Effect of the Surface Roughness of Conducting Polypyrrole Thin-Film Electrodes on the Electrocatalytic Reduction of Nitrobenzene

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ABSTRACT: Conducting polypyrrole (PPy) thin-film electrodes were prepared by the electropolymerization of pyrrole on gold-coated glass plates. Films of various roughnesses were obtained by the variation of the scan rates during electropolymerization. These thin films were modified by doping with $6mM$ of the dopant $NiCl_2$. The surface morphology of the films was studied by scanning electron microscopy and atomic force microscopy (AFM), which suggested films prepared with a high scan rate were rougher in nature than the films produced with a low scan rate. The electrocatalytic reduction of nitrobenzene was carried out with these electrodes with the cyclic voltammetry technique in acetonitrile containing $0.1M$ $HClO_4$ as a supporting electrolyte. The various results obtained show that the conducting PPy thin-film electrodes were catalytically active toward the electroreduction process. The modified PPy film electrodes doped with $NiCl_2$ were more active toward nitrobenzene electroreduction than the PPy film alone. The results indicate that the roughness of the films played a very important role in determining their catalytic activity. The PPy films that were more rough in nature were catalytically more active than the smooth films; this may have been due to the availability of more reactive sites in the case of rough films. The apparent diffusion coefficients of the PPy film electrodes were also calculated. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1875–1881, 2012

Key words: atomic force microscopy (AFM); conducting polymers; diffusion; surface modification; thin films

INTRODUCTION

Conducting polymers, such as polypyrrole (PPy), polyaniline, and polythiophene, can be used as catalysts because of their ion and electron conductivity, and these materials show excellent reversible redox behavior. In general, conducting polymers have been studied extensively in recent decades for various applications, including light-emitting diodes,[1,2] electromagnetic interference shielding and electrostatic charge dissipation,[3] sensors and actuators,[4–6] energy conversion systems,[7,8] catalysts,[9–11] and corrosion protection.[12,13] The advantage of using conducting polymers is that the electrical properties of these materials can be reversibly controlled; this is because of their reversible redox properties, easy interfacing with electronic device, flexibility, long life, high stability, and environmental friendliness.

Conducting polymers, when used as catalysts, have an added advantage over commonly known polymer supported catalysts: these are sufficiently stable under the experimental conditions employed, permeable to electroactive species, and sufficiently conductive for current flow between the solution substrate, the electrocatalyst, and the current collector. The advantage of the use of such materials lies also in their fibrillar nature, which can be exploited to provide a large surface area for depositing particulate catalysts.

We reported previously that conducting PPy films modified by doping with $PdCl_2$ showed catalytic activity toward methanol electrooxidation and that the catalytic activity increased several times when these films were modified by ion-beam irradiation.[10] The better catalytic activity in the case of irradiated film samples was explained on the basis of better complexation between Pd and nitrogen atoms of the PPy chain. We also reported in one of our previous communications that in the electrochemical oxidation of methanol by conducting PPy doped with a series of metal halide dopants having different electronegativities, such as $ZrCl_4$, $NiCl_2$, and $CuCl_2$, the electronegativity of the dopant ions played an important role in the electrocatalytic activity, the results of which

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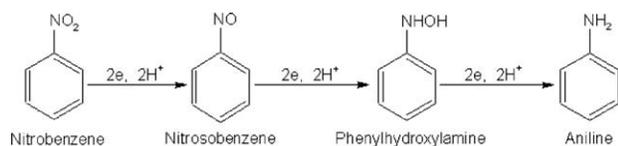
Scheme 1 Nitrobenzene electrochemical reduction reactions.

were explained on the basis of the charge-transfer efficiency at the electrode–electrolyte interface with an energy-level diagram.[11]

In the year 1898, Haber for the first time studied the electrochemical reduction of nitrobenzene. Haber[14] used a platinized platinum electrode for the electrochemical reduction of nitrobenzene.

