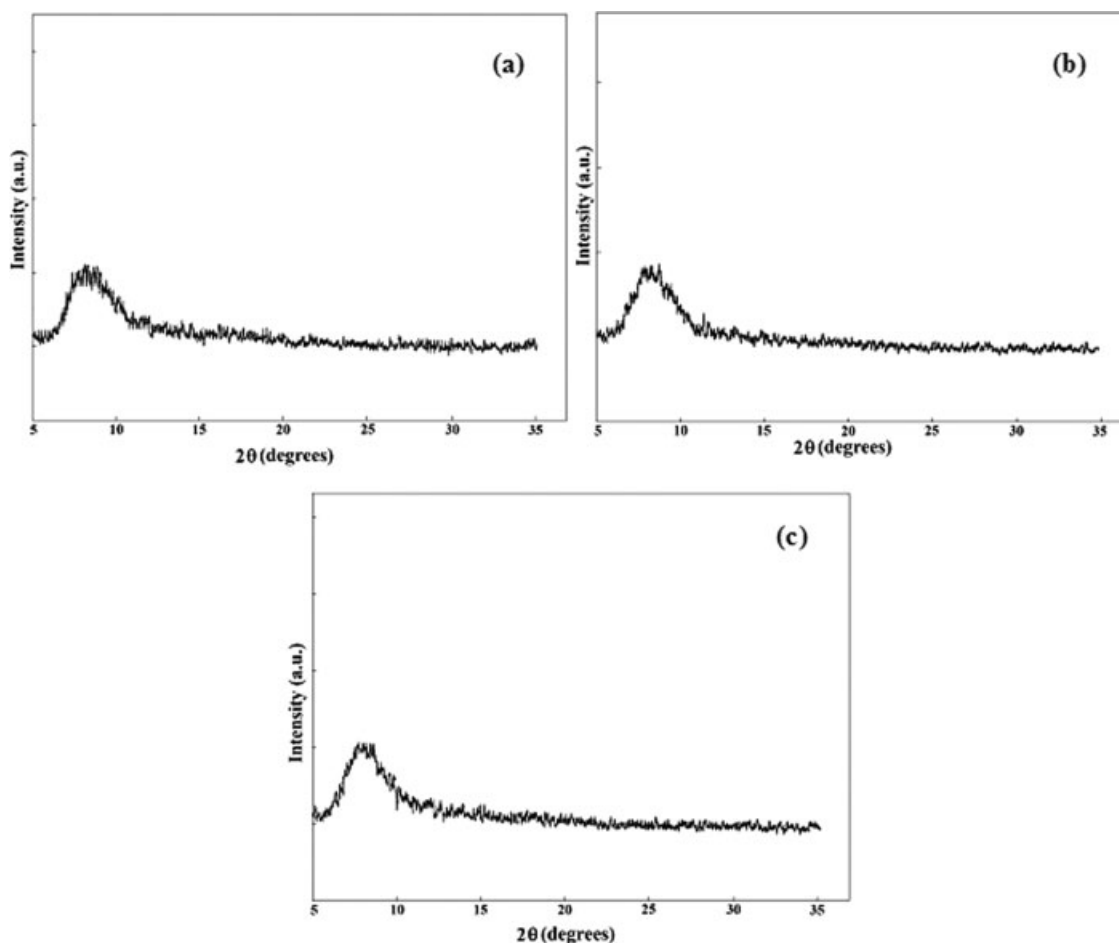


Figure 4 Typical XRD pattern of (a) PANI, (b) POT, and (c) PANI/POT/SiO₂.

the diffraction patterns of the PANI/POT/SiO₂ and the other samples studied are likely to be dominated by the response made by the polymer component.

The direct-current conductivities of the PANI, POT, PANI/POT, and PANI/POT/SiO₂ samples in the compressed pellet geometries measured at room temperature by a conventional two-point probe technique were 4.21×10^{-3} , 5.44×10^{-3} , 4.72×10^{-3} , and 2.19×10^{-3} S cm⁻¹, respectively. The observed conductivity of the present PANI pellet was found to be consistent with previous work.³⁶ However, the magnitude of conductivities for the homo- and copolymers were reported to be higher in their film geometry measured by four point-probe technique.²⁶⁻²⁸ Although, the incorporation of SiO₂ lowers the conductivity of the present composite, its conductance exists still in the range of the conductivities of the conventional inorganic semiconductors. The lower conductance of the PANI/POT/SiO₂ composite is presumably due to the interparticle resistance arising from the incorporation of insulating SiO₂ particles in the PANI matrix.^{19,37} As the electrical behavior of the composite is so far controlled by the polymer components, the mechanism of conduc-

tion is expected to be similar to those of the bulk polymer.

