

A novel one-pot synthesis of free standing Pd–PPy films: Observation of enhanced catalytic effect by Pd–Ppy layers

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Abstract

A novel one-pot method to synthesize palladium nanoparticles incorporated polypyrrole films (Pd–Ppy) is described. The films are homogeneous with palladium particles and can be peeled from the electrode surface as a free standing films. Novelty of this procedure is that the palladium particles are prepared and stabilized in presence of the surface-active dopant, dodecylbenzene sulphonic acid sodium salt (NaDBSA), and are incorporated in to the polymer matrix along with dopant during the growth of the film. It is observed that the incorporation of palladium is uniform and homogeneous. An unprecedented catalytic activity by these Pd–Ppy composite layers in enhancing the rate of polymer deposition is observed. The films also electrocatalyze the oxidation of hydrazine more effectively than do the pure Ppy films.

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1. Introduction

Micro/nano metal particles dispersed on electrodes provide a large surface area on which many reactions are reported to proceed at accelerated rates [1–3]. The importance of noble metals, such as Ru, Rh, Pd and Pt in heterogeneous catalysis and electrocatalysis, especially in the research of fuel cells, is widely recognized [4,5]. Since then, there is a strong resurgence in the method of fabricating such systems offering highly dispersed metal particles that can provide large surface areas necessary for efficient catalysis.

Intrinsically conducting polymers (ICP) have attracted the scientific community ever since when polyacetylene was first synthesized by Shirakawa et al. in 1977 [6]. Soon after this, many new conducting polymers, under the name ‘synthetic metals’, such as polyaniline (PANI), polypyrrole

(Ppy) and polythiophene (PTh) were discovered [7]. Soon these polymers became foci of materials science and many applications are in vogue such as electrochromic displays [8], corrosion protection [9], electrostatic discharge, EMI shielding [10], batteries [11,12], sensors and electrocatalysis [13,14]. Thus the term ‘synthetic metal’ is slowly fading away and is being substituted by ‘advanced materials’. Palladium is a catalytically active metal which is useful for many organic transformation where new C–C bond is formed [15]. The cost of this metal is prohibitive for its generous usage and hence is dispersed as fine particles on conductive or inert supports. Palladium is also known to store highest volumes of hydrogen by a way of adsorption [16] and can act as good ‘hydrogen sensor’ under suitable conditions. Thus, choosing a suitable conducting polymer, namely polypyrrole and fine particles of palladium, a best combination for an effective sensor/electrocatalyst systems can be manipulated.

Polypyrrole is chosen for its excellent conductivity and film formation properties. There are many reports on the synthesis of palladium–polyaniline (Pd–Pani) [17–19] and

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palladium–polypyrrole [Pd–Ppy] systems [20,21] as a powder material. In contrast, very few reports are available on synthesis of Pd–Pani/ or Pd–Ppy films [22,23]. In studies related to synthesis of Pd–Ppy [24,25], the films were not homogeneous as the palladium depositions were only on the surface of the Ppy films. This process involved in two steps i) deposition of polypyrrole layer of suitable thickness and ii) electrodeposition of palladium particles on Ppy film. In the second step, palladium is deposited from an aqueous solution of a palladium salt [26] or from a solution of stabilized Pd⁰ nanoparticles [24]. The novelty in the present communication is one-pot synthesis of Pd–Ppy composite film. The Pd particles are stabilized by a surfactant which is also the dopant, i.e., sodium salt of dodecylbenzene sulphonic acid (NaDBSA) in aqueous medium. The palladium nanoparticles are incorporated into the Ppy film along with the dopant during electropolymerisation step. The results are presented and discussed.

2. Experimental section

All chemicals are analytical grade. Pyrrole and hydrazine salt were obtained from C.D.H chemicals (India). NaDBSA was purchased from Aldrich chemical company. Electrochemical experiments were performed on Solartron SI 1287 interface using three electrode assembly containing platinum foil working electrode (5 mm × 5 mm), platinum wire auxiliary electrode and saturated calomel (S.C.E) reference electrode. Electrooxidation of hydrazine was tested by taking 1 mM of hydrazine hydrochloride in 0.5 M KCl aqueous solution. FT-IR spectrum of the film was recorded on model no. Paragaon-500 of Perkin–Elmer. SEM images for film were taken on Hitachi 3000 H instrument. For obtaining better quality SEM pictures at high magnifications, samples were gold sputtered on JEOL-FINE COAT ion sputter (model no. JFC-1100) for three minutes. Palladium was estimated by atomic absorption spectroscopy (AAS) after leaching a 2.5 cm × 2.5 cm measuring Pd–Ppy film in concentrated nitric acid for 48 h on Varian, model no. 220 instrument. X-ray diffraction experiments were conducted on PANalytical's X'Pert PRO instrument.