The reduction of nitroaromatic compounds is of considerable interest because these are common groundwater contaminants, and reduction reactions can play a central role in their environmental fate or cleanup. Sources of nitroaromatic contaminants include activities associated with the production or utilization of explosives, dyes, agrochemicals, and pesticides. Reduction products of nitrobenzene are nitrosobenzene, phenyl hydroxylamine, aniline, and coupled products, such as azoxybenzene, azobenzene, and hydrazobenzene. The course of reactions varies with the reaction conditions, such as the temperature and pH, and also depends on the choice of electrode material, electrode potential, and electrolyte solutions.[15,16]

In this work, the electrochemical reduction of nitrobenzene (Scheme 1) was carried out with conducting PPy modified by doping with metal halide $NiCl_2$. Various reports exist in the literature about the reduction of nitrobenzene at various electrodes, mainly, Pt, Ni, Cu, and so on.[17–21]

The reduction of various organic molecules on modified conducting polymers has been done,[22–25] but a much lower number of references are found in the literature on the use of conducting polymer electrodes for the electrochemical reduction of nitrobenzene.[26–28] In this work, PPy film electrodes modified with $NiCl_2$ were found to exhibit high electrocatalytic activity toward nitrobenzene reduction as compared to the PPy film alone or the undoped one.

The effects of the roughness of the conducting PPy films on the electrocatalytic reduction reactions were also investigated. For that purpose, conducting PPy films of different roughnesses were prepared and modified by doping with $NiCl_2$. These films were employed to study the electrocatalytic reduction of nitrobenzene. It was observed that the greater the roughness of the films was, the greater was the catalytic activity.

The electrocatalytic behavior of any material depends on various factors, including (1) the posi-

tion of the energy levels involved for the reactive species and the electrode material, (2) the charge-transfer process across the interface of the electrode and electrolyte, (3) the diffusion of the reactive species into or through the polymer electrode, and (4) the surface morphology of the electrode. The first two factors were discussed in our previous communication,[29] and in this communication, second two factors are examined detail.

EXPERIMENTAL

Materials

The chemicals used for they synthesis of conducting PPy were monomer pyrrole (99.0% purity, SRL Chemicals, Mumbai, India, which was distilled before use) and sulfuric acid (H_2SO_4; Merck India, Mumbai, India, purity $\approx$ 98%). The transition-metal dopant $NiCl_2$, the reactant nitrobenzene ($C_6H_5NO_2$), the solvent acetonitrile (CH_3CN), and the electrolyte perchloric acid ($HClO_4$, 70%) were obtained from Merck India and were used as received. The water used in this work was ultrapure water (Milli Q).

Preparation of the conducting PPy electrodes

The conducting polymer-coated electrodes were prepared by the electropolymerization of pyrrole by a standard conventional route in a single-compartment, three-electrode cell connected to computer-controlled potentiogalvenostat (Vibrant EC2010 Lab India).[30] Pyrrole polymerization was carried out on gold-coated (vacuum-deposited) glass plates in an aqueous electrolyte containing $0.1M$ pyrrole and $0.1M$ H_2SO_4 with a platinum counter electrode at a 0.7-V [saturated calomel electrode (SCE)] constant potential for 120 s when the PPy films (ca. 0.5 μ m thick) got deposited. The area of the PPy thin-film electrodes prepared was 1×2 cm^2.

These PPy films as prepared were then undoped by the application of negative potential to the films. The electrochemical cell contained an aqueous solution of $0.1M$ H_2SO_4, and the potential applied was −0.7 V (cathodic) for 60 s. These films were then rinsed in distilled water and dried.

These undoped PPy films were then modified by redoping with the metal halide dopant $NiCl_2$ by placement of the films in 6 mM $NiCl_2$ solutions for 30 min; we then drained the excess liquid and dried the films. In one of our previous studies of nitrobenzene electrocatalytic reduction with different metal halide dopants, it was proven that $NiCl_2$-doped PPy was catalytically more active compared to the different dopants investigated, and hence, in this investigation, $NiCl_2$ was chosen as the dopant for the different experiments.[29] A dopant concentration of 6

mM was chosen to dope the PPy films, as previous investigations showed that this dopant concentration gave the highest catalytic activity for the reactants.[10,11,29] These films were employed to check the electrocatalytic activity of the PPy films, and the electrocatalytic reduction of nitrobenzene for different concentrations of the reactant.

