

# Electrocatalytic properties of monometallic and bimetallic nanoparticles-incorporated polypyrrole films for electro-oxidation of methanol

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## Abstract

Oxidative electrochemical polymerization of pyrrole at indium-doped tin oxide (ITO) is accomplished from a neat monomer solution with a supporting electrolyte (0.3 M *n*-tetrabutyl ammonium tetrafluoroborate) by multiple-scan cyclic voltammetry. Polypyrrole (Ppy) films containing nanometer-sized platinum and Pt/Pd bimetallic particles are electro-synthesized on ITO glass plates by voltammetric cycling between  $-0.1$  and  $+1$  V (versus Ag/AgCl/3 M NaCl). The electrocatalytic oxidation of methanol on the nanoparticle-modified polypyrrole films is studied by means of electrochemical techniques. The modified electrode exhibits significant electrocatalytic activity for methanol oxidation. The enhanced electrocatalytic activities may be due to the uniform dispersion of nanoparticles in the polypyrrole film and a synergistic effect of the highly-dispersed metal particles so that the polypyrrole film reduces electrode poisoning by adsorbed CO species. The monometallic (Pt) and bimetallic (Pt/Pd) nanoparticles are uniformly dispersed in polypyrrole matrixes, as confirmed by scanning electron microscopic and atomic force microscopic analysis. Energy dispersive X-ray analysis is used to characterize the composition of metal present in the nanoparticle-modified electrodes. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Electrocatalytic activity; Methanol oxidation; Polypyrrole; Platinum nanoparticles; Platinum/palladium bimetallic nanoparticles; Fuel cell

## 1. Introduction

There is increasing interest in the electro-oxidation of methanol because of the development of direct methanol fuel cells (DMFCs) as power sources for electric vehicles and electronic devices. The DMFC is a promising future technology as an alternative to conventional energy-generating devices due to its higher energy-conversion efficiency, low-to-zero pollutant emissions, ready availability of methanol fuel, ease in distribution, and high energy [1]. Platinum is used in such fuel cells on the basis of its activity for methanol oxidation. There is, however, a particular difficulty, namely, the poisoning of anode catalysts by adsorbed carbonyl species that are derived from methanol oxidation. To improve the catalytic performance and to decrease the poisoning effect of the anode catalyst, composite catalytic sys-

tems such as Pt/Ru [2,3] and Pt/WO<sub>3</sub> [4] have been investigated. An alternative approach is the dispersion of precious metals such as Pt, Ru, Au and Pd on to a conducting matrix such as carbon or graphite. Such electrodes are not easy to fabricate due to the high carbon/graphite concentrations that are required for conductivity. To overcome such difficulties, conducting polymers have been used as a substrate for the incorporation of metal particles. These systems present a new and novel class of electrode materials.

Conducting polymers offer great advantages over other materials since they are permeable to electroactive species, readily modified by different techniques, and easy to coat on various substrates. The polymers possess high electronic conductivity and a porous structure, which can accommodate a dispersed catalyst with a large surface area that is necessary for efficient electrocatalysis. Conducting polymers with porous structures and high surface areas, such as polyaniline and polypyrrole (Ppy), are usually employed as matrix to incorporate noble metal catalysts for the electro-oxidation of small molecules such as hydrogen,

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methanol and formic acid [5–15]. The reason for incorporating metallic particles into porous matrixes is to increase the specific area of these materials and thereby improve catalytic efficiency. Another reason is the higher tolerance of the platinum particles to poisoning due to the adsorption of CO species, in comparison with the serious problem of poisoning of bulk platinum electrodes.

Polypyrrole is one of the most attractive polymers due to its stability and easy processibility at ambient conditions. The electrocatalysis of the reduction of oxygen [16–18], the oxidation of hydrogen [18,19] and the oxidation of methanol [20,21] has been investigated by using Pt microparticles incorporated in a polypyrrole film. Nanotechnology imparts a well-developed surface chemistry [22], a controllable geometry [23], rigidity and chemical stability [24]. It is an excellent tool to evaluate the contribution of conformational entropy in polyvalent binding, as elucidated by Whitesides et al. [25,26]. The improvement of catalysis at the nanoscale domain is mainly necessary for economic reasons. Metals in the form of nanoparticles are expected to play an important role in electrocatalytic reactions. With this in view, the present work is undertaken to investigate the catalytic activity of an electrochemically-synthesized polypyrrole film modified with monometallic and bimetallic nanoparticles towards the electro-oxidation of methanol. Three electrodes were fabricated, namely, indium-doped tin oxide (ITO) modified with Ppy, Ppy–Pt(0) and Ppy–Pt/Pd(0), have been used for the investigation of methanol oxidation. The surface morphology of the nanoparticle-coated electrodes was characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The presence of metallic particles was confirmed by means of X-ray (EDAX) analysis.

## 2. Experimental

Hexachloroplatinic acid and trisodium citrate were obtained from Merck. Pyrroles and *n*-tetrabutyl ammonium tetrafluoroborate were received from Aldrich. All the solvents were distilled prior to use. The solutions were prepared with millipore water. All the electrochemical measurements were carried out under a nitrogen atmosphere at room temperature.

Electropolymerization of pyrrole was studied using an ITO (1 cm × 1 cm) glass plate as the working electrode in 0.3 M *n*-tetrabutyl ammonium tetrafluoroborate as electrolyte. An Ag|AgCl (3 M NaCl) and Pt electrode served as the reference electrode and counter electrode, respectively. All potentials in this work are reported with respect to the Ag|AgCl scale. The electrochemical measurements were performed with a CHI600B instrument.