2.1. Preparation of NaDBSA stabilized Pd nanoparticles (Pd–NaDBSA) dispersion

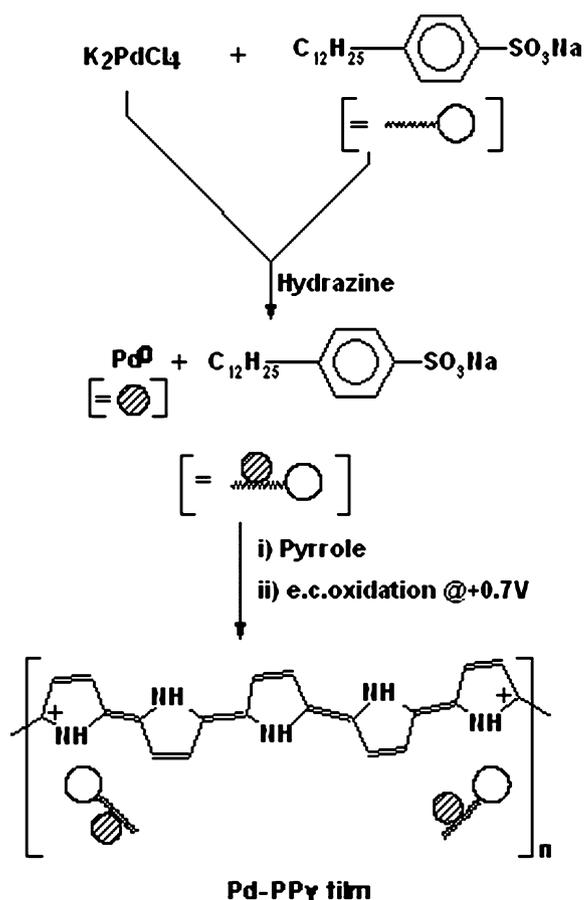
Dodecylbenzene sulphonic acid, sodium salt (NaDBSA) stabilized palladium nanoparticle dispersion is synthesized as follows. To an aqueous NaDBSA solution (57 mM, 50 ml), K₂PdCl₄ (0.07 mM) was added and heated on water bath to get clear yellow solution. To this was added an aqueous solution of hydrazine hydrochloride (0.047 M, 10 ml) with stirring. After few minutes, the colour of solution turned to black–brown suggesting reduction of palladium ions to palladium metal. This solution was further heated for 2–3 h to remove/decompose excess of hydrazine and was finally filtered for a clear solution.

2.2. Electrosynthesis of Pd–Ppy films

Pd–Ppy films were synthesized from the above Pd–NaDBSA solution. After cooling the solution to room temperature, pyrrole (0.4 mM) was added and Pd–Ppy films were grown by potentiostatic deposition at 0.7 V on platinum or S.S electrodes (316 grade) (2.5 cm × 2.5 cm). The deposition was carried out for a minimum period of 30 minutes. The electrode was taken out and washed with copious amounts of distilled water, dried at room temperature and desiccated. Whenever needed, the free-standing films are readily obtained by carefully peeling the film from the base electrode with help of a razor blade.

3. Results and discussion

Scheme 1 explains the strategy for the synthesis of palladium incorporated Ppy films. Palladium nanoparticles are obtained by reducing K₂PdCl₄ with hydrazine in presence of dodecylbenzene sulphonate which acts as stabilizer for the nanoparticles and also dopant for polypyrrole. The formation of the nanoparticles is evident from appearance of black–brown colour from initial yellow colour originating from tetrachloropalladate ions. After addition of required amount of pyrrole monomer to this black solution, polypyrrole films containing palladium are obtained on to the



Scheme 1. Strategy showing synthesis of Pd–Ppy films.