PPy films of various roughnesses were also prepared by the use of the cyclic voltammetry (CV) technique instead of the normally used chronoamperometry technique. These were prepared by the scanning of the potential from 0 to 0.7 V (vs SCE) at various scan rates ranging from 10 to 150 mV/s. The deposition time was the same for all of the films (120 s). The same procedure was followed to modify films of various roughnesses with NiCl$_2$ dopant, as mentioned previously. These PPy thin-film electrodes prepared at various scan rates were used to investigate the effect of the roughness of the electrodes on the electrocatalytic reduction of nitrobenzene.

Electrocatalytic reduction of nitrobenzene

The electrocatalytic activity of the PPy doped with the NiCl$_2$ film electrode was studied with the CV technique at a scan rate of 50 mV/s from -1500 to $+1500$ mV. The electrocatalytic reduction reaction was carried out in a single-compartment, three-electrode cell (described previously) with aqueous 0.1M HClO$_4$ as the electrolyte and nitrobenzene as the reactant in the acetonitrile medium. The solution was purged with nitrogen before every run. The reactant nitrobenzene concentration was varied from 0.01 to 0.5M in the electrochemical reaction when the effect of the concentration of the reactant was being investigated; otherwise, the concentration of the reactant was constant at 0.1M.

Investigation of the surface morphology

The surface morphology of the PPy films was investigated with scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM instrument used in this investigation was a Leica Stereoscan 440 model manufactured by M/S Leica Cambridge, Ltd. (United Kingdom), and AFM imaging was done by a Nanoscope III Veeco (Digital Instruments, Plainview, NY).

AFM is a scanning probe technique that allows one to obtain a nondestructive three-dimensional picture of the surface. AFM does not require the surface to be conductive, and it has become a widespread method for characterizing surfaces. The AFM imaging in this work was done in air in contact mode. In contact mode, the tip is brought in contact with the surface, and the cantilever deflection is kept constant during scanning. The contrast of the image depends on the applied force, which, in turn, depends on the cantilever spring constant.

RESULTS AND DISCUSSION

Surface morphology investigation

SEM and AFM images were recorded for the films deposited at various scan rates. SEM images of the films deposited at 20, 30, and 60 mV/s are shown in Figure 1, whereas the AFM topography images of PPy films deposited at 20, 30, and 100 mV/s are shown in Figure 2. From the SEM and AFM images, it could be observed that the films deposited at a higher scan rate were more rough in nature than the films deposited at lower scan rates.

The AFM topography images were obtained by the scanning of an area of 10 $\times$ 10 μm^2. AFM imaging was done in air in contact mode. Different roughness parameters, such as root mean square (R_q), average height, average roughness (R_a), maximum deviation, and average height difference (R_z), were obtained from AFM data and are given in Table I.

To calculate the average height from the AFM topography images, the lowest point in the image was assigned the height of zero, and all other points in the image were higher than zero, whereas R_q was the standard deviation of the all of the Z (height) values. R_a was the average deviation from the mean surface plane. The maximum deviation was the furthest data point above or below the mean image plane, and R_z was the average difference in height between the five highest peaks and the five lowest valleys relative to the mean plane.

From the AFM data, it was observed that the conducting PPy films deposited at a higher scan rate were rougher compared to the films deposited at a lower scan rate.