Figure 5 shows the CVs of (a) PANI/POT and (b) PANI/POT/SiO₂ composite film coated Pt electrodes in a monomer free aqueous solution containing 0.8M H₂SO₄. Under the similar condition, the CV of PANI and POT taken separately were found to be identical to that of the PANI/POT film [Fig. 5(a)] indicating that the copolymer film can be oxidized and reduced electrochemically with concomitant color change. The redox peaks as observed in the CV correspond to copolymer oxidation (doping) and reduction (dedoping). Alike the PANI/POT copolymer film, the CV of PANI/POT/SiO₂ film [Fig. 5(b)] also indicates that the composite matrix can also be switched between its oxidized and reduced states. Color of the PANI/POT/SiO₂ film changed from deep blue to greenish-yellow during electrochemical switching from oxidized to reduced state, respectively. These observations for the composite seem to be identical with the characteristics features of PANI, POT, and PANI/POT and thus may suggest that anodic oxidation and cathodic reduction of the PANI/POT/SiO₂ film lead it to be doped and dedoped, respectively.

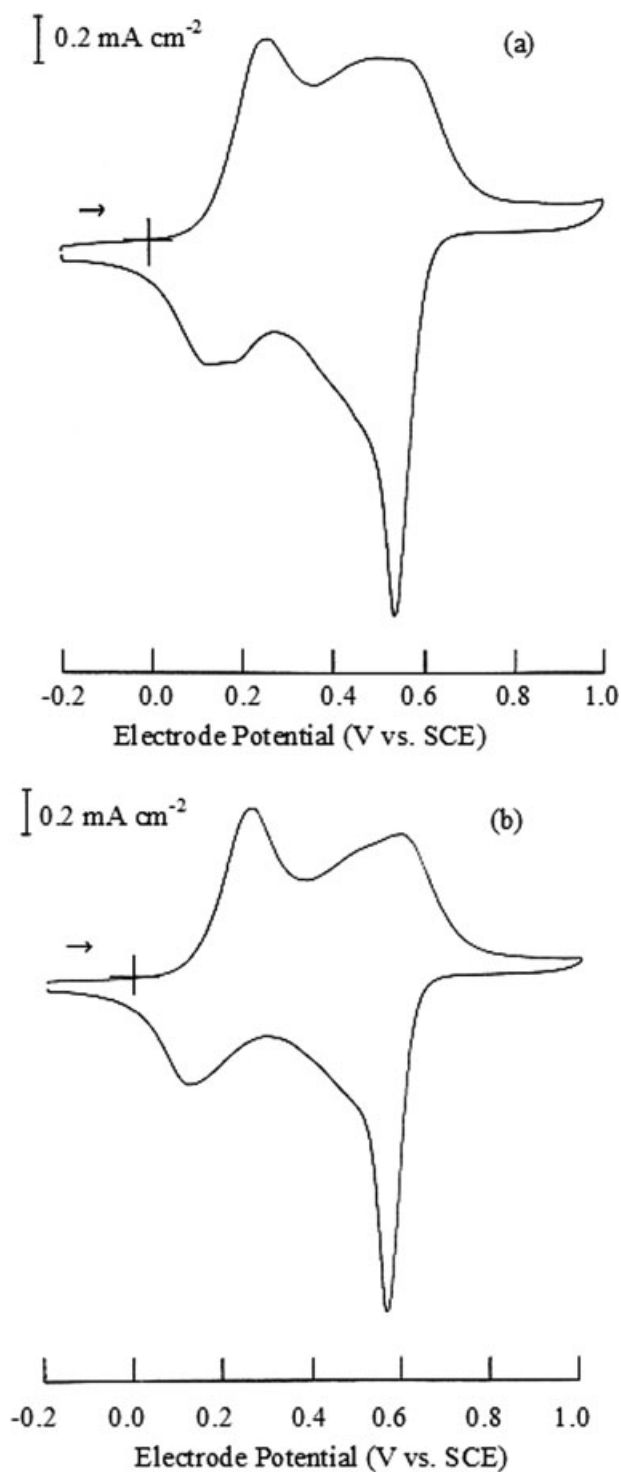


Figure 5 CV of (a) PANI/POT and (b) PANI/POT/SiO₂ films on a Pt electrode in 0.8M H₂SO₄.

