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Electrochemical preparation and characterization of polypyrrole films in an aqueous solution containing a biocompatible surfactant

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ABSTRACT

Polypyrrole (PPy) films were synthesized electrochemically by the direct anodic oxidation of pyrrole in an aqueous solution containing the environmentally friendly surfactant sodium dodecyl sulfate (SDS). The PPy/SDS films were characterized by cyclic voltammetry (CV), in situ UV-visible spectroscopy, and scanning electron microscopy (SEM), and were then contrasted with PPy films prepared under identical conditions in the absence of SDS. The results obtained show that the rate of electropolymerization increases in the presence of SDS with the electroactive, adhesive, and homogenous polymer films onto the electrode surface. Also we found that the optimized concentration of pyrrole for electropolymerization decreases in the presence of SDS. The CVs for the PPy/SDS films recorded at different scan rates reveal that the anodic peak currents increase with increase in the scan rate, and that the redox process is surface-controlled. The effects of electropolymerization parameters on the morphology obtained are discussed. It is proposed that the electropolymerization rate and polymer stiffness are the important factors in controlling the morphology. SEM images show that the PPy/SDS films take a small size, and extend surface particles with better diffusivity which is affected by stabilizers. The model of the polymer growth is flowers-like in the absence of SDS, and it is string-like in the SDS medium. © 2014 Trade Science Inc. - INDIA

KEYWORDS

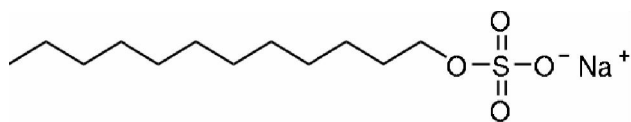
Polypyrrole (PPy);
Sodium dodecyl sulfate
(SDS);
Cyclic voltammetry (CV);
Morphology.

INTRODUCTION

The chemical and electrochemical synthesis of conducting polymers continues to receive great attention in fundamental as well as applied studies. In particular, micro- and nanostructures of conducting polymers are under active investigation because of the many existing and new possibilities for applications in optical, electri-

cal, and sensing devices^[1-10]. The formation of these structures in the presence of active surface materials in aqueous media has received less attention in spite of the obvious economical advantages. Among all the conducting polymers, polypyrrole (PPy) is the one most studied for its ease of preparation, high electronic conductivity, and good stability in air and aqueous media.

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Scheme 1 : Chemical structure of SDS

Electrochemical polymerization of pyrrole is the main method in the preparation of PPy films. The polymerization parameters such as solvent,^[11-14] temperature,^[15] potential or current density,^[16] monomer concentration^[17] supporting electrolyte^[18] and nature of working electrode^[19] have strong effects on the polymerization processes of pyrrole.

Polymeric as well as non-polymeric surfactants have been used to make colloidal PPy. The presence of a surfactant or polyelectrolyte significantly modifies both the microscopic and macroscopic properties of the final polymer^[20-28]. Sodium dodecyl sulfate (SDS) has been used extensively as a surfactant for micellar/emulsion polymerization for a series of monomers using both the chemical and electrochemical polymerization routes^[22-28]. SDS is an anionic surfactant having a bulky hydrocarbon tail and a sulfonate group in its polar head (Scheme 1). It has been postulated that pyrrole is solubilised in the micellar assembly formed on the substrate leading to a highly concentrated monomer. The chemical synthesis of PPy has been performed in the presence of surfactants, where they act as a co-dopant together with the anion of the oxidising agent^[29,30]. In contrast, the electrochemical synthesis allows incorporation of SDS as a unique dopant. The electrodeposition of PPy onto stainless steel in organic media containing surfactant for the construction of a single-layer actuator has also been reported^[31].

In this work, the investigation was extended by analyzing the first stages of PPy electrosynthesis in the SDS solution in different electrochemical techniques. We report the detailed mechanistic investigations of the effect of varying the amount of SDS on the rate of polymerization of pyrrole. Different PPy/SDS morphologies were formed, which were characterized by varying electrosynthesis parameters. Cyclic voltammetry (CV) was used to investigate the electrochemical behavior of the modified electrode. Furthermore, the composite structure and electrical properties were compared with the pure PPy using the UV-visible and SEM techniques.

MATERIALS AND METHOD

Chemicals and materials

Pyrrole (Merck) was distilled under reduced pressure before use. SDS and other chemicals were analytical grade reagents (Merck), and were used as received. Deionized water from a Millipore purification system was used for the preparation of the solutions.