Electrocatalytic reduction of nitrobenzene

The modified conducting-PPy-coated electrodes were employed for the electrochemical reduction of nitrobenzene. Figure 3 shows the CV for the bare Au electrode; undoped PPy-coated electrode, and PPy with doped NiCl$_2$ for nitrobenzene reduction reaction. The electrochemical activity in these cases was observed to clearly be enhanced with the modification of the electrodes, as evidenced by the enhancement of the current. The peak current at -500 mV for the NiCl$_2$-doped PPy electrode was greater compared to that of the undoped PPy electrode. To identify the nature and origin of the cathodic current, the concentration of nitrobenzene (reactant) in the electrolyte was increased from 0.01 to 0.5M, and CV was recorded for each with the
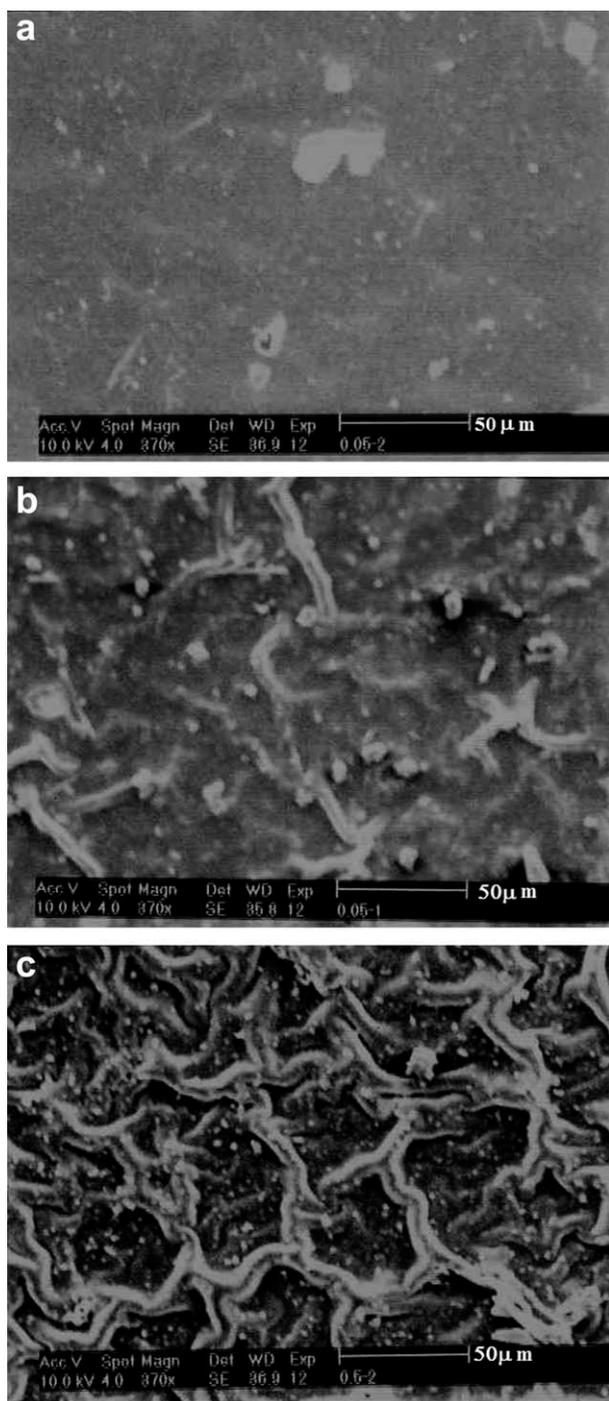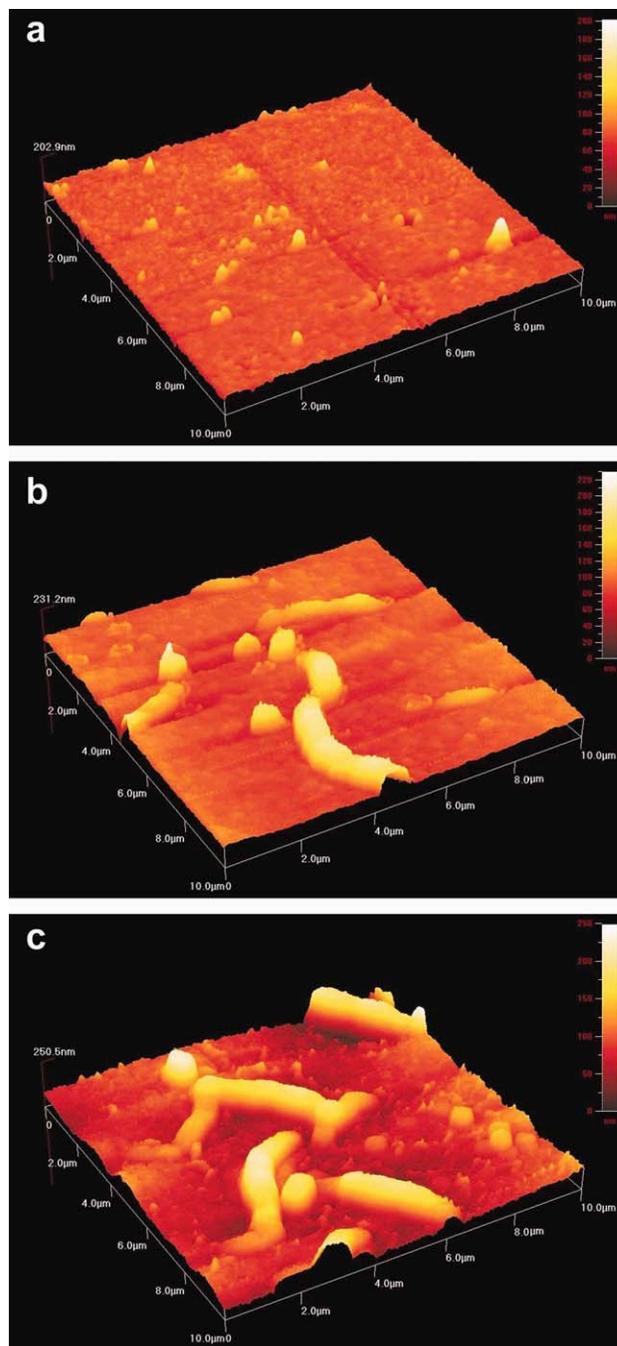
Figure 1 SEM images of PPy thin films prepared at different scan rates: (a) 20, (b) 30, and (c) 60 mV/s.