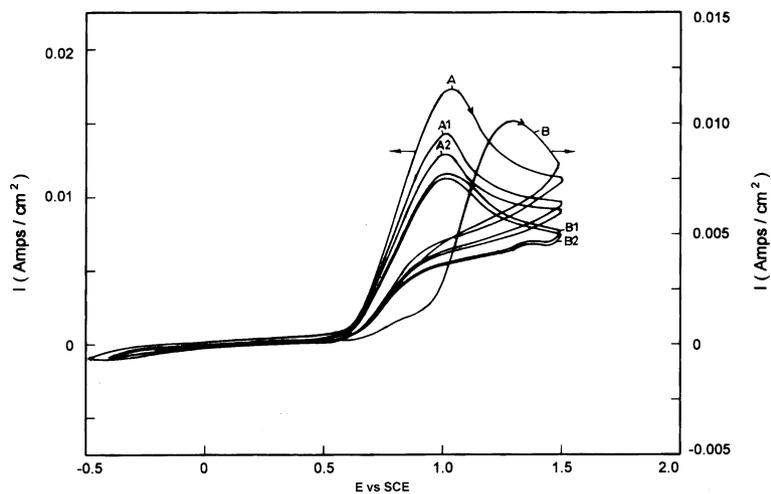


Fig. 1. Cyclic voltammetric deposition of (A) Pd-Ppy (B) pure Ppy film on platinum electrode. The scan rate is 50 mV/s.

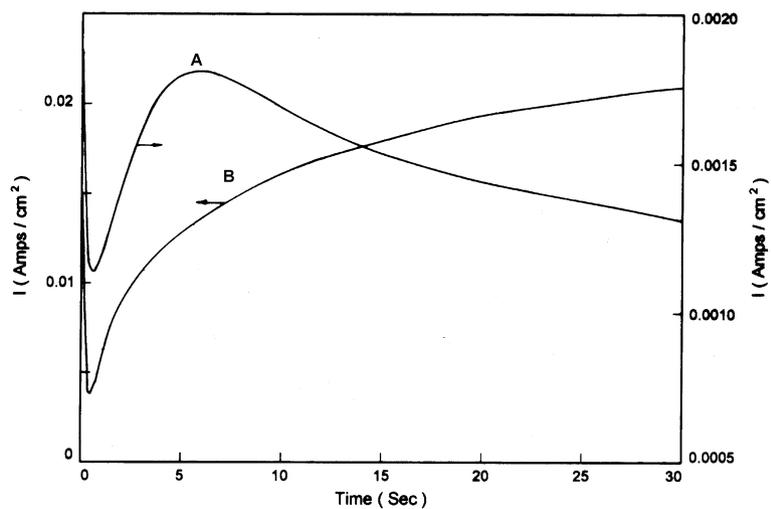


Fig. 2. Current–time profiles for potentiostatic deposition of (A) Pure Ppy (B) Pd-Ppy films at 0.7 V vs SCE on platinum electrode.

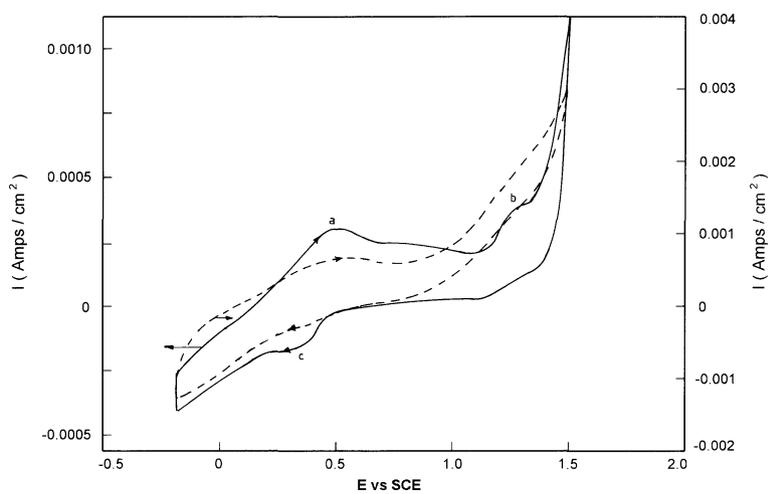


Fig. 3. Cyclic voltammograms exhibited by Ppy and Pd-Ppy films in 1 M sulphuric acid solution. The scan rate is 50 mV/s.

platinum (or stainless steel) electrode by potentiostatic deposition at 0.7 V vs SCE. The films can be grown up to a minimum of 50–60 μm thickness, dried and can be peeled from the substrate. To increase the percentage of active palladium particles on the surface of the films, it is recommended that a final conditioning of the film is recommended. The conditioning is done by treating the grown film potentiostatically in the range -0.5 to -0.3 V for few minutes in the same solution. This process facilitates deposition of free palladium nanoparticles on the Pd-Ppy film, which are otherwise co-deposited along with polymer.