Instrumentation

A standard three-electrode cell was used with a glassy carbon, gold or platinum disk as the working electrode, a saturated calomel electrode (SCE) as reference, and a platinum wire as the counter electrode. The working electrode had a surface area of 0.20 cm². Before each experiment, the working electrode was polished mechanically with 1.0 mm diameter alumina powder, washed, and then rubbed against a smooth cloth. All the electrochemical measurements were carried out using the electrochemical system Behpajuh Electric (Iran) with a PC and electrochemical set-up that was controlled with the software. Except otherwise stated, all the experiments were carried out at room temperature (25 ± 0.1 °C), and all potentials were referred to the SCE. The UV-visible transmission spectra were recorded using a Shimadzu (M-160) spectrometer. The SEM images were taken using a Hitachi instrument (S-4160) at various magnifications.

Preparation of PPy/SDS composite films

The PPy/SDS films were formed on the Pt working electrode by three electrochemical techniques including potentiodynamic, potentiostatic, and galvanostatic in an aqueous solution containing KNO₃ (0.2 M).

RESULTS AND DISCUSSION

Electrochemical preparation of PPy/SDS films in aqueous media

Electrochemical synthesis of PPy was performed by the CV method from the solution of pyrrole (0.07 M) in KNO₃ (0.2 M) on a Pt electrode with and without the presence of SDS (0.1 mM) using a potential sweep rate of 100 mVs⁻¹ between -1 and +1 V. Figure 1a shows the influence of SDS on cyclic voltamogram of PPy films with respect to that obtained

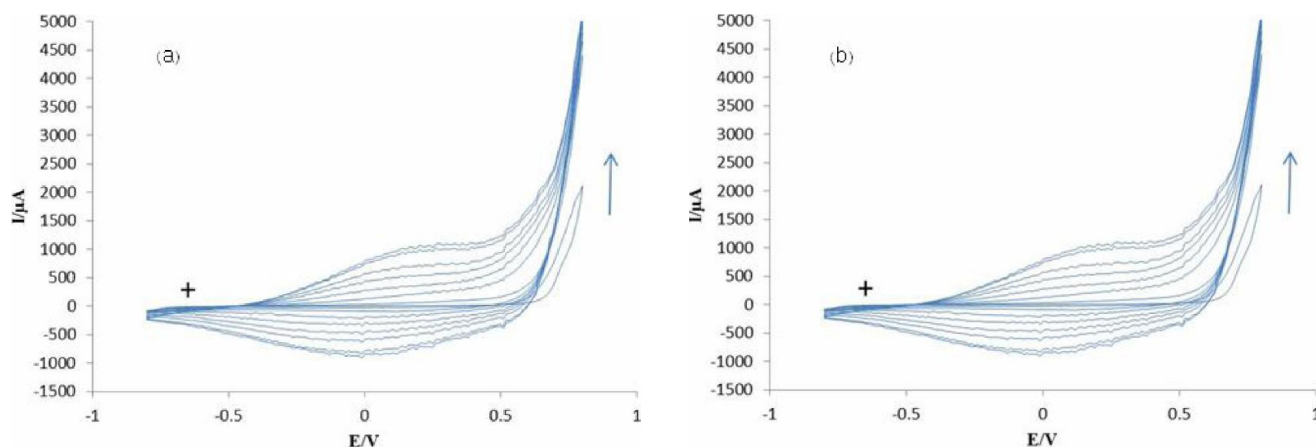


Figure 1 : CVs for (a) PPy/SDS film on Pt electrode in 0.07 M Py/0.2 M KNO_3 /0.1 mM SDS aqueous solution, (b) PPy film in the absence of SDS at scan rate of 100 mV s^{-1} in the potential range of -1.0 to 1.0 V for cycles 1, 3, 5, 7, 9, 11, 13, and 15.

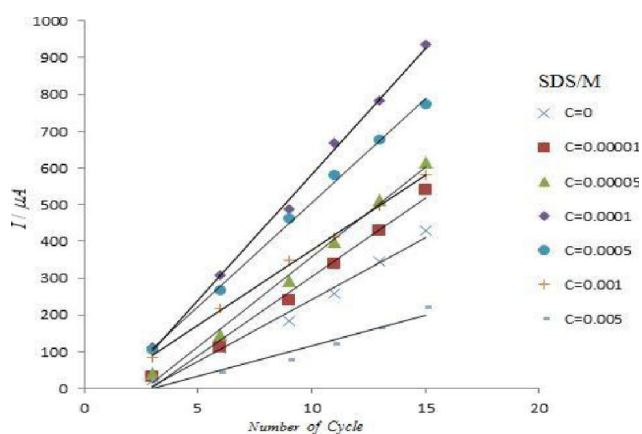


Figure 2 : Plot of peak current against scan numbers during PPy/SDS electrodeposition in the presence of SDS with the concentration in the range of 1×10^{-5} - 1×10^{-3} M from the 0.07 M Py/0.2 M KNO_3 aqueous solution at scan rate of 100 mV s^{-1} .

