

Dopants Dependent Ion Sensitivity of Polypyrrole-Modified Electrode: Case of pH Sensing

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ABSTRACT: The polypyrrole (PPY)-modified electrode made through electropolymerization of pyrrole monomer is found sensitive to different cations depending on the dopants present within microstructure of polymeric domain. When *p*-toluenesulfonate (PTS) anion is doped, the modified electrode is sensitive to proton whereas, under similar conditions, in the presence of tetraphenylborate (TPB) anion, the same is sensitive to zinc ion. A comparative study on ion sensing behavior of PPY-modified electrodes is reported in this communication. The electro-polymerization of PTS-doped PPY-modified electrode, made under both potentiodynamic and potentiostatic conditions, are studied. The modified electrode is characterized by scanning electron microscopy and cyclic voltammetry and compared with those recorded for TPB-

doped PPY-modified electrode made under similar conditions. The results based on scanning electron microscopy and cyclic voltammetry suggested; (i) dependence of microstructure based on mode of electropolymerization; (ii) dopant-dependant ion sensitivity of PPY-modified electrode, (iii) variation in the redox behavior of the PPY-modified electrode based on dopants and mode of electropolymerization. Typical results on pH sensing together stability of PPY-based pH sensor are reported and compared with those recorded for polyaniline (PANI)-based pH sensor. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2594–2599, 2008

Key words: polypyrrole; electro-polymerization; pH sensor; polymer-modified electrode; ion-selective electrode

INTRODUCTION

Amongst the various conjugated polymers, polypyrrole (PPY) is one of the most widely investigated conducting polymers due to its chemical and thermal stability.¹ The mechanism of conduction in this polymer and the dependence of the conductivity on parameters like microstructure, mode of polymerization and medium of polymerization, nature of the oxidant, and pH of the environment² provided valuable information for several technological applications. The effect of pH on the conductivity of PPY has been widely reported^{3,4} and have been exploited for the fabrication of pH sensors^{5–12} in which PPY has been grafted onto an electrode, either chemically or electrochemically.

We have recently reported the electro-polymerization of aniline, indole, cyclohexylthiophene, and pyrrole.^{13–21} The results recorded on these monomers revealed interesting finding on the variation of polymeric microstructures on the following parameters: (1) the mode of electro-polymerization, (2) nature of solvent, (3) current density, and (4) nature of dopants. Further it has been also reported that many conduct-

ing polymer could be utilized in the evolution of the various components of chemical sensors especially as sensing element and transducers.²² It is indeed an important requirement to understand the ionophoric properties of the film for technological applications whether such materials could be used as sensing element or dipolar layer or as transducer. We have been working on these lines using polyindole,^{13–16} polypyrrole,²⁰ polythiophene,²¹ polyaniline.^{17–19} Amongst various organic conducting polymers, PPY has been one of the most versatile polymer for various applications. The finding related to the morphological variations on dopants has remained point of further investigation. Initial investigation on these lines by Malhotra and coworkers²³ has been reported on enhanced loading of glucose oxidase in PPY films via manipulation of the polymer morphology using *p*-toluene sulfonate and ferricyanide as dopant during electropolymerization. Pruneanu et al.²⁴ reported marked increase in molecular anisotropy, with the increase of electrolyte concentration while making PPY–polyvinyl composite. The reaction rate of the iodide/tri-iodide redox couple dissolved in acetonitrile has been quantified on several electrode materials including PPY by AC impedance spectroscopy as a function of the electrode potential by Bay et al.²⁵ Density function theory simulation was used to understand the effect of the dopants on the solid structure, optical absorption, and energy band structures of PPY.²⁶ The results demonstrated in these publications