NiCl$_2$-doped, PPy-coated electrode as shown in Figure 4. It could be seen that there was a distinct peak appearing at the −500 mV (SCE) region, and the cathodic current at this potential increased with the increase in the concentration of nitrobenzene. Thus, the cathodic peak current at −500 mV was associated with the reduction of nitrobenzene; this was in agreement with electroreduction potential reported for this reactant.[31]

Effect of the surface roughness of the PPy films

As it was known that the surface morphology of the electrocatalyst plays an important role in electrochemical reactions, further reactions were carried out with conducting PPy electrodes of various roughnesses. PPy films of various roughnesses were prepared with different scan rates of deposition during electrosynthesis. The effect of the scan rate on

Figure 2 AFM topography images of PPy thin films prepared at different scan rates: (a) 20, (b) 30, and (c) 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Scan Rates for the PPy Film Deposition with Values of Average Height, R_q,
Mean Deviation, Maximum Deviation, and R_z Calculated from the
AFM Topography Images

Scan rate employed for the preparation of the films (mV/S)	Average height (nm)	R_q (nm)	R_a (nm)	Maximum deviation (nm)	R_z (nm)
10	77.7	7.77	4.9	125.2	202.9
30	96.1	19.9	12.2	135.1	231.2
50	159.9	25.7	14.8	231.7	391.5
100	174	59.6	38.1	818.7	992.8

the morphology of the PPy films could be seen in the SEM and AFM images. The PPy films deposited at higher scan rates were rougher than the films deposited at lower scan rates. The PPy films of various roughnesses were then doped with $NiCl_2$ and were employed to study the effects on the electroreduction of nitrobenzene. CV of the PPy–$NiCl_2$ films of various roughnesses for $0.1M$ nitrobenzene is shown in Figure 5. From CV, it could be observed that the cathodic peak current was greater for films that were more rough in nature than for the smooth films.