Again, since the CV is composed of two redox couples, it indicates the presence of variable electroactive regions in the PANI/POT/SiO₂ composite film. Further, the result also suggests that even after incorporating insulating SiO₂ particles in the composite matrix, it can perform electrode activity as

high as PANI, POT and PANI/POT showing normal oxidation (doping) and reduction (dedoping) of the polymer component.

The stability of PANI/POT/SiO₂ composite film electrode in an electrochemical system at the very high positive potentials was examined. This was done by biasing the electrode potential at +1.0 and +2.0 V, and potential was then immediately allowed to sweep toward the negative potential at -0.2 V. The result is shown in Figure 6. On biasing the composite electrode at +1.0 V for 60 s, the CV (curve 1) shows normal redox characteristics as expected for a conducting polymer. Further, when the electrode was biased for the same duration at positive potential of as high as +2.0 V (curve 2), the electrode gives an identical redox response as that observed in curve 1 though a small shift of the reduction peak at *ca.* +0.45 V toward negative direction of potential is observed. It is interesting to note that the calculated charges of the reduction and oxidation peaks are comparable (integrated charge ratio for reduction peaks is 1.008 : 1.000 while that for oxidation peaks is 1.01 : 1.00) when the electrodes were biased at +1.0 and +2.0 V, indicating the normal oxidation

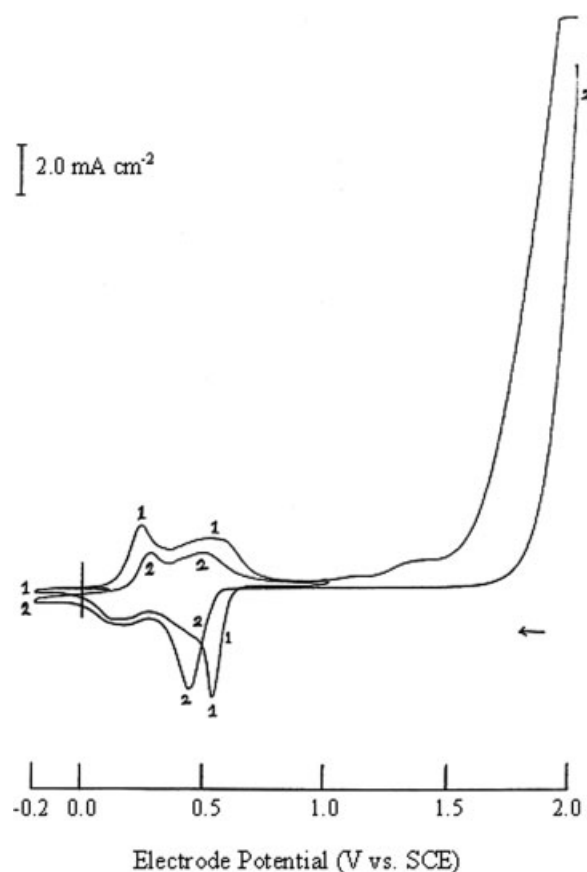


Figure 6 CV of PANI/POT/SiO₂ in 0.8M H₂SO₄ solution. Switching potentials: 1.0 V (curve 1) and 2.0 V (curve 2). Biasing time: 60 s.