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and also reported in our laboratory,¹³⁻²¹ as well, justified the use of these polymers as immobilization matrix for (i) contact layer for maintaining constant dipolar potential across electrode/polymer interface and (ii) as a sensing element itself. We got interesting observations on the use of sodium tetrphenylborate as bathing electrolyte during electropolymerization of aniline and pyrrole. Tetrphenylborate (TPB)-doped PPY is sensitive to zinc ion whereas TPB-doped polyaniline (PANI) has been found as pH sensor. Such observations have directed our attention on the use of PTS as dopant during the electropolymerization of pyrrole and aniline with special attention to ion-sensing behavior. Accordingly it is intended to study the following: (1) variation of electrochemical oxidation of pyrrole in acetonitrile in the presence of PTS anion and TPB anion, if any; (2) variations in the electrochemical performance of PTS doped-PPY and TPB-doped PPY, if any; (3) variation of the microstructures of PPY film doped with these two anions; (4) variations in the ion sensing behavior of these anions doped PPY-modified electrodes. Indeed we got very interesting observations on these lines and reported in this communication. We observed significant variation in the pattern of growth of the polymeric microstructure and the electrochemical behavior of PTS-doped PPY-modified electrodes when developed under potentiodynamic and potentiostatic mode of electropolymerization. The TPB-doped PPY is found sensitive to zinc ion where as the same when doped with PTS is sensitive to pH. The results on the PTS-doped PPY based on scanning electron microscopy and cyclic voltammetry are reported. The pH sensing behavior of PTS-doped PPY-modified electrode is also reported.

EXPERIMENTAL

Materials and methods

Pyrrole and tetrabutylammonium *p*-toluenesulfonate (PTS) were obtained from Aldrich Chemical; sodium tetrphenylborate (TPB) was obtained from E-Merck India Limited. All other chemicals were of analytical reagent grade. Pyrrole was distilled prior to use.

Electrochemical polymerization of PPY

The electrochemical synthesis of PPY was performed with a Solartron Electrochemical Interface (model 1287, Solartron, UK) connected to a PC through the serial port. All electrochemical experiments were carried out in a three electrode single-compartment cell with a working volume of 5 mL. A Pt disk electrode system (diameter = 3 mm) as working electrode, Ag/AgCl reference electrode, and a platinum foil auxiliary electrode were used for the measurements. The working

electrode was made from a Teflon™ cylinder. The exposed diameter of the platinum disk to be used as an active surface for polymerization was 2 mm. The platinum surface was polished with alumina slurry to a mirror finish followed by drying under a nitrogen stream. The electrochemical polymerization of PPY was carried out in acetonitrile containing 0.1M tetrabutylammonium PTS and 0.2M pyrrole through both potentiodynamic and potentiostatic modes of electropolymerization. The potentiodynamic mode of electropolymerization was conducted by cycling the potential of working electrode between -0.7 and 1 V vs. Ag/AgCl at the scan rate of 50 mV/s whereas potentiostatic mode of the same was made at constant potential of 0.9 V vs. Ag/AgCl. The film was highly stable for practical application and was characterized based on cyclic voltammetry in monomer free acetonitrile containing 0.1M tetrabutylammonium PTS.

Scanning electron microscopy

The growth pattern of the polymeric microstructure was characterized by scanning electron microscopy.

Measurements of the ion sensing behavior of PPY-modified electrode

The PTS-doped PPY-modified electrode prepared through either potentiodynamic or potentiostatic mode of electropolymerization was examined for ion sensitivity. The PTS-doped PPY-modified electrode was washed in acetonitrile and the same was incubated in 0.01M KCl for 24 h at room temperature (25°C). The electrode responses were recorded with a Keithley 2000 multimeter connected to a PC through the serial port. The potentiometric response of ion sensor was carried out in 0.01M Tris-HCl buffer, pH 7.0 using Ag/AgCl reference electrode with the cell assembly.

Reference electrode/KCl_{sat}/0.01M Tris-HCl buffer, pH 7.0/test solution/polymer-modified electrode.

The PTS-doped PPY-modified electrode together with a double junction reference electrode was dipped in the stirred electrochemical cell with a working volume of 5 mL. At the steady-state potentiometric response, varying concentrations of the ionic solution was injected into the cell and the new steady-state potential was recorded.