FT-IR spectrum of Pd-Ppy film exhibited broad band at 3435 cm^{-1} due to $-\text{NH}-$ stretching. A couple of bands at 2850 and 2918 cm^{-1} are due to $-\text{C}-\text{H}$ stretching mode originating from ring carbons of pyrrole are observed. The absorption bands appearing at 1587 and 1531 cm^{-1} are from the combination of an intra-ring $\text{C}=\text{C}$ vibration and an inter-ring $\text{C}-\text{C}$ stretch. Bands at 1432 and 1380 cm^{-1} are due to $\text{C}=\text{N}$ stretching. These are all found in accordance with reported data [26,27] and hence confirm the formation of polypyrrole film. The diffuse reflectance spectrum of the free-standing film exhibited bands at 388 nm due to valence \rightarrow conduction band ($\pi \rightarrow \pi^*$) and a high intense band which onsets at 450 nm . This band extends into near IR region and is originating from charge carriers [27,28], implying conductive state of the polymer.

Fig. 1 shows the cyclic voltammetric deposition of Pd-Ppy film at 50 mV/s on platinum electrode. Without the addition of palladium, the oxidation of pyrrole (i.e., first radical cation formation) took place at 1.28 V in the first scan (curve B, Fig. 1) and subsequently reduced to 1.0 V from second scan onwards (curves B1, B2). When polymerization is carried out in presence of palladium particles, the initial oxidation (radical cation formation) of pyrrole took place at lower potential, i.e., 1.03 V (curve A, Fig. 1) and decreased to 1.0 V in the second scan onwards (curves A1, A2). Fig. 2 shows potentiostatic deposition of pure Ppy and Pd-Ppy films. The growth of pure Ppy gave char-

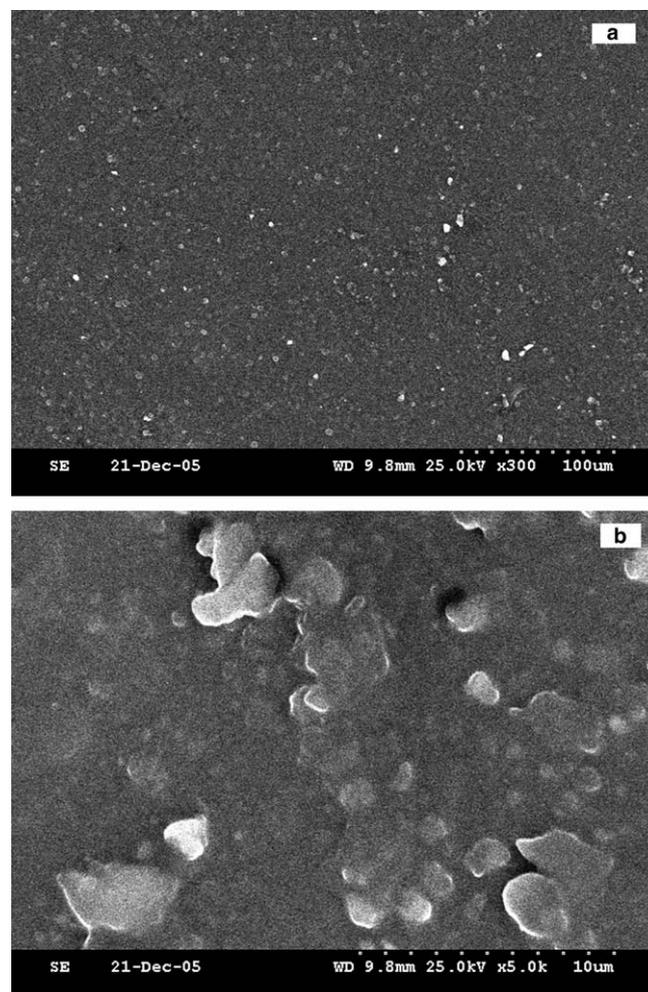


Fig. 5. Scanning electron micrographs of free standing Pd-Ppy films (a) at 300 and (b) at 5000 magnifications.