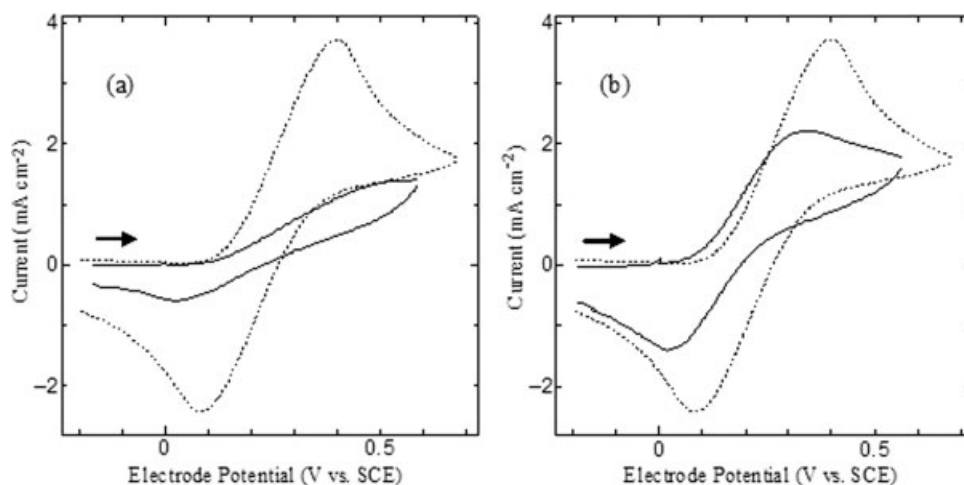


Figure 7 CV of (a) PANI/POT and (b) PANI/POT/SiO₂ film electrodes (solid lines) in an aqueous solution containing 0.1M K₄[Fe(CN)₆]. The dotted line shows the CV of bare Pt electrode in the same solution. (The magnitude of current for the CV of PANI/POT is twice than that shown in the vertical axis).

and reduction processes of the PANI/POT/SiO₂ film electrode even after biasing it at +2.0 V. The bulk polymer electrodes, *viz.* PANI, POT were reported not to be stable under the similar electrochemical condition at +2.0 V¹⁹ and were found to be lost or reduced the electroactivity of the electrodes to show normal redox process after biasing at high positive potentials. Thus, the present PANI/POT/SiO₂ electrode system indicates a superior electrochemical stability over the bulk PANI or POT electrodes at high positive potential.

The superior electrochemical stability and electroactivity of the polymer matrices studied in this work prompted us to examine their performance as electrode modifier. For this purpose, the films of PANI, POT, PANI/POT, and PANI/POT/SiO₂ coated on

the Pt electrodes were employed for investigating the redox activity of Fe²⁺/Fe³⁺ and H₂Q/Q couples. Figure 7 shows the CVs of PANI/POT and PANI/POT/SiO₂ electrodes in the K₄[Fe(CN)₆] solution. The oxidation and reduction peaks as observed in both the CVs indicate the one electron redox reaction of Fe²⁺ and Fe³⁺: Fe²⁺ - e⁻ = Fe³⁺. From the results, it can also be seen that oxidation potential of the Fe²⁺/Fe³⁺ system is slightly lower at the PANI/POT/SiO₂ electrode compared with that at the PANI/POT electrode. It indicates that the oxidation of ferrous to ferric on the PANI/POT/SiO₂ is more favorable than that on the PANI/POT one. The polymeric modifier was also used in investigating the redox behavior of H₂Q/Q redox system. The result is presented in Figure 8. The oxidation and reduction