Surface analysis was carried out with a LEO-stereoscan 440 scanning electron microscope. The presence of metal nanoparticles in the polymer matrix was investigated by means of energy dispersive X-ray analysis (INCA200). An AFM (NANOSCOPE IIIa, Digital instrument) with a 90 μm scan range was used to view the surface morphology of the polymer electrodes. Images were obtained by scanning at a rate of 1.5 Hz using the contact mode technique. A 3D height mode was used to

characterize all the samples where bright colours indicated the higher regions, while darker regions were lower regions of the samples. UV–vis spectroscopy (PERKIN ELMER LAMBDA 25) was used to study the optical properties of the metal nanoparticles and their size was confirmed with transmission electron microscopy (TECHNIE 10) with 80-kV accelerating voltage.

The Pt colloid was prepared via a standard protocol method [27]. H<sub>2</sub>PtCl<sub>6</sub> (4 cm<sup>3</sup> of 5% (w/w) aqueous solution) was added to freshly-distilled water (340 cm<sup>3</sup>) and heated to 80 °C with efficient stirring. Sodium citrate (60 cm<sup>3</sup> of a 1% (w/w) aqueous solution) was added and heating was continued for about 4 h. The resultant Pt colloid was transparent and had a weak absorption tail stretching across the UV region but no absorption at λ > 200 nm. The colloid was found to be stable for months.

Colloidal suspensions of Pt/Pd bimetallic nanoparticles were prepared using a modified procedure based on that reported elsewhere [28]. Fifty milliliters of 9.3 × 10<sup>−4</sup> M PdCl<sub>2</sub> (0.016 g in 2 ml of 1 N HCl and made upto 100 ml) and 100 ml of 3.4 × 10<sup>−2</sup> M tri-sodium citrate were taken in a round bottom flask and stirred for 15 min. 212.5 ml of 1.4 × 10<sup>−3</sup> M chloroplatinic acid and 37.5 ml of 3.4 × 10<sup>−2</sup> M tri-sodium citrate

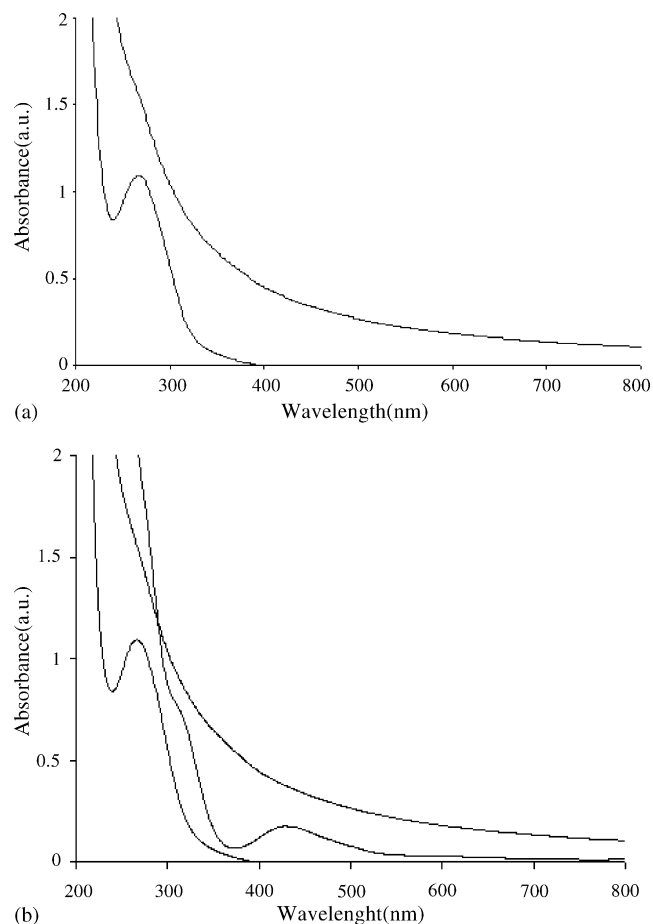


Fig. 1. UV–vis spectrum of citrate stabilized metallic nanoparticles: (a) platinum and (b) Pt/Pd bimetallic.

were added and the solution was further diluted to 100 ml and refluxed at 90 °C under stirring for 6 h until a brown colour had developed. The solution was then filtered and stored for further use.

### 3. Results and discussion

The UV–vis spectra for the platinum (Pt) and the Pt/Pd (0) nanoparticles are shown in Fig. 1(a) and (b), respectively. Absorptions were observed at 260 and 425 nm and can be attributed to ligand-to-metal charge transfer transitions of  $[\text{PtCl}_6]^{2-}$  and  $[\text{PdCl}_4]^{2-}$  ions. The absorption peaks due to platinum and palladium ions completely disappear after refluxing the solution, which indicates the complete reduction of the precursor metal ions. This is also further confirmed using TEM analysis (Fig. 2(a) and (b)) that show an average size of  $\sim 5$ –6 and  $\sim 8$ –9 nm for monometallic and bimetallic nanoparticles, respectively.