acteristic $I-t$ curve [29–31] (Fig. 2, curve A) showing that there is random nucleation of polymer phase and three dimensional growth. In presence of palladium (Fig. 2,

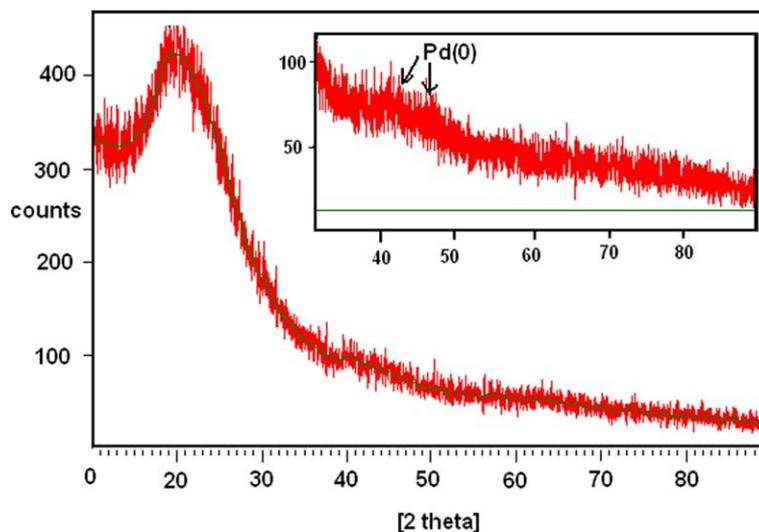


Fig. 4. X-ray diffractogram of Pd-Ppy free-standing film. Inset diagram shows broad peaks due to incorporated palladium metal.

curve B), the current keeps increasing indicating that better ordered polymer with layered structure is formed.

The evidence for the presence of incorporated palladium in the polymer matrix comes by performing cyclic voltammetry (CV) and X-ray diffraction for Pd–Ppy film. Fig. 3 exhibits CV of Pd–Ppy film in 1 M sulphuric acid solution. It is clearly seen that the Ppy matrix undergoes oxidation around 0.47 V (peak 'a', $\text{Ppy} \rightarrow \text{Ppy}^+$). The incorporated palladium particles undergo oxidation at 1.3 V (peak 'b', $\text{Pd}^0 \rightarrow \text{PdO}$) which later on the reversal of the potential, undergo reduction (peak 'c', $\text{PdO} \rightarrow \text{Pd}^0$) at 0.32 V. These peaks are absent in pure Ppy film (Fig. 3). More over, the oxidation peak at 1.3 V (peak 'b') and the corresponding reduction peak at 0.32 V (peak 'c') are also present in the Pd–DBSA dispersion. This observation is similar to the report available in literature [25], expect that the oxidation process arising from palladium nanoparticles is a well resolved peak at 1.4 V. In the present Pd–Ppy system, this oxidation peak is not well resolved and occurs at 1.3 V. This is due to the reason that the palladium particles are embedded in the polymer matrix and enjoy different environment compared to the literature system.

X-ray diffraction (Fig. 4) of the free-standing Pd–Ppy film exhibited broad pattern spread over in 2θ range = 15–30° due to polypyrrole and low intensity broad diffraction (inset, Fig. 4) at around $2\theta = 40^\circ$ arising from the incorporated palladium metal. The broad nature of the peak suggests that very fine particles of palladium are present in the polymer matrix.

The conductivity of the Pd–Ppy films at room temperature, measured by four-probe method, is found to be around 50 S/cm, which is higher than pure polypyrrole film

(1 S/cm) grown under same experimental conditions. This is due to the incorporation of palladium particles homogeneously throughout the polymer matrix. The loading of palladium metal into the polymer matrix, analyzed by AAS, is in the range 38–50 $\mu\text{g}/\text{in}^2$ (or 6–8 $\mu\text{g}/\text{cm}^2$). It is observed that increase in concentration of palladium loading resulted in brittle films. More over it is difficult to get stabilized Pd nanoparticles with higher concentrations of K_2PdCl_4 as most of it precipitates as palladium black.