The catalytic efficiency of the films of various roughnesses was calculated with the cathodic peak current for nitrobenzene reduction. The catalytic efficiency in these cases was expressed with respect to the bare Pt electrode. Although platinum is considered to be an inert metal, it is surface is known to be covered with a thin oxide or hydroxide film. The PPy films were free from such surface films, and the electron exchange for Eq. (1) occurred without hindrance. Moreover, the high porosity and hence high

surface area of the conducting PPy, which could be due to the long polymer chain, promoted the catalysis of Eq. (1) on the PPy surface. The catalytic efficiency (γ) of PPy toward the reduction of nitrobenzene could be defined as

$$\gamma = \frac{100[I_P(\text{PPy}) - I_P(\text{Pt})]}{I_P(\text{Pt})} \tag{1}$$

where $I_P(\text{PPy})$ and $I_P(\text{Pt})$ are the peak current values of nitrobenzene reduction on the PPy and Pt electrodes, respectively, at -500 mV. The graph for the catalytic efficiency toward nitrobenzene reduction against PPy–$NiCl_2$ films of different surface roughnesses with respect to the bare platinum electrode are given in Figure 6. From the graph, it was observed that the catalytic efficiency was greater for the PPy film electrodes with high roughness (high scan rate of deposition). With increasing roughness of the film, the surface area increased, and this resulted in an increase in the number of sites for interaction with the reactant and gave rise to improved catalytic activity.
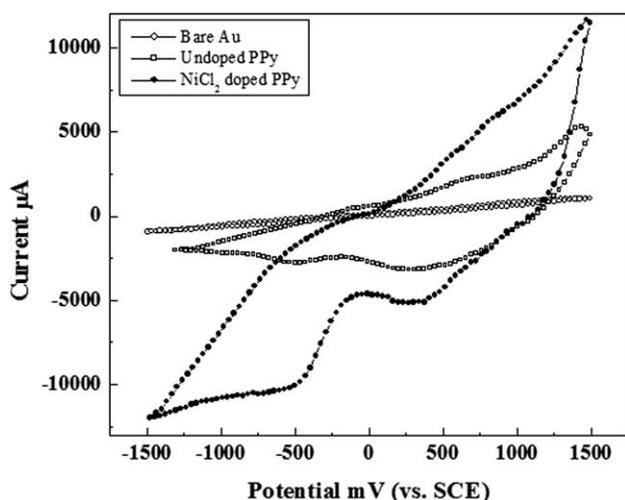

Figure 3 CV for the electrocatalytic reduction of nitrobenzene with Au, undoped PPy, and PPy–$NiCl_2$ doped electrodes. $HClO_4$ was used as a supporting electrolyte, and the nitrobenzene concentration was $0.1M$ in the reaction mixture. The reference electrode was SCE, and the counter electrode was Pt foil.
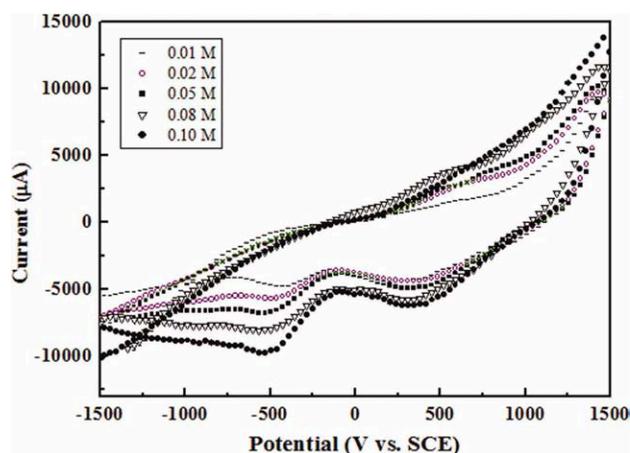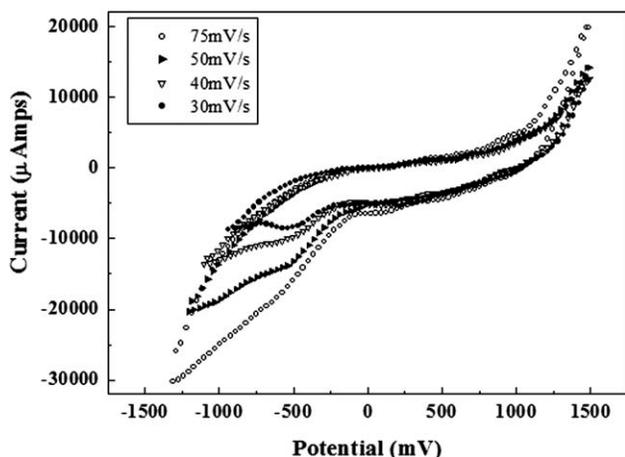