RESULTS AND DISCUSSION

Electropolymerization of PTS doped PPY

We first investigated on the electropolymerization of pyrrole in the presence of PTS anion both by potentiodynamic and potentiostatic modes of electropolymerization. Figure 1 shows the results on

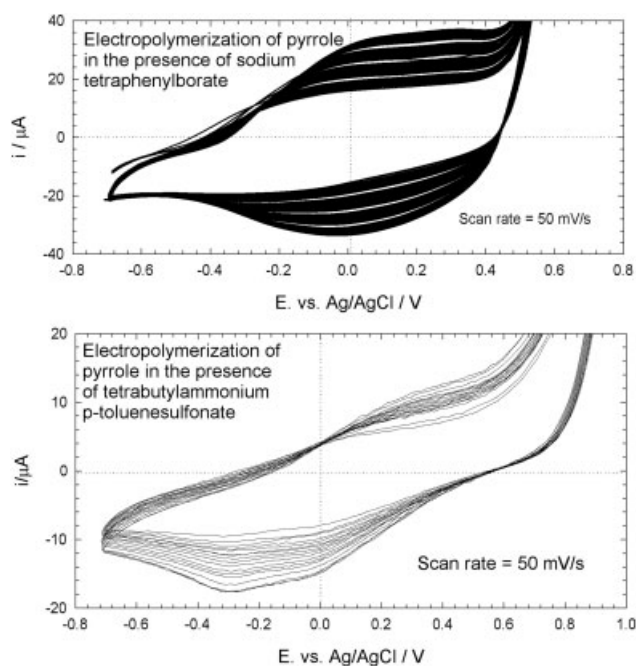


Figure 1 Potentiodynamic electropolymerization of 0.2M pyrrole in acetonitrile containing 0.1M tetrabutylammonium *p*-toluenesulfonate.

potentiodynamic electropolymerization by cycling the electrode potential between -0.7 and 1.0 V vs. Ag/AgCl in the presence of two different electrolytes tetrabutylammonium PTS and sodium tetrabutylammonium tetraphenylborate. There are remarkable dependence of the nature of bathing electrolyte on the electro-oxidation of pyrrole and these are as follows: (1) relatively much larger anodic current is observed in the presence of TPB anions ($>40 \mu\text{A}$) as compared with that in the presence of PTS anions ($<20 \mu\text{A}$) even keeping same concentrations of pyrrole and electrolytes; (2) oxidation of pyrrole is triggered <-0.2 V in the case of TPB anion whereas same is >0.2 V in the presence of PTS anion while keeping similar other conditions; (3) even at lower current density better yield of polymer formation is observed in the presence of PTS as compared with that in the presence of TPB anions; (4) reduction wave is apparently visible >-0.2 V in the case of PTS anions whereas the same is <0.0 V vs. Ag/AgCl in the presence of TPB anions. The bathing electrolyte dependent process of electropolymerization which ultimately affect in electro-oxidation of pyrrole monomers generate altered microstructure along with variable redox properties. The electrochemical performances and ion sensitivity of PPY-modified electrode are discussed *vide infra*.

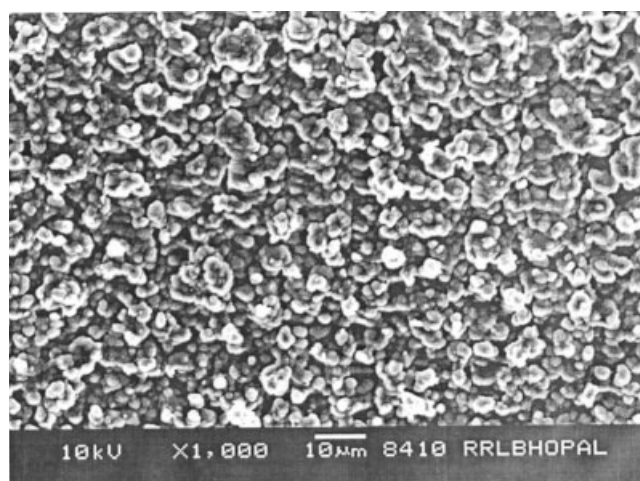
Characterization of PTS doped PPY

The PPY film made through electropolymerization has been characterized by scanning electron micros-