For the fabrication of Ppy films, the working electrodes were typically cycled between +1000 and –1000 mV at  $100 \text{ mV s}^{-1}$  in order to effect polymerization. Oxidative elec-

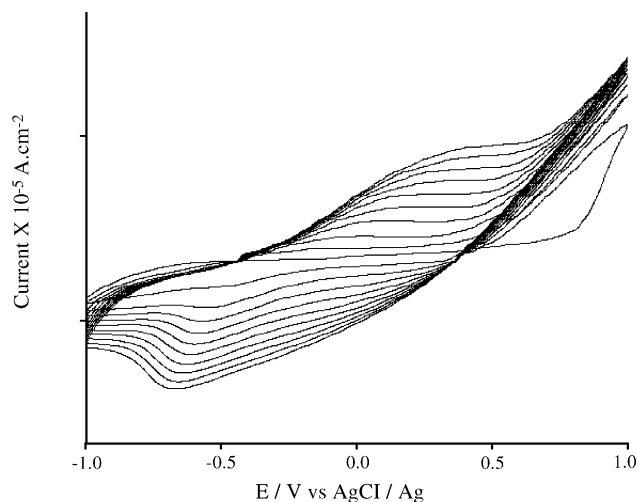


Fig. 3. Electro-polymerization of polypyrrole at ITO from neat polypyrrole containing 0.3 M TBABF<sub>4</sub> at  $100 \text{ mV s}^{-1}$  between 1 and –1 V.



Fig. 2. Transmission electron microscopic images of citrate stabilized metallic nanoparticles: (a) platinum and (b) Pt/Pd bimetallic.

trochemical polymerization of pyrrole at ITO has been accomplished from neat monomer solution containing only added electrolyte (0.3 M *n*-tetrabutyl ammonium tetrafluoroborate) for 10 continuous cycles. Representative data for the electropolymerisation of pyrrole containing 0.3 M TBABF<sub>4</sub> on ITO is shown in Fig. 3. On the first anodic scan, a single anodic wave is observed at a relatively high potential. This is due to the oxidation of pyrrole monomer to produce the radical cations. Upon reduction, two cathodic waves are observed due to reduction of the radical cation and the oxidized polymer, respectively. With each successive scan, the peak current associated with both the anodic and cathodic waves of the polymer increases continuously, which suggests the growth of the polymer film. With repetitive cycling, an increasingly thick, dark-black film is deposited on the working electrode. Once polymerization is accomplished, the polypyrrole-coated electrode is removed from the cell and rinsed copiously with acetone and deionized water. The electrode is then characterized by cyclic voltammetry in the same range at a scan rate of 100 mV s<sup>-1</sup> in an aqueous monomer-free 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Voltammograms for polypyr-

role films exhibit fairly well-defined oxidation and reduction peaks.

Nanoparticle-dispersed polypyrrole electrodes were prepared by electrodepositing the prepared nanoparticles during the course of polymerization. The electro-oxidation of a nanoparticle-modified polypyrrole electrode shows a high elec-

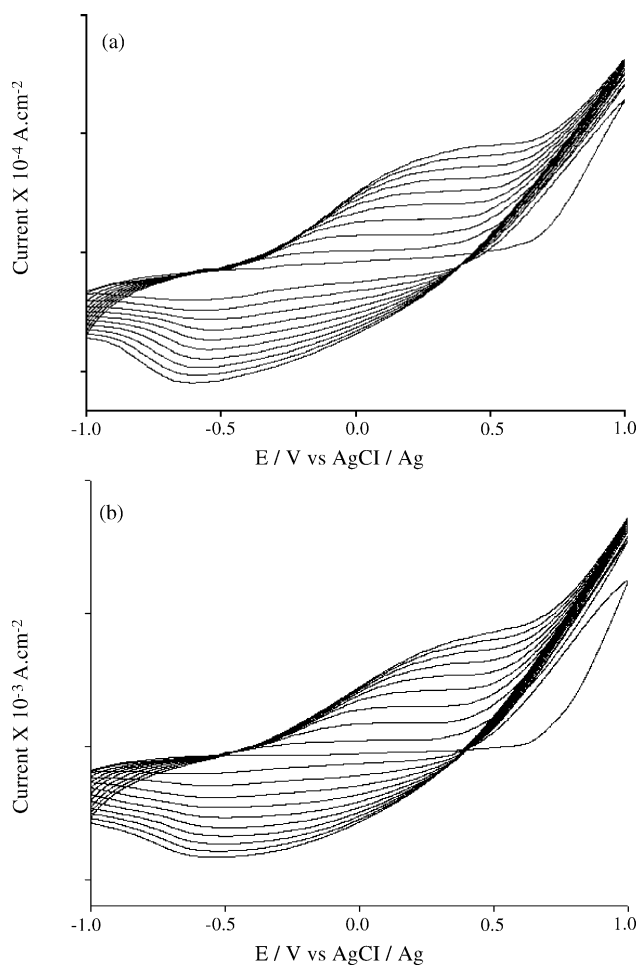


Fig. 4. Electro-polymerization of modified polypyrrole with (a) Pt(0) and (b) Pt/Pd(0) at ITO from neat polypyrrole containing 0.3 M TBABF<sub>4</sub> at 100 mV s<sup>-1</sup> between 1 and -1 V.