Figure 4 CV for the electrocatalytic reduction of nitrobenzene with $NiCl_2$-doped PPy electrodes for different concentrations of the reactant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
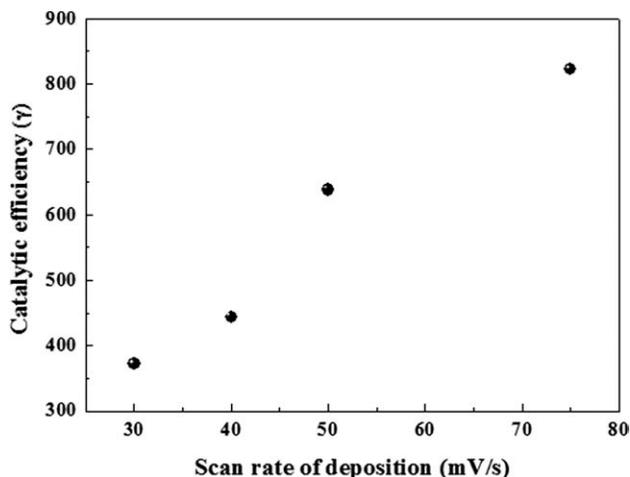
Figure 5 CV for the electroreduction of nitrobenzene ($0.1M$) with PPy films of various roughnesses (various scans of deposition).

The apparent diffusion coefficient (D_{app}) values of the films of different roughnesses were also calculated with Eq. (2) and are given in Table II:[32,33]

$$I_P = (2.69 \times 10^5)n^{3/2}AD_{app}^{1/2}c^0v^{1/2} \qquad (2)$$

where I_P is the peak current values of nitrobenzene reduction on different electrodes at -500 mV, n is the number of electrons transferred up to the rate-determining step, A is the area of the electrode, c^0 is the analyte concentration, and v is the scan rate. From the table, we observed that diffusion coefficient was greater in the case of films that were deposited at a higher scan rate; that is, D_{app} was greater for rougher films; this resulted in a higher catalytic activity. The D_{app} values obtained were in the range 10^{-8} to 10^{-9} cm^2/s; this was in agreement with literature.[34,35] Thus, the surface morphology of the electrode is also one of the important factors in

Figure 6 Graph of the catalytic efficiency versus scan rate of deposition (various roughnesses) of the PPy films toward the electrocatalytic reduction of nitrobenzene.

TABLE II
Peak Current and D_{app} Values of PPy Films of Different Roughnesses

Scan rate employed for the preparation of the films (mV/S)	D_{app} (cm^2/s)
30	5.09×10^{-9}
40	6.77×10^{-9}
50	1.25×10^{-8}
75	1.81×10^{-8}

designing an electrocatalyst apart from the energy level of the electrode–reactant and the rate of charge transfer across the electrode–electrolyte interface.

CONCLUSIONS

We observed in these studies that the conducting polymer PPy properly modified with dopant could be employed as a catalyst for the reduction of nitrobenzene. The surface morphology of the electrode played an important role in the electrolytic reduction with the conducting polymer. PPy films that were rougher in nature were catalytically more active than the smooth films; this may have been due to the availability of more reactive sites in the case of rough films. The effect of roughness was explained by the calculation of the diffusion coefficients of the films. It was shown in our previous communications that the energy level of the electrodes and charge-transfer process across the electrode–electrolyte interface appeared to be the main factor that determines the rate of the reaction. So, in the case of conducting polymer thin-film electrodes, the electrocatalytic behavior also depended on factors such as (1) the position of the energy levels involved for the reactive species and the electrode material, (2) the charge-transfer process across the interface of the electrode and the electrolyte, (3) the diffusion of the reactants into or near the electrode surface, and (4) the surface morphology of the electrode.

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