in the same conditions in the absence of SDS (Figure 1b). It is clear from the figure that the oxidation peak current for PPy in all cycles increases in the presence of SDS. Therefore, SDS has a good catalytic effect on the electropolymerization of pyrrole. As reported,^[32] the surfactant is adsorbed on the metal substrate and also on the growing polymer layer during the electrochemical polymerization. Thus the initial stage of polymerization is influenced because the substrate is modified, and the number of active sites for the electrochemical polymerization is affected. The following stages could also be influenced: electron transfer; surfactant interacting with the growing polymer and incorporation of ion; transport of the monomer towards the electrode; and solubilization of the reaction products such as oligomers, and their loss into the solution.

The effect of different SDS concentrations (from

1×10^{-5} to 5×10^{-3} M) on the oxidation peak current of pyrrole (0.07 M) was studied by the CV method in an aqueous KNO_3 solution (0.2 M). The direct proportionality of the amount of polymer to the positive peak current is fundamentally important for studying the PPy electropolymerization. The positive peak current is employed directly to determine the amount of polymer deposited on the electrode surface^[33,34]. The anodic peak currents were measured and plotted as a function of cycle number (i.e. the reaction time), and presented in Figure 2. According to this figure, in all the SDS concentrations studied, the polymer films produced increase linearly with the cycle number. The figure also shows that the slope of variation of I_p versus cycle number increases with concentration of SDS until 1×10^{-3} M, but this behavior is inverted with increase in SDS more than 1×10^{-3} M. However, for all concentrations in the range of 1×10^{-5} - 1×10^{-3} M, the rate of polymerization is higher than that in the absence of SDS. It is clear that the increase in the rate of polymerization is attributed to the interaction between anionic surfactant and pyrrole monomer or its oxidation radical cation. The surfactant tends to accumulate at the electrode/electrolyte interface, and draws in the monomer, thereby enhancing the local concentration. The supply of monomer to the electrode is now limited by the diffusion of the micelles. In view of their large size, the rate of arrival of monomer towards the electrode is low, which results in lowering the polymerization rate. On further increasing the SDS concentration ($>5 \times 10^{-3}$ M), the number of micellar structures increases, and on further increasing the concentration, an emulsion is formed. At this concentration of

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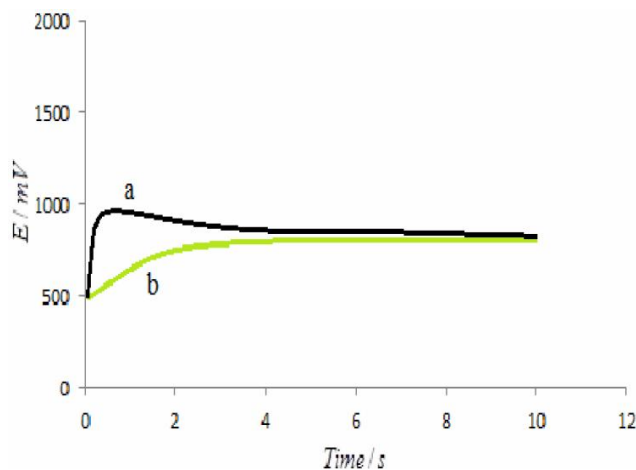


Figure 3 : Galvanostatic charge-discharge curves for (a) PPy/SDS film and (b) PPy film at 0.1 mA

SDS, the solution forms a two-phase medium, and consequently, I_{p_a} reduces considerably compared with that in the absence of SDS.

To illustrate the performance of the resulting electrodes in supercapacitors, constant current charge-discharge cycling was performed to measure the capacitance in aqueous solutions containing KNO_3 (0.2 M). Typical galvanostatic charge-discharge curves at a current of 0.1 mA are shown in Figure 3. It can be clearly seen that the PPy/SDS films present a higher capacitance than the pure PPy one, and this can be considered as the contribution of faradic pseudocapacitance of PPy/SDS films. Generally, the galvanostatic technique can produce adhesive and uniform deposited polymer films on the electrode surface. The electrochemical behavior of PPy/SDS films deposited galvanostatically from aqueous solutions containing SDS was investigated by the CV method, and the results

obtained were shown in Figure 4. According to the CVs in this figure, I_{p_a} increases linearly with scanning rates, which indicates that redox processes were not controlled by diffusion of counter ions. These films can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials. Moreover, it is clear that the anodic currents increase slightly with increased cycles due to the lower doping level of the PPy/SDS films.