During the growth of Ppy film it is observed that in presence of fresh palladium nanoparticles, the rate of deposition of film is increased. Moreover, the film is uniform throughout the electrode. This effect is clearly observed on catalytically inactive substrates such as S.S. In presence of palladium particles, when Ppy film is deposited potentiostatically at 0.7, a 45 μm thick Pd–Ppy film is formed on 1 cm^2 S.S electrode in 30 min. In the absence of palladium particles, only 30 μm thick film was formed on S.S. electrode. As shown in the Scheme 1, the palladium nanoparticles are co-deposited along with the growing polymer chain, to form a composite layer of Pd–Ppy. This layer has greater catalytic activity than pure Ppy layer and hence acts as a better catalytic surface for the growth of fresh layers of Pd–Ppy. Thus the rate and hence thickness of Ppy layer are increased. To the best of our knowledge on conducting polymers, this observation is unprecedented.

Figs. 5 and 6 show the surface morphology of the free standing Pd–Ppy film as observed by SEM and AFM techniques, respectively. The film is smooth, uniform at lower magnifications (Fig. 5 (a) and (b)) and has regular globular structures, typical of conducting polypyrrole. Fig. 6 shows atomic force micrograph of the same film. The film is char-

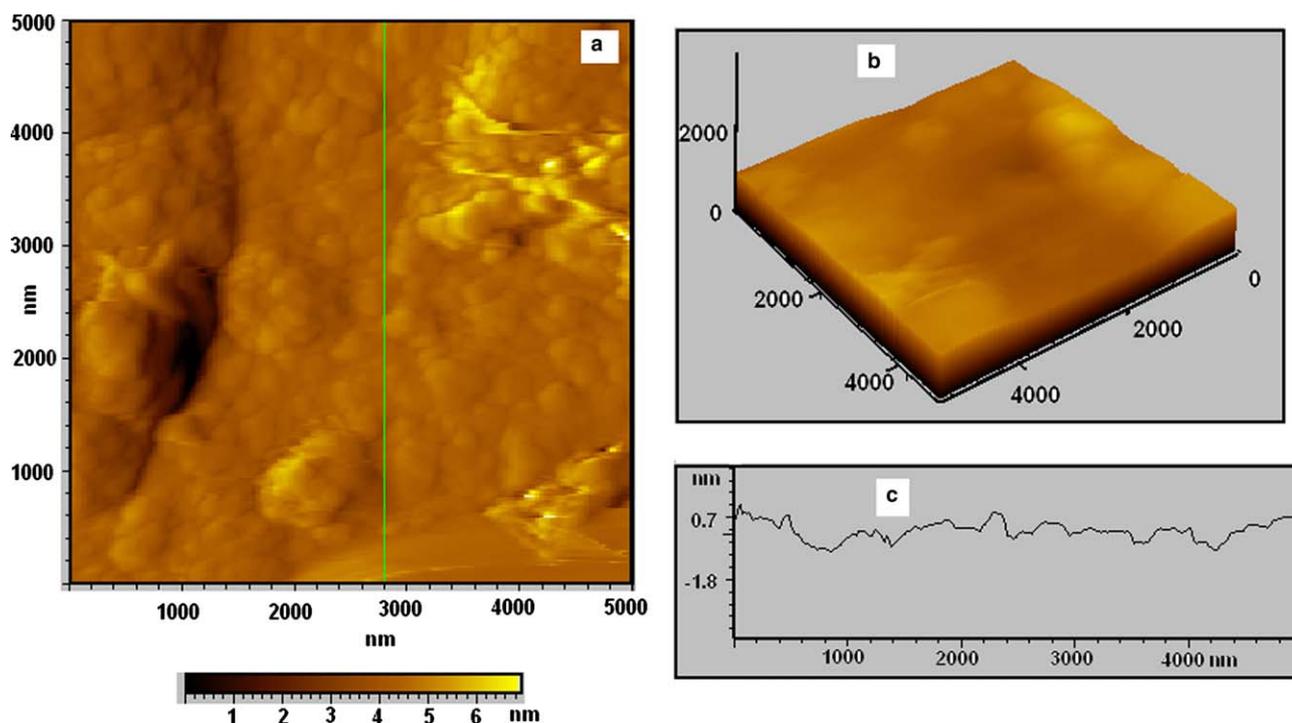


Fig. 6. (a) Surface appearance (b) topography and (c) vertical cross section of Pd–Ppy film as probed by AFM.