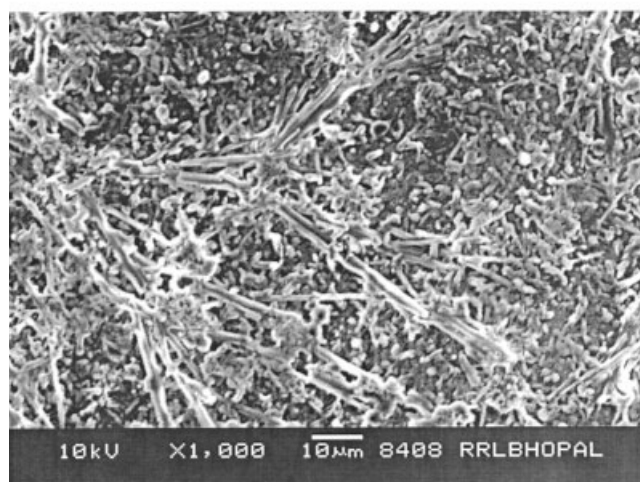
copy. The scanning electron microscopy of TPB-doped PPY has been reported in earlier publication.^{20,21} The SEM of PTS-doped PPY is shown in Figure 2. The microstructure of PPY film made through potentiodynamic mode of electropolymerization is shown in Figure 2(a) whereas the same made through potentiostatic mode of electropolymerization is shown in Figure 2(b). The growth patterns of PPY network are entirely different in these two cases. There is globular morphology when made through potentiodynamic mode of polymerization whereas the same is fibrous under potentiostatic mode of polymerization.

Electrochemical characterization of PTS doped PPY

The results based on cyclic voltammetry on the electrochemical performances of PTS-doped PPY made



(a)



(b)

Figure 2 (a) Scanning electron micrograph of PTS-doped PPY made by potentiodynamic mode of electropolymerization, (b) scanning electron micrograph of PTS-doped polypyrrole polymerized by potentiostatic mode of electropolymerization.

through potentiodynamic mode of electropolymerization are shown in Figure 3(a) and compared with that of electrochemical performance of TPB-doped PPY. The electrochemistry of PPY-modified electrodes is different when PTS anions are doped as compared with that of TPB-doped PPY-modified electrode. The TPB-doped PPY shows better oxidation whereas PTS doped PPY shows pronounced reduction and supported the electrochemical observation of the redox behavior. The differential electrochemical doping–dedoping kinetics of these two different dopants within polymer interstices could be diagnosed from; (i) relatively higher magnitude of both anodic and cathodic current ($>40 \mu\text{A}$) in the case of TPB-doped PPY as compared to that of PTS-doped PPY ($<18 \mu\text{A}$) made under potentiodynamic mode of electropolymerization [Fig. 3(a)]; (ii) the electrochemistry of PTS anions-doped PPY-modified electrode made under potentiostatic condition is much better in term of reversible redox behavior of the polymer as compared with that of TPB-doped PPY [Fig. 3(b)]; (iii) both anodic and cathodic current have larger magnitude when PTS anions are doped as compared with that of TPB doped PPY-modified electrode [Fig. 3(b)] when made through potentiostatic mode of electropolymerization which are opposite to that of PPY-modified electrode made under potentiodynamic mode of electropolymerization. Such variation in electrochemistry of these two different dopants based PPY-modified electrode is basically due to variation in size and polarity of these two anions leading to the differential dynamics of doping–dedoping reactions.

Ion-sensing behavior of PTS doped PPY

Before going ahead on ion sensing behavior of such film it is important to review some of our earlier finding conducted on these lines. The previous results available on the ion-exchange capacity of TPB-impregnated within PVC matrix membrane has been very well documented. However, when TPB is doped within polymeric interstices, its ion-exchange behavior has not been studied so far. We have studied the ion sensing behavior of both TPB-doped PPY-modified electrode as well as PTS-doped PPY-modified electrode. The variations in morphology of polymeric structure as shown is SEM observations (Fig. 1) at least suggested that ion-exchange property of the polymer concern to the dipolar charge separation created during the growth of polymeric domains. The TPB-doped PPY-modified electrode is found sensitive to Zinc ion^{20,21} whereas PTS-doped PPY-modified electrode is sensitive to pH which are one of the remarkable observation on the contributions of doped electrolyte on the establishment of spatial charge distribution across polymer/solution