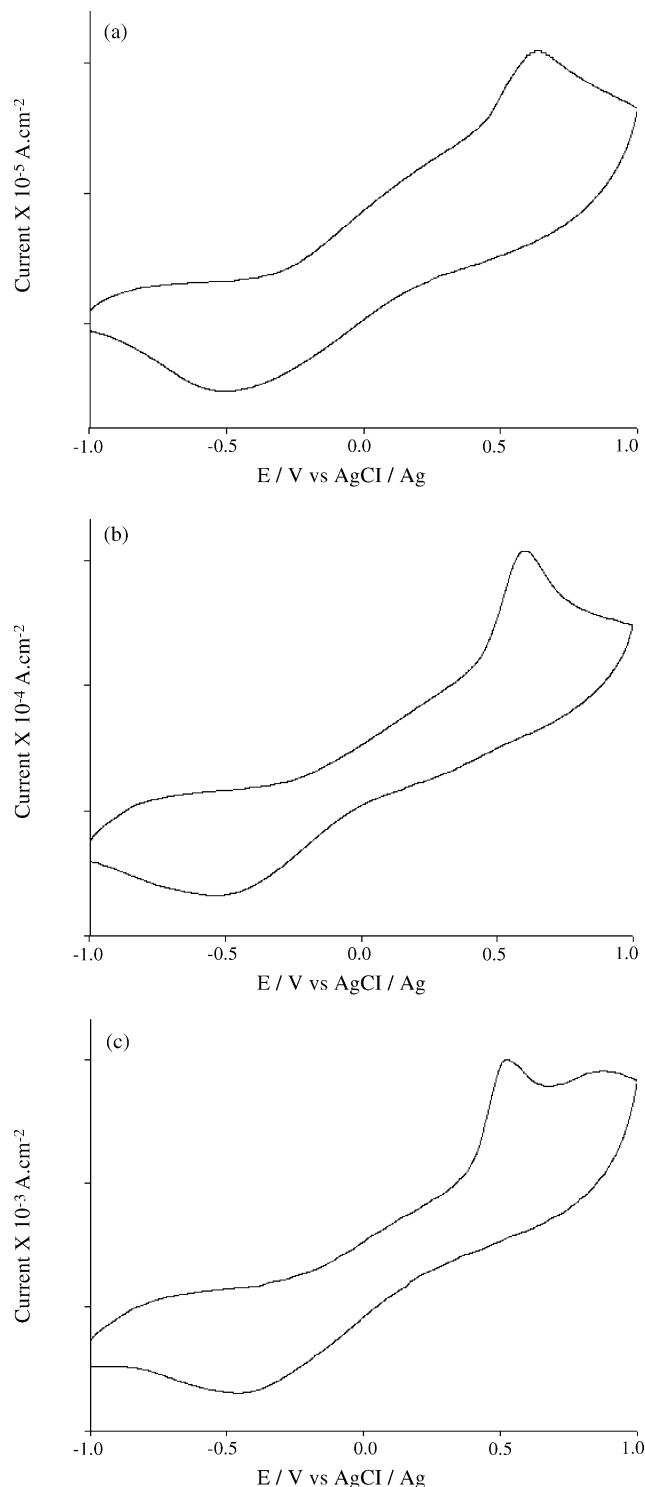
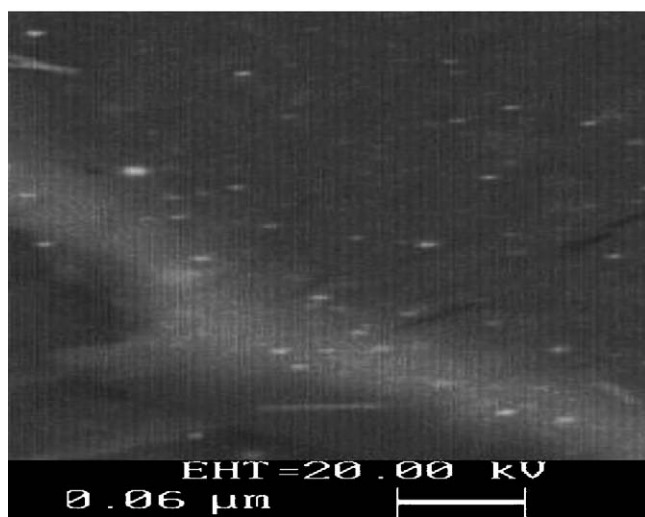


Fig. 5. Cyclic voltammograms of polypyrrole: (a) ITO/Ppy, (b) ITO/Ppy/Pt(0) and (c) ITO/Ppy/Pt-Pd(0). Electrolyte is 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH.

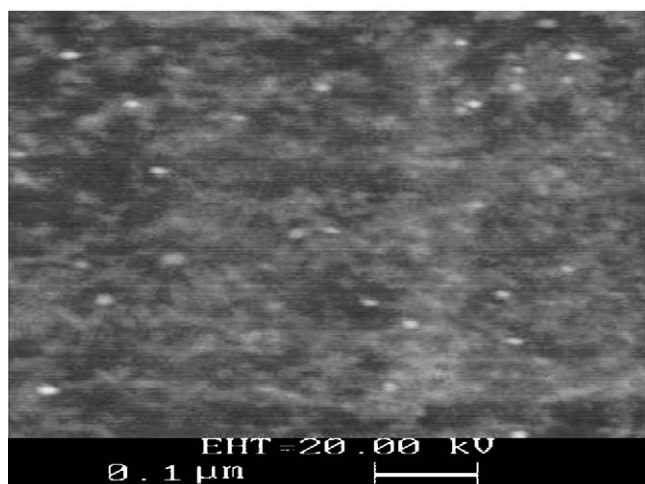
Table 1  
Methanol oxidation activity on Pt and Pt/Pd(0)-incorporated polymer matrixes