A set of current transients during electropolymerization of pyrrole (0.07 M) containing different concentrations anionic SDS–aqueous solution at an applied potential of 0.8 V versus SCE on a Pt electrode is shown in Figure 5. Two or more stages can clearly be observed at different SDS concentrations. The initial stage of electrodeposition was a combination of instantaneous 2-D and 3-D mechanisms since electrodeposition was undercharge transfer control rather than diffusion; in later stages, layer-by-layer growth mode was in accordance with the Stranski–Krastanov model^[35,36]. It is an important feature that the layer-by-layer growth mode demonstrates the electrochemical feasibility of ultrathin PPy/SDS films, and these ultrathin films play an important role in modern biosensors^[35,36].

Moreover, the amount of charge passed was monitored, and the total time taken to produce a finite thickness polymer (correspond to 30 mC charge) was taken as the index for the rate of polymerization. A plot of the time taken to form the polymer films is shown in Figure 6. It is clear from the figure that the rate of polymerization increases as the concentration of SDS increases

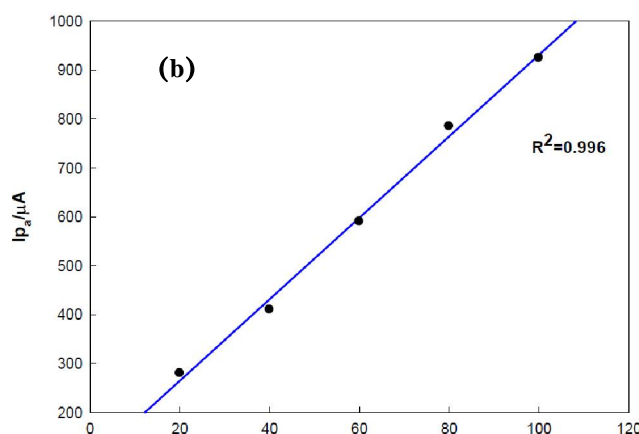
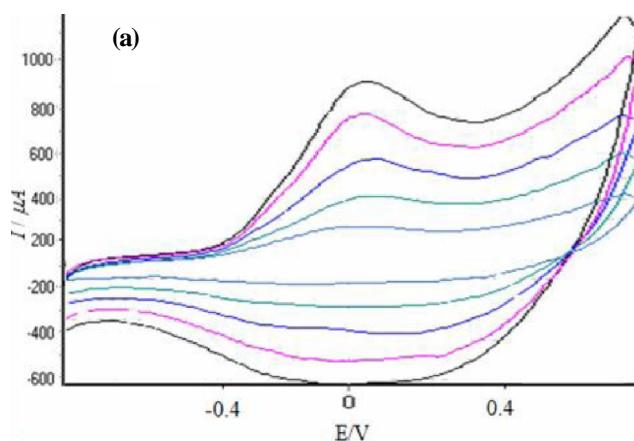


Figure 4 : (a) Effect of scan rate on the first cycle of PPy/SDS film activity in KNO_3 (0.2 M) solution, and (b) dependence of the anodic peak current (I_{p_a}) of the first cycle of the PPy/SDS film activity on the scan rate

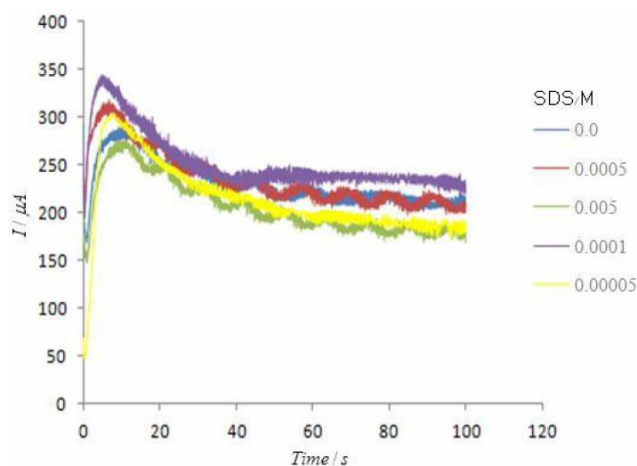


Figure 5 : Chronoamperograms of pyrrole (0.07 M) in KNO_3 (0.2 M) aqueous solution containing SDS with the concentration in the range of 1×10^{-5} - 1×10^{-3} M at an applied potential of 0.8 V vs. SCE