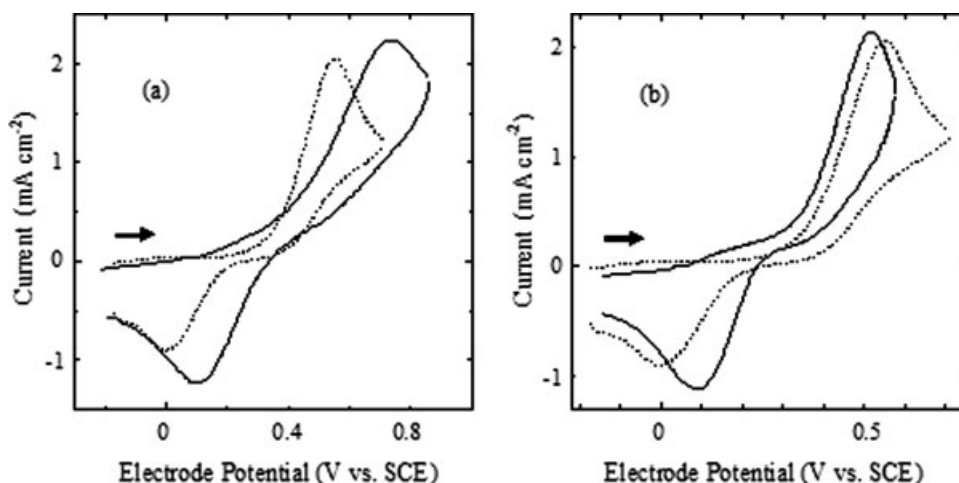


Figure 8 CV of (a) PANI/POT and (b) PANI/POT/SiO₂ film electrodes (solid lines) in an aqueous solution containing 0.01M Hydroquinone + 0.1M Na₂SO₄. The dotted line shows the CV of bare Pt electrode in the same solution.

TABLE I
Redox Behavior of Modified Electrodes in Different Electrolytic Media

Electrolyte solution	Oxidation potential (V)					Reduction potential (V)				
	Bare Pt	PANI	POT	PANI/POT	PANI/POT/ SiO ₂	Bare Pt	PANI	POT	PANI/POT	PANI/ POT/SiO ₂
0.1 M [K ₄ Fe(CN) ₆]	+0.40	+0.48	+0.47	+0.50	+0.35	+0.09	+0.09	+0.09	+0.02	+0.03
0.01 M H ₂ Q+ 0.1 M Na ₂ SO ₄	+0.55	+0.72	+0.73	+0.75	+0.51	+0.00	+0.13	+0.12	+0.10	+0.09

processes for this two electron redox reaction: $Q + 2H^+ + 2e^- = QH_2$, are well exhibited in the CV. However, the oxidation potential is seen to be slightly lower when PANI/POT/SiO₂ film electrode was used and thus indicates that the oxidation process of the system is comparatively favorable at this electrode. The results of redox behavior for Fe⁺²/Fe⁺³ and H₂Q/Q systems at different electrodes are summarized further in Table I. From the data, it seems that redox reactivity of the electrode matrices varies considerably. Peak separation, i.e., the difference between the potentials of anodic and corresponding cathodic peak, is considered to measure the reversibility of a redox process. For the Fe⁺²/Fe⁺³ process, peak separation with the Pt electrode seems to be lower than that each of the PANI, POT, and PANI/POT matrices while it is comparable with that of PANI/POT/SiO₂ electrode. This means that the reversibility of the process with Pt is comparable with the PANI/POT/SiO₂ electrodes, whereas the process proceeds with less reversibility with the PANI, POT, and PANI/POT electrodes. Such dissimilar redox reactivity can also be realized for the H₂Q/Q process. In this case, the PANI/POT/SiO₂ electrode seems to show relatively better reversibility than the Pt one while the process becomes less reversible when PANI, POT, and PANI/POT electrodes are employed. The reason for the superior redox activity of PANI/POT/SiO₂ electrode has not been investigated further in this work; however, the incorporation of SiO₂ particles into the matrix may influence the surface properties of the composite electrode and thus modify the electrode activity for reactions.

CONCLUSIONS

PANI/POT/SiO₂ composite film can be prepared by a simple electrochemical route from an aqueous acidic solution containing colloidal dispersion of silica, aniline and *o*-toluidine. The polymeric composite thus obtained is electronically conductive and corresponds to the range of conventional semiconductors. The PANI/POT/SiO₂ film is electroactive and can be used as an electrode modifier for

performing Fe⁺²/Fe⁺³ and H₂Q/Q redox processes on its surface. The anodic and cathodic processes involved in these redox reactions were comparable to that performed on the noble Pt metal surface. Thus, the use of PANI/POT/SiO₂ composite film as the electrode modifier could be interesting to be examined for other electrochemical processes too.