Electrode	Onset potential for CH <sub>3</sub> OH oxidation vs. Ag AgCl	Peak curve density, $\times 10^{-5} \text{ A cm}^{-2}$
ITO/Ppy	0.4890	1.0418
ITO/Ppy/Pt(0)	0.4248	9.6830
ITO/Ppy/Pt–Pd(0)	0.3500	17.1509

troactive response that might be due to the oxidation of a pyrrole moiety on the surfaces of the nanoparticles. A further increase is observed in the case of a bimetallic nanoparticle-modified polypyrrole electrode since the catalytic activity is higher on a bimetallic nanoparticle surface than on a monometallic nanoparticle surface [29–31]. Corresponding data obtained for both monometallic and bimetallic nanoparticle-modified polypyrrole electrodes in aqueous electrolyte solution are shown in Fig. 4 (a) and (b), respectively.



(a)

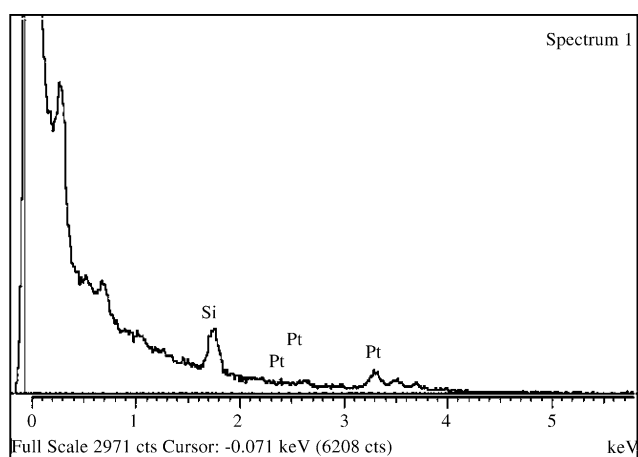


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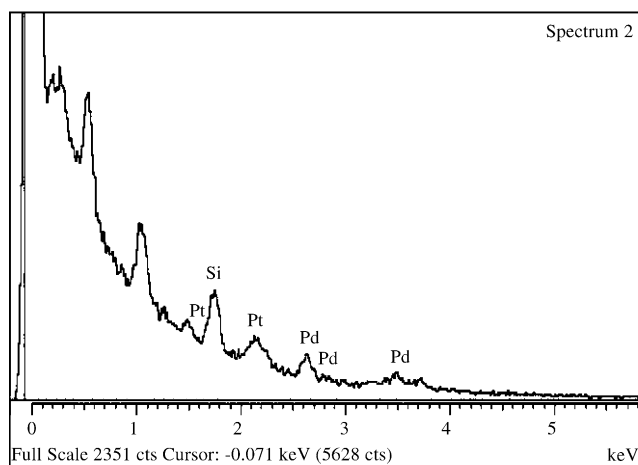
Fig. 6. Scanning electron micrograph of pyrrole matrix with incorporated metallic nanoparticles: (a) ITO/Ppy/Pt(0) and (b) ITO/Ppy/Pt–Pd(0).

Electro-oxidation of methanol on monometallic and bimetallic nanoparticle-modified polypyrrole electrodes was performed in 0.5 M CH<sub>3</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup> (Fig. 5(a–c)). The voltammograms clearly show an oxidation peak around 0.6 V in the anodic scan region. This is ascribed to the oxidation of adsorbed carboxyl species that result from the dissociative adsorption of methanol. The current density is about 1.5 mA cm<sup>-2</sup> in the case of the unmodified polypyrrole matrix and is increased to about 5.2 mA cm<sup>-2</sup> when Pt(0) is electrodeposited on to the pyrrole electrode. A further increase in current density to about 9.4 mA cm<sup>-2</sup>, which corresponds to the oxidation of methanol, is observed for the bimetallic-modified polypyrrole electrode. In the case of nanoparticle-incorporated polymer modified electrodes, the metal–polymer interaction inhibits the formation of strongly chemisorbed species that may be responsible for higher stability and increased catalytic activity.

During oxidation, methanol undergoes dissociative adsorption that results in the formation of carboxyl intermediates together with the formation of strongly adsorbed CO species. To oxidize further such intermediates to CO<sub>2</sub>, the



(a)

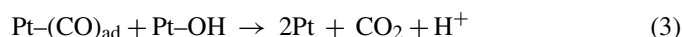
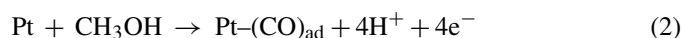


(b)

Fig. 7. EDAX pattern for Pt and Pt/Pd(0)-modified polypyrrole films on ITO electrode: (a) ITO/Ppy/Pt(0) and (b) ITO/Ppy/Pt–Pd(0).