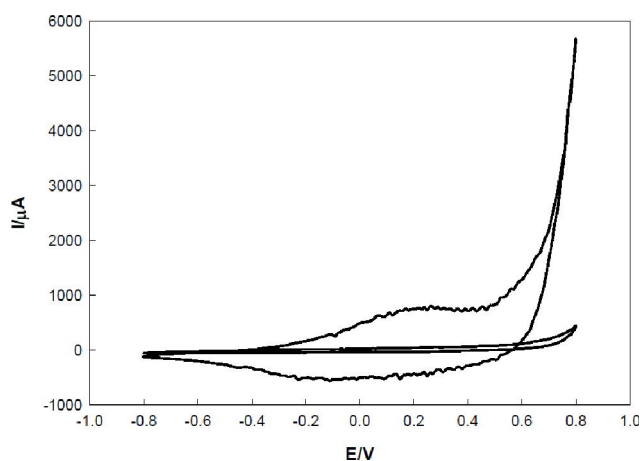


Figure 7 : Comparative CVs (10th cycle) for electrosynthesis of pyrrole (0.2 M) in the presence of SDS (0.1 mM) and its absence at scan rate of 100 mV s^{-1} in the potential range from -1.0 to 1.0 V

and reaches a maximum around 1×10^{-4} M. The rate of polymerization then decreases on further increase of SDS. The horizontal line represents the polymerization time at 30 mC in the absence of SDS. Figure 6 confirms that the polymerization rate is lower than that in the absence of SDS, where its concentration increases above 5×10^{-3} M. The supply of monomer to the electrode is now limited by the diffusion the micelles. In view of their large size, the rate of arrival of the monomer towards the electrode is low, which results in lowering the polymerization rate.

Influence of SDS on limiting concentration of monomer for electropolymerization

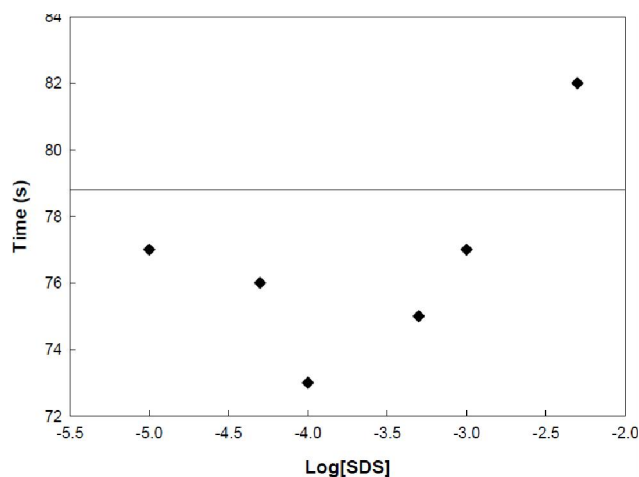


Figure 6: Amount of time taken to produce a finite thickness polymer (30 mC) as a function of SDS concentration for the electropolymerization of pyrrole. The horizontal line represents the polymerization time in the absence of SDS

It is clear from the results mentioned above that the rate of polymerization of the pyrrole monomer increases in the presence of SDS, and that the PPy/SDS films have modified the electroactive properties. SDS can also decrease the minimum limit of monomer concentration to prepare the optimum polymer films. It was found that at an applied monomer concentration less than 0.3 M, polymerization does not occur on the electrode surface from aqueous solution in the absence of SDS. Once the limiting concentration of monomer for obtaining the polymer reduced to 0.2 M, a proper quantity of SDS was added to the aqueous solution. Figure 7 compares the 10th cycle number of voltammograms of electrosynthesis of 0.2 M pyrrole in the presence and absence of SDS. As we can observe in this figure, the anodic oxidation potential or activated potential of electropolymerization of monomer was reduced in the presence of SDS. This is due to the tendency of surfactant to accumulate at the electrode/electrolyte interface, and draws in the monomer, thereby enhancing the local concentration. Presence of pyrrole in the oil phase of the micellar solution was confirmed spectrophotometrically. The UV-visible spectrum of pyrrole in the aqueous phase of a monomer solution containing SDS shows a band absorption of 1.251 at 220 nm compared with the monomer solution in the absence of SDS (with a band absorption of 1.575 at 220 nm). It was revealed that the micellar solution contained a considerable part of monomer in the surfactant medium (oil phase), which