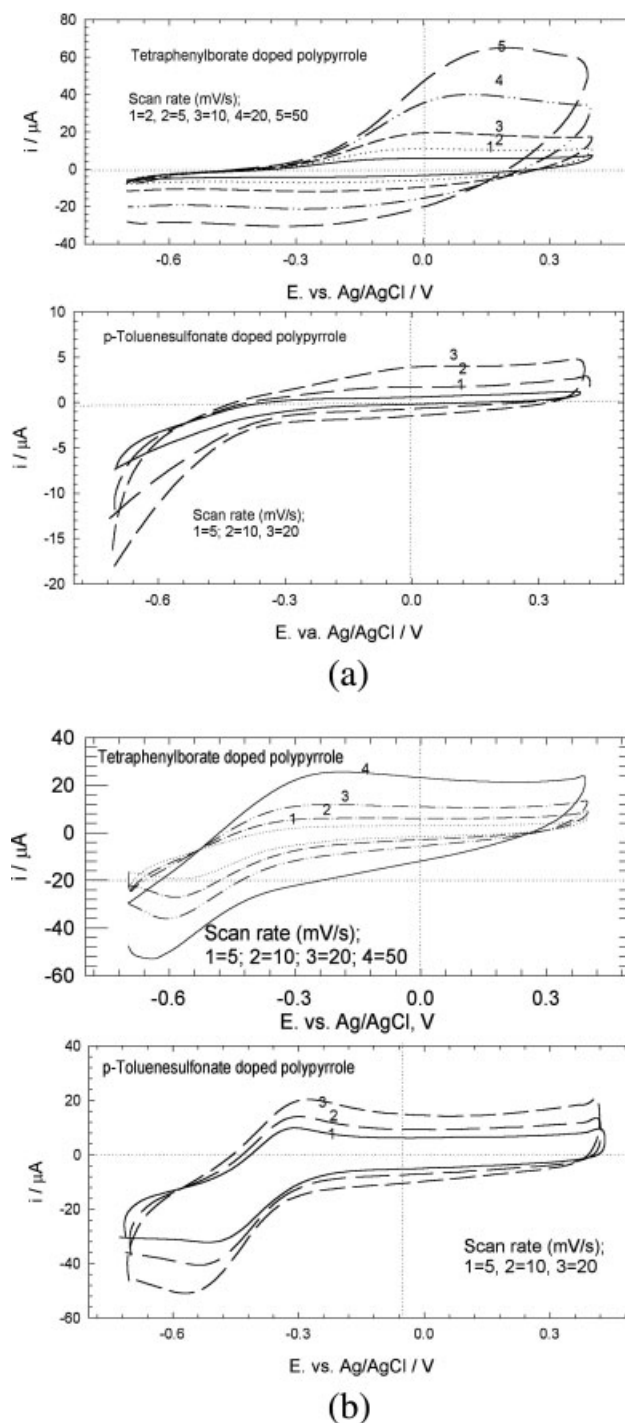


Figure 3 (a) Cyclic voltammogram of PTS-doped and TPB-doped PPY-modified electrode made through potentiodynamic mode of electropolymerization at various scan rates in acetonitrile containing 0.1M tetrabutylammonium *p*-toluenesulfonate/sodium tetraphenylborate. (b) Cyclic voltammogram of PTS-doped/TPB-doped PPY-modified electrode made through potentiostatic mode of electropolymerization at various scan rates in acetonitrile containing 0.1M tetrabutylammonium *p*-toluenesulfonate/sodium tetraphenylborate.

TABLE I
Dependence of Ion Sensing Behavior of Polypyrrole Synthesized Under Different Experimental Conditions

Polymer type	Pyrrole (molar)	Electrolyte (molar)	PS/PD	Potential (V) vs. Ag/AgCl	Ionic sensitivity
Polypyrrole-I	0.8	0.1M TPB	PD	-0.7 to 1.0	Zn ⁺⁺
Polypyrrole-II	0.8	0.1M TPB	PS	0.9	Zn ⁺⁺
Polypyrrole-III	0.8	0.1M TPB	PS	0.6	Zn ⁺⁺
Polypyrrole-IV	0.4	0.1M TPB	PS	0.9	Zn ⁺⁺
Polypyrrole-V	0.2	0.1M PTS	PD	-0.7 to 1.0	pH
Polypyrrole-VI	0.2	0.1M PTS	PS	0.9	pH

interface. The zinc ion sensing of TPB-doped PPY-modified electrode has been reported in details.^{20,21} The zinc ion sensing of TPB-doped PPY was even sensitive to mode of electropolymerization^{20,21} basically due to variation in microstructure of the polymer leading to differential localized charge distribution within polymer interstices that contribute ion sensitivity. The comparison of ion sensing behavior of PPY film made under varying experimental conditions is shown in Table I. The pH sensing behavior of PTS-doped PPY-modified electrode is reported herein. First the potentiometric response of the modified electrode in different buffer ranging between pH 3 and pH 10 has been recorded. The potentiometric signal versus pH is shown in Figure 4(a). The slope of the curve is 59 mV justifying