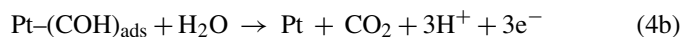
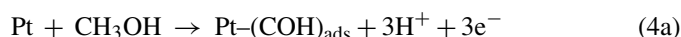


adsorbate must react with oxygen-containing species such as  $\text{OH}_{\text{ad}}$  or  $\text{H}_2\text{O}$  in aqueous solutions. Hence, a good catalyst for methanol electro-oxidation should easily adsorb methanol molecules, intermediates and oxygen-containing species. The Ppy/Pt(0) electrodes possess such a bifunctional character, i.e.,



This reaction involves a large number of steps that yield different intermediate products and finally results in the formation of  $\text{CO}_2$ . Methanol is adsorbed on the nanoparticle metal surface followed by the dehydrogenation of adsorbed species. The substrate reacts with catalytically-active sites immobilized in the film rather than at the underlying support electrode. Therefore, the electrochemistry of the substrate reaction is governed by the redox properties of the deposited nanoparticles. The immobilized redox site mediates the electron transfer between the electrode and the substrate. The reason for the higher activ-

ity and stability is that there may be some interaction between the metal nanoparticles and the polymer that inhibits the formation of strongly-bound chemisorbed species. Since metal nanoparticles are incorporated during the course of polymerization, the interaction between the polymer and the nanoparticles increases, and thus leads to higher activity and greater stability for methanol oxidation. For bimetallic nanoparticles, the synergistic effect due to the presence of palladium in the system enhances the overall electrocatalytic activity [32]. In the case of Pt(0)-incorporated polypyrrole matrixes, the platinum particles on the electrode surface are covered by strongly adsorbed  $(:\text{COH})_{\text{ads}}$  species. In such case, the adsorbed species requires three neighbouring Pt sites for adsorption and thereby, the electrode surface becomes slowly covered with this poison, i.e.,



In the case of Pt/Pd nanoparticle-incorporated polypyrrole films, there is an enhancement in the oxidation of methanol. Palladium is inactive in acid medium. In the Pt/Pd(0) system, the

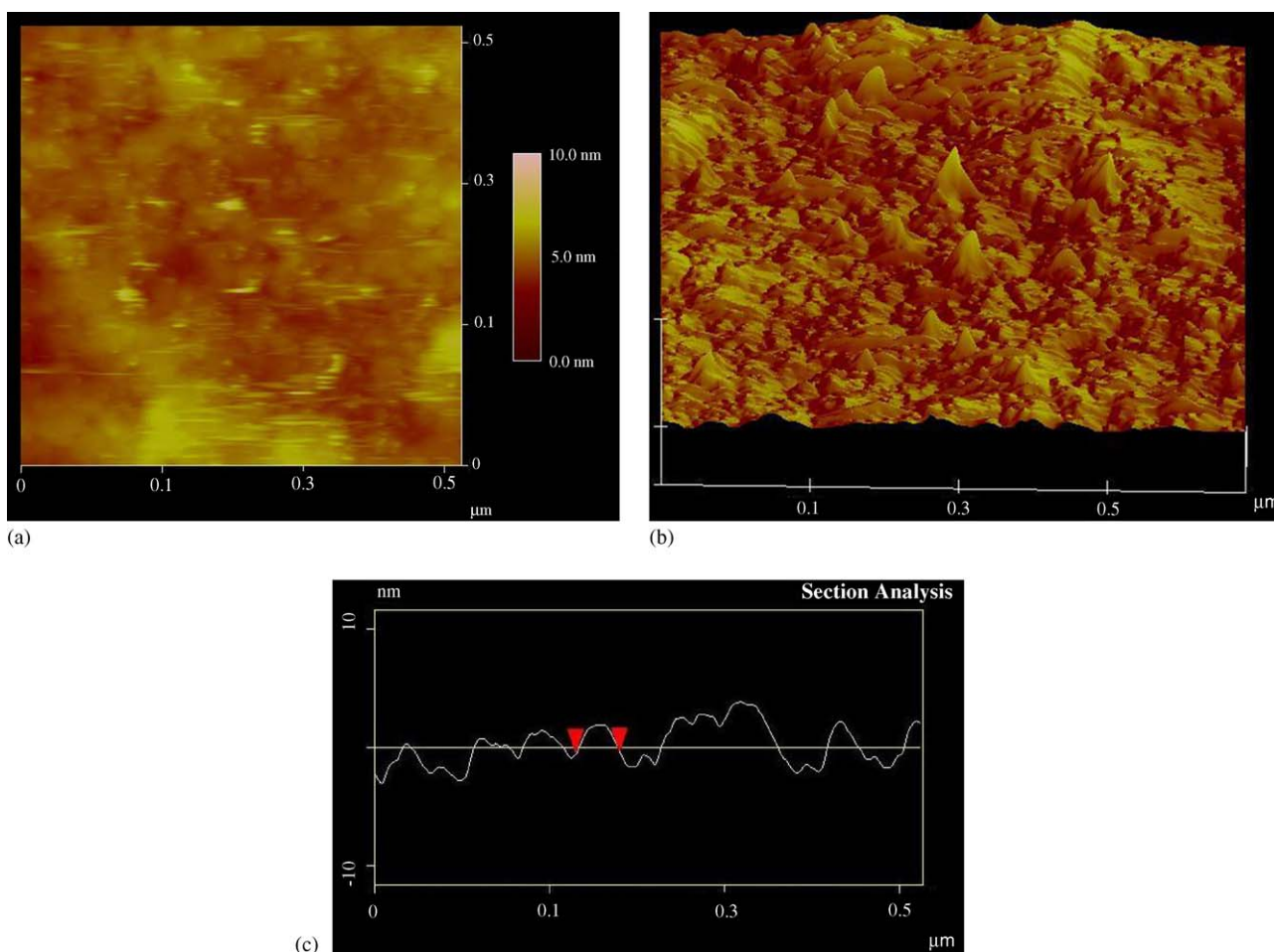


Fig. 8. Atomic force micrographs of polypyrrole film on ITO electrode: (a) normal surface view (scanning area,  $0.6 \mu\text{m} \times 0.6 \mu\text{m}$ ), (b) cross-section of image and (c) RMS graph.