References

1. Tourillon, G. In Handbook of Conducting Polymers; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 293.
2. Jasne, S. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1988; Vol. 51.
3. Yoshino, K. Synth Met 1989, 28, 669.
4. Om. Bockris, J.; Miller, D. In Conducting Polymers: Special Applications; Alcaer, L., Ed.; Reidel: Dordrecht, 1989; Vol. 1.
5. Yonezawa, S.; Kanamura, K.; Takehara, Z. J Electrochem Soc 1993, 140, 629.
6. Palmisano, F.; De Benedetto, G. E.; Zamboni, C. G. Analyst 1997, 122, 365.
7. Özden, M.; Ekinçi, E.; Karagözler, E. J Appl Polym Sci 1999, 71, 2141.
8. Nugay, N.; Küçükyavuz, Z.; Küçükyavuz, S. Polymer 1993, 34, 4649.
9. Özyağcı, M.; Küçükyavuz, Z. Synth Met 1997, 87, 123.
10. Yıldırım, P.; Küçükyavuz, Z. Synth Met 1998, 95, 17.
11. Sankır, M.; Küçükyavuz, Z.; Küçükyavuz, S. J Appl Polym Sci 2003, 87, 2113.
12. Wei, Y.; Hariharan, R.; Petal, S. A. Macromolecules 1990, 23, 758.
13. Mattoso, L. H. C.; Osvaldo, N.; Oliveira, Jr.; Faria, R. M.; Manohar, S. K.; Epstein, A. J.; Macdiarmid, A G Polym Int 1994, 35, 89.
14. Savitha, P.; Sathyanarayana, D. N. Polym Int 2004, 53, 106.
15. Huang, M. R.; Li, X. G.; Yang, Y. L.; Wang, X. S.; Yan, D. J Appl Polym Sci 2001, 81, 1838.
16. Rao, P. S.; Sathyanarayana, D. N. J Polym Sci Polym Chem Ed 2002, 40, 4065.
17. Maeda, S.; Armes, S. P. Synth Met 1995, 73, 151.
18. Chowdhury, A.-N.; Rahman, J. M. A.; Rahman, M. A. Indian J Chem 2002, 41, 1789.
19. Chowdhury, A.-N.; Rahman, J. M. A. J Electrochem Soc India 2002, 51, 66.
20. Jang, S. H.; Han, M. G.; Im, S. S. Synth Met 2000, 110, 17.
21. Ita, M.; Uchida, Y.; Matsui, K. J Sol-Gel Sci Technol 2003, 26, 479.
22. Lu, X.; Manners, I.; Winnik, M. A. Macromolecules 1997, 30, 34.
23. Ritchie, M. C.; Bochas, L. G.; Olin, T.; Sikdar, S. K.; Bhattacharyya, D. Langmuir 1999, 15, 6346.

24. Oh, I.-S.; Park, N.-H.; Suh, K.-D. *J Appl Polym Sci* 2000, 75, 968.
25. Gupta, S. D.; Roy, S. K. In *Chemical Analysis of Ceramic and Allied Materials*; Ganguly, D., Kumar, S., Ed.; Indian Institute of Ceramics: Calcutta, 1985; p 38.
26. Borole, D. D.; Kapadi, U. R.; Kumbhar, P. P.; Hundiwale, D. G. *Mater Lett* 2002, 57, 844.
27. Borole, D. D.; Kapadi, U. R.; Kumbhar, P. P.; Hundiwale, D. G. *Mater Lett* 2003, 57, 3629.
28. Borole, D. D.; Kapadi, U. R.; Kumbhar, P. P.; Hundiwale, D. G. *Mater Lett* 2006, 60, 2447.
29. Chowdhury, A.-N.; Yousuf, M. A.; Rahman, M. M.; Hasan, A. Q. M. Q. *Indian J Chem A* 2002, 41, 1562.
30. Stejskal, J; Kratochvil, P.; Jenkins, A. D. *Polymer* 1996, 37, 367.
31. Abdiryim, T.; Xiao-Gang, Z.; Jamal, R. *J Appl Polym Sci* 2005, 96, 1630.
32. Atobe, M.; Chowdhury, A.-N.; Fuchigami, T.; Nonaka, T. *Ultrason Sonochem* 2003, 10, 77.
33. Dyar, J. R. *Application of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New Delhi, 1991.
34. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
35. Cao, Y.; Li, S.; Xue, Z. Guo, D. *Synth Met* 1986, 16, 305.
36. Chowdhury, A.-N.; Islam, M. S.; Azam, M. S. *J Appl Polym Sci* 2007, 103, 321.
37. Zhang, Z.; Wan, M. *Synth Met* 2003, 132, 205.