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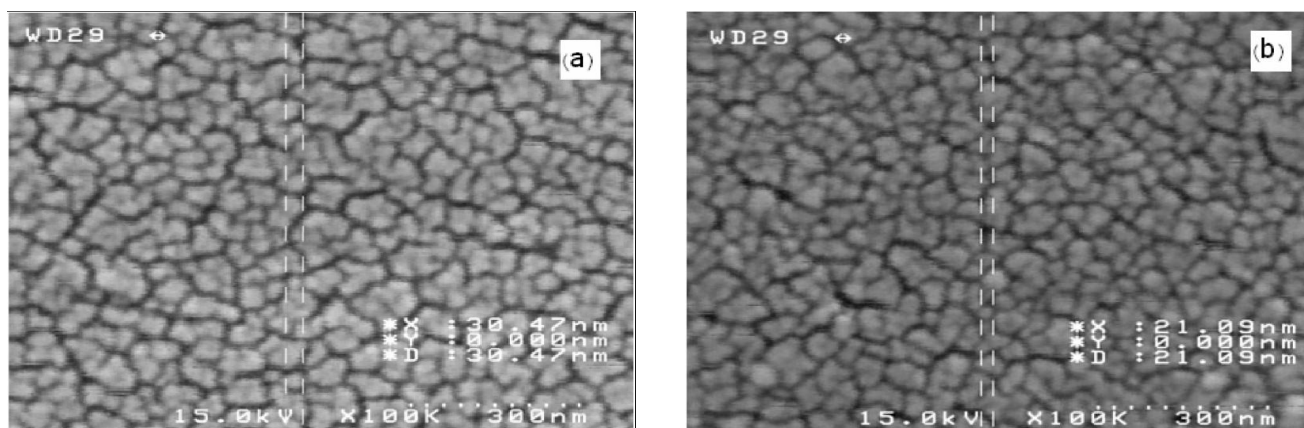


Figure 8 : SEM images for electrode surface solution of (a) PPy film and (b) PPy/SDS film prepared by the CV technique

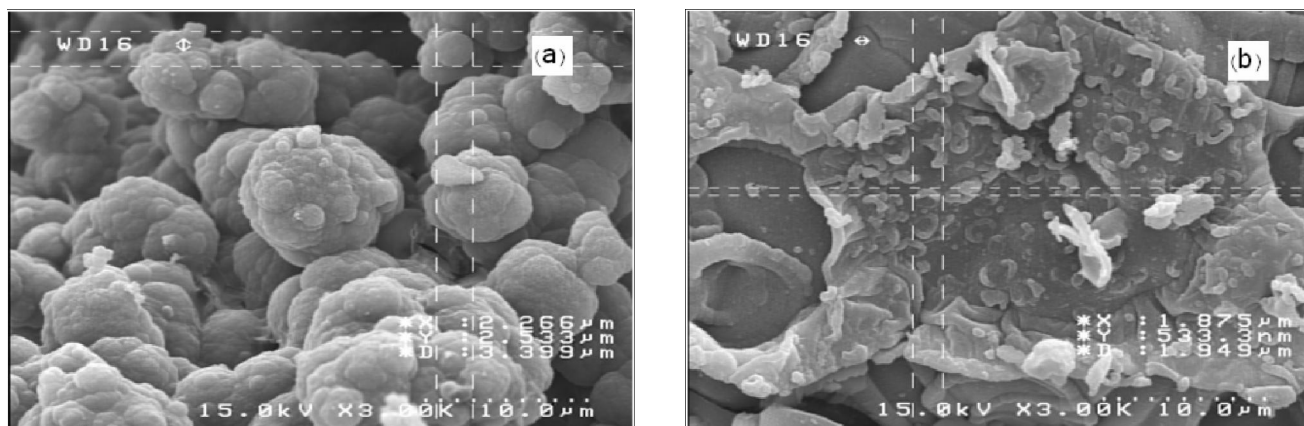


Figure 9 : SEM images for surface solution of (a) PPy film and (b) PPy/SDS film prepared by the potentiostatic technique at an applied potential of 0.8 V

tends to accumulate at the electrode/solution interface, and then the polymerization rate of the PPy/SDS films increases.

Surface morphology of deposited films

It is clear from the above mentioned results that the PPy/SDS films have modified the microscopic and macroscopic properties. Thus the surface morphologies of the PPy/SDS films were visualized by SEM. Figs. 8a and 8b show the SEM images of the PPy and PPy/SDS films, grown during 15 scans from aqueous solution, respectively. These images reveal the morphology of electrode surface of the polymer films. The uniform growth of the polymer films on the surface can be observed in these images since the surface is progressively covered by all the polymer films. However, SDS is loosely bound to the polymer chain, and leaches out by repeated cycling of the film between the reduced and oxidized states in aqueous solution. SDS can also leach out by dedoping the film in aqueous solution for a

long time. The PPy/SDS modified polymer shows a more porous and open structure compared with the PPy films.