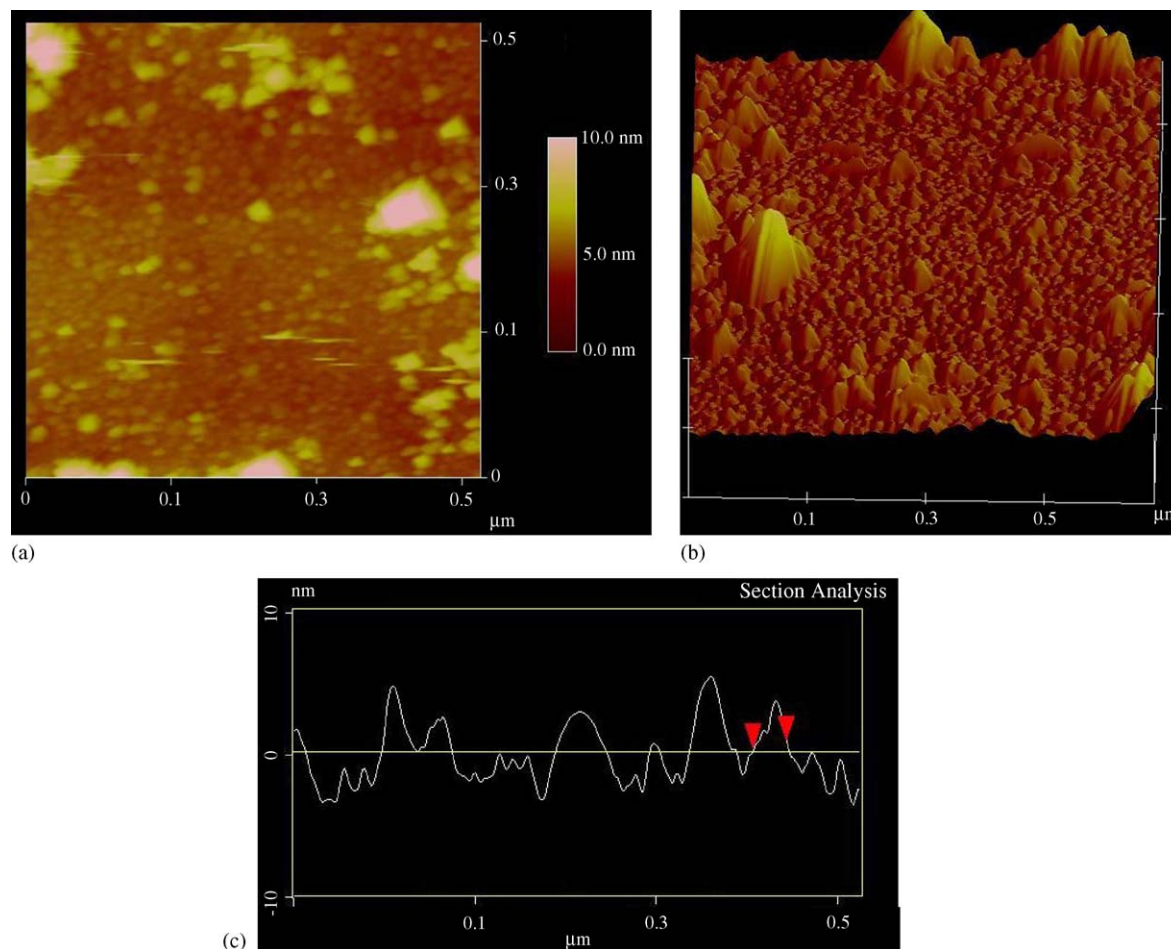
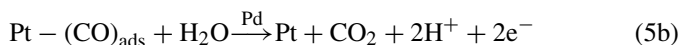
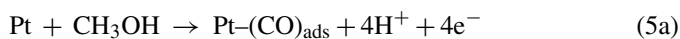


Fig. 9. Atomic force micrographs of Pt-modified polypyrrole film on ITO electrode: (a) normal surface view (scanning area,  $0.6 \mu\text{m} \times 0.6 \mu\text{m}$ ), (b) cross-section of image and (c) RMS graph.

presence of palladium helps in diluting the platinum sites and prevents the presence of three adjacent Pt sites that are necessary for the adsorption of poison species on the electrode surface. Now only two neighbouring Pt sites are available for  $\text{CH}_3\text{OH}$  adsorption and this favours the formation of  $(:\text{CO})_{\text{ads}}$  species. This leads to a new mechanism, which is responsible for overall enhancement of the electrooxidation of  $\text{CH}_3\text{OH}$ , i.e.,



The rate of reaction (5b) is greater than that of (4b) thereby enhancing the overall rate of the reaction in Pt/Pd-dispersed polymer electrodes. Thus, the presence of Pd in the polymeric matrix increases the rate of oxidation of methanol by decreasing the poisoning of the electrode surface.

As demonstrated by the data given in Table 1, the onset potential for methanol oxidation shifts to a more negative potential in the case of nanoparticle-dispersed polymer films that are found to be applicable in the fuel-cell applications.