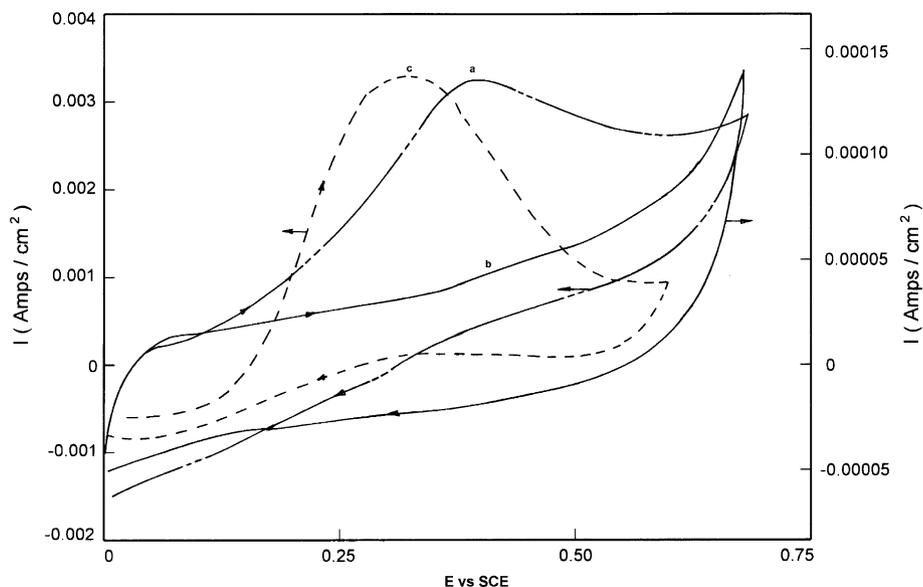


Fig. 7. Cyclic voltammogram of 1 mM hydrazine hydrochloride in 0.5 M KCl solution at (A) Pd–Ppy film (B) pure Ppy film and (C) pure Pd metal. The scan rate is 50 mV/s.

acterized by kinks/folds and over grown patches (up to 6 nm) of the polymer. The topography of the film is shown in Fig. 6(b).

4. Catalytic activity towards oxidation of hydrazine

Hydrazine, an important high-performance fuel in energy storage and conversion, is found to be electrocatalytically oxidized on this type of Pd particle modified Ppy. Electrooxidation of hydrazine occurs at 0.4 V on the Pd–Ppy electrode (curve A, Fig. 7) while hydrazine shows no response on bare Ppy deposited electrode in the potential range from 0.0 to 0.6 V (curve B, Fig. 7). The electrocatalytic activity of the pure palladium film is also tested (Fig. 7, curve C). On pure palladium film, the oxidation of hydrazine occurred at 0.38 V with lower current intensity, demonstrating only marginal difference in the catalytic activity compared to Pd–Ppy film. The difference is due to the lower size particles of Pd in Pd–Ppy compared to the polycrystalline nature of the Pd film. The low potential of electrooxidation and large anodic current exhibited by Pd–Ppy film compared to pure Ppy film, indicate high electrocatalytic activity of the Pd nano particles in the Ppy film. Moreover, we observed that the current decreases and the peak potential shifts negatively with the increasing of potential cycles. Considering the existence of some impurities in the solution of hydrazine, it is reasonable to suggest that the decreasing of the electrocatalytical current results from the contamination of the solution. Thus Pd–Ppy film electrode can be used to detect the traces of hydrazine with good reproducibility and stability [32].

5. Conclusion

We have demonstrated a process for one-pot synthesis of palladium incorporated polypyrrole films that exhibited

higher electronic conductivity. These films are homogeneous in palladium composition and can be separated from the base electrode. Interestingly, unprecedented catalytic effect by Pd–Ppy layers is observed in deposition of further layers of polypyrrole. These Pd–Ppy films are good electrocatalysts for hydrazine oxidation and the activity is comparable to the pure palladium metal. The films promise for a good hydrogen sensor activity.

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