The SEM images of the solution surface of polymer films prepared by the potentiostatic method at a constant potential of 0.8 V are shown in Figure 9. In general, nodular surface and flower-like structures were observed for the PPy films. However, the PPy/SDS polymer demonstrated less diameter for the particle usually with extended surface. As shown in this figure, PPy/SDS films comprise mainly ordered molecular strands anchored directly on the electrode surface with respect to the pure PPy films. The diffusion and exchange of ions and dopants in this ordered PPy/SDS films should be very fast, and entrapment of the ions should be small. Similar results can be observed in Figure 10, where the galvanostatic technique at a constant current of 0.1 mA was applied to produce the polymer films. It is interesting that the PPy/SDS films prepared from aqueous solution were regular and smooth, pre-

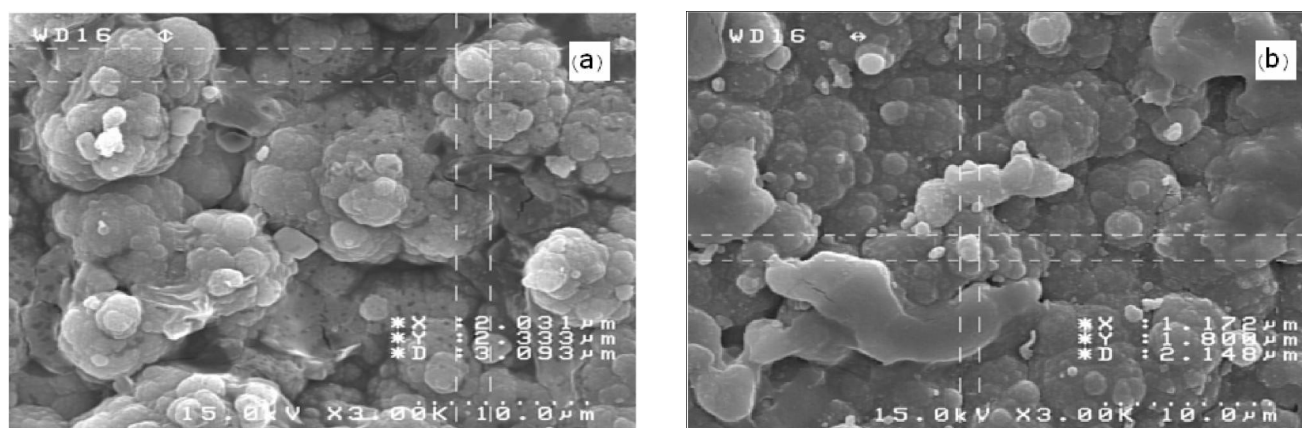


Figure 10 : SEM images for surface solution of (a) PPy film and (b) PPy/SDS film prepared by the galvanostatic technique at a constant current of 0.1 mM.

sending dense, compact, and homogeneous structures.

CONCLUSION

In this paper, we showed that polymerization of pyrrole in the presence of SDS proceeds mainly with the complex formed between pyrrole and SDS. The rate of polymerization initially increases with increase in the SDS concentration and passes through a maximum at 0.1 mM. The current time profile and SEM studies indicate that the mechanism of growth and morphology of the PPy/SDS films are different from those for PPy. The electrochemical, structural, and morphological studies indicated that the PPy films prepared in the presence of SDS had a better electrochemical response at different scan rates, higher current density, lower resistance, and uniform structure with a high electrocatalytic effect compared with the pure PPy polymer. SDS enhanced the local concentration of pyrrole between the electrode/solution interface, and also lowered the limiting concentration and E_{ox} of monomer for the electropolymerization. The successful electropolymerization of pyrrole in SDS aqueous solution proved that SDS can facilitate the biocompatibility of pyrrole with biologically active species, and that these results will benefit further agricultural applications of PPy/SDS biosensors.