The morphology of the nanoparticle-modified polypyrrole films was studied using SEM (Fig. 6(a) and (b)) and the corresponding EDAX images are shown in Fig. 7(a) and (b), which indicate the presence of Pt and Pd in the system. Polymer morphology was investigated by means of contact mode AFM Figs. 8–10. Images for the modified films show a homogeneous coverage of metal nanoparticles. The Pt and Pt/Pd nanoparticles are clearly seen to be embedded in the polypyrrole matrix with average sizes of about  $\sim 6$  and  $\sim 10$  nm, respectively. An image for the unmodified polypyrrole film has been given for comparison. In order to estimate the surface morphology of the polymer films, root mean square (RMS) analysis was performed. In the absence of nanoparticles, the polymer shows very smooth morphology with a RMS smaller than  $0.15$  nm (Fig. 8(a–c)). The RMS surface roughness of platinum and Pt/Pd-incorporated polypyrrole matrixes is  $1.9$  and  $2.7$  nm, respectively. The RMS roughness increases with deposition of nanoparticles on the polypyrrole film. Cross-sections taken from the images (Figs. (8c), (9c) and (10c)) clearly show that the polymer gains height and width during deposition of metal nanoparticles.

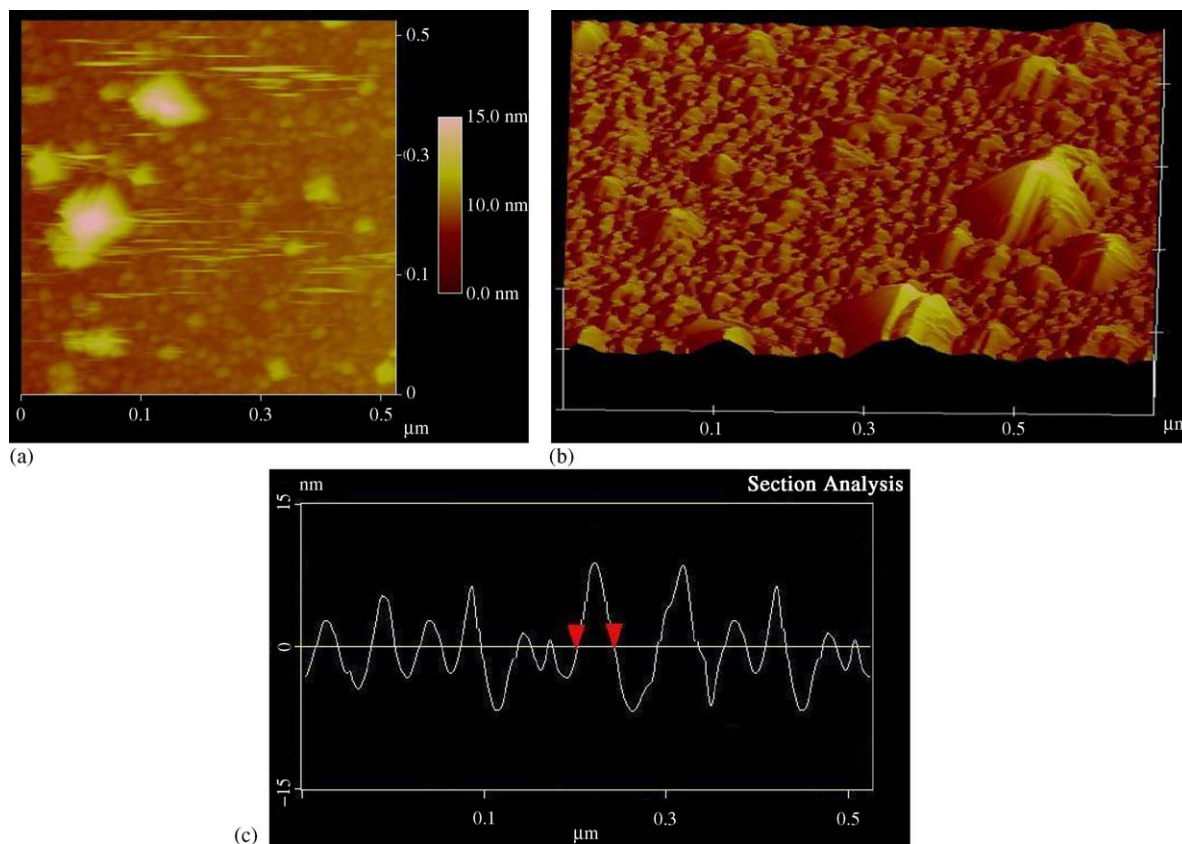


Fig. 10. Atomic force micrographs of Pt/Pd-modified polypyrrole film on ITO electrode: (a) normal surface view (scanning area,  $0.6 \mu\text{m} \times 0.6 \mu\text{m}$ ), (b) cross-section of image and (c) RMS graph.

#### 4. Conclusions

Polypyrrole, a conducting polymer matrix, is found to be an ideal material for the incorporation of monometallic (Pt) and bimetallic (Pt/Pd) nanoparticles. Nanoparticle-modified polypyrrole films show better electrocatalytic activity than unmodified polymers. This is considered to be due to stabilization of the nanoparticles in the polymeric matrix. Further, it has been shown that the electrocatalytic oxidation of methanol is more effective in the case of a bimetallic system. This is due to the rate of decrease of electrode poisoning by CO species that result from the dissociative adsorption of methanol. Polypyrrole with incorporated monometallic (Pt) or bimetallic (Pt/Pd) nanoparticles shows better electro-oxidation than a polypyrrole thin film on an ITO glass plate. The enhanced electrocatalytic activity may be due to the observed uniform dispersion of nanoparticles in polypyrrole films.

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