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REFERENCES

- [1] H.Shirakawa; *Angew.Chem.*, **113**, 2642 (2001).
- [2] T.A.Skotheim, R.L.Elsenbaumer, J.R.Reynolds; *Handbook of Conducting Polymers*, Marcel Dekker, New York, **1/2**, (1997).
- [3] H.S.Nalwa; *Handbook of Organic Conductive Molecules and Polymers*, Wiley, Chichester, 1–4 (1997).
- [4] B.D.Malhotra, A.Chaubey, S.P.Singh; *Anal.-Chim.Acta*, **578**, 59 (2006).
- [5] B.D.Malhotra, R.Singhal, A.Chaubey, S.K.Sharma, A.Kumar; *Curr.Appl.Phys.*, **5**, 92 (2005).
- [6] S.Andreescu, O.A.Sadik; *Pure Appl.Chem.*, **76**, 861 (2004).
- [7] L.A.Terry, S.F.White, L.J.Tigwell; *J.Agric.Food Chem.*, **53**, 1309 (2005).
- [8] N.K.Guimard, N.Gomez, C.E.Schmidt; *Prog.-Polym.Sci.*, **32**, 876 (2007).
- [9] K.S.Ryu, K.M.Kim, S.G.Kang, G.J.Lee, J.Joo, S.H.-Chang; *Synth.Met.*, **110**, 213 (2000).
- [10] A.Talei, J.Y.Lee, Y.K.Lee, J.Jang, J.A.Romagnoli, T.Taguchi, E.Maeder; *Thin Solid Films*, **363**, 163 (2000).
- [11] K.Imanishi, M.Satoh, Y.Yasuda, R.Tsushima, S.Aoki; *J.Electroanal.Chem.*, **260**, 469 (1989).
- [12] R.Cervini, R.J.Fleming, B.J.Kennedy, K.S.Murray; *J.Mater.Chem.*, **41**, 87 (1994).
- [13] J.Ouyang, Y.Li; *Polymer*, **38**, 1971 (1997).
- [14] J.Tietje-Girault, C.Ponce de Leon, F.C.Walsh; *Surf.Coat.Technol.*, **201**, 6025 (2007).
- [15] W.Liang, J.Lei, C.R.Martin; *Synth.Met.*, **52**, 227 (1992).
- [16] D.S.Maddison, J.Unsworth; *Synth.Met.*, **30**, 47 (1989).
- [17] M.Ogamasawara, K.Funahashi, T.Demyra,

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- T.Hagiwara, K.Iwata; Synth.Met., **14**, 61 (1986).
- [18] R.Qian, J.Qiu; Polym.J., **19**, 157 (1987).
- [19] B.Sun, D.P.Schweinsberg; Synth.Met., **68**, 49 (1994).
- [20] A.Buffenoir, G.Bidan; J.Chim.Phys., **95**, 1547 (1998).
- [21] Y.Kang, M.H.Lee, S.B.Rhee; Synth.Met., **52**, 319 (1992).
- [22] S.Mafe, J.A.Manzanares, H.Reiss; J.Chem.Phys., **98**, 2408 (1993).
- [23] J.C.Michaelson, A.J.McEnvoy, N.Kuramoto; Reactive Polym., **17**, 197 (1992).
- [24] N.Kuramoto, A.M.Genies; Synth.Met., **68**, 191 (1995).
- [25] L.T.Cai, S.B.Yao, S.M.Zhou; Synth.Met., **88**, 209 (1997).
- [26] S.L.de Albuquerque Maranhao, R.M.Torresi; Electrochim.Acta, **44**, 1879 (1999).
- [27] B.J.Kim, S.G.Oh, M.G.Han, S.S.Im; Langmuir, **16**, 5841 (2000).
- [28] B.J.Kim, S.S.Im, S.G.Oh; Langmuir, **17**, 565 (2001).
- [29] M.A.DePaoli, R.C.D.Peres, S.Panero, B.Scrosati; Electrochim.Acta, **37**, 1173 (1992).
- [30] R.C.D.Peres, M.A.De Paoli, P.M.Torresi; Synth.-Met., **48**, 259 (1992).
- [31] K.Naoi, Y.Oura, M.Maeda, S.Nakamura; J.Electrochem.Soc., **142**, 417 (1995).
- [32] V.Tsakova, S.Winkels, J.W.Schultze; Electrochim.Acta, **46**, 759 (2000).
- [33] J.Heinze; Electrochemically conducting polymers, in: Topic in Current Chemistry, **152**, Springer, Berlin, (1990).
- [34] Y.Wei, Y.Sun, X.Tang; J.Phys.Chem., **93**, 4878 (1989).
- [35] H.Randriamahazaka, V.Noel, C.Chevrot; J.Electroanal.Chem., **472**, 103 (1999).
- [36] J.A.Venables, G.D.T.Spiller, M.Hanbucken; Rep.-Prog.Phys., **47**, 399 (1984).