Nernstian behavior of the modified electrode involving one-electron/per proton transfer. We have also studied pH sensing behavior of PANI-modified electrode made through similar protocol of preparation.¹⁷ The slope recorded for PANI-modified electrode is found to be 90 mV/pH and suggested that the redox reaction involve the transfer of three protons per two electrons during PANI-based pH sensing whereas transfer of one proton per electron in case of PTS-doped PPY.

Typical results on acid and base sensing are shown in Figure 4(b,c). The response was recorded on the addition of acidic acid and ammonium hydroxide, respectively. The results justify the usability of new PTS-doped PPY-modified electrode as pH sensor. The dependency of polymeric microstructure on differen-

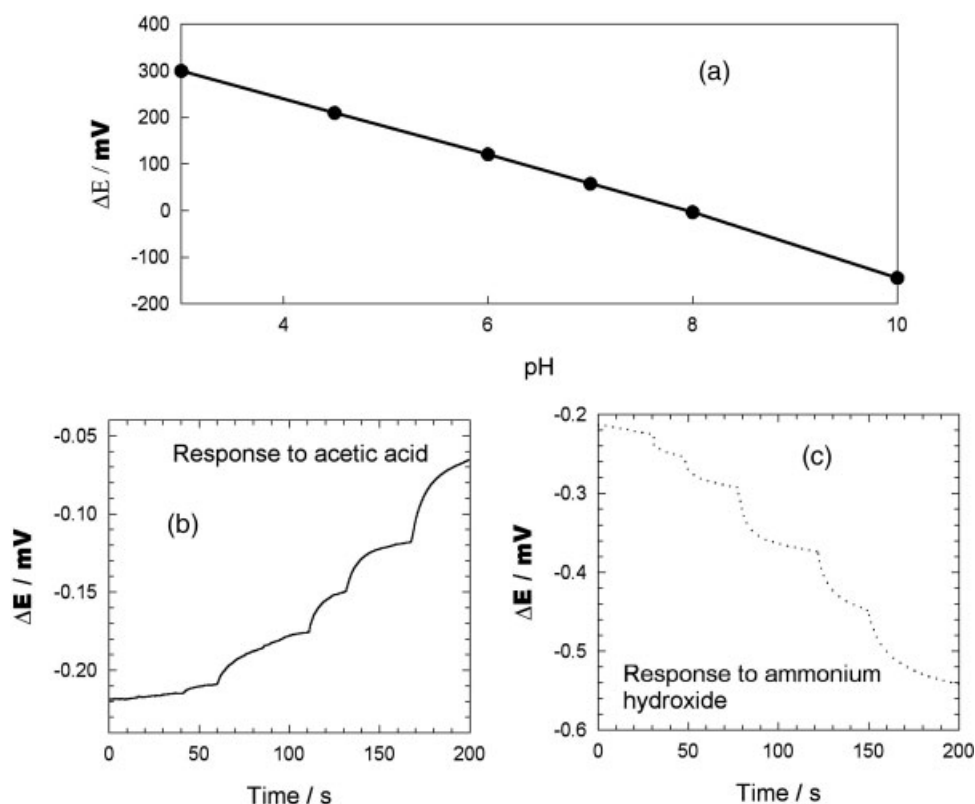


Figure 4 (a) Potentiometric response of PTS-doped PPY-modified electrode versus pH. Typical potentiometric response of the PTS-doped PPY modified electrode on the addition of increasing concentration of acetic acid (b) and ammonium hydroxide (c) in 0.001M Tris-HCl buffer pH 7.0 and at 25°C.

tial ion sensitivity justified further exploration of research program to be undertaken really to understand the specificity of polymeric domains to selective ions. The reasons for selective interaction of proton with PTS-doped-PPY is under investigation.

CONCLUSION

The electrochemical synthesis of PTS-doped PPY is reported and the new conducting polymer is characterized based on SEM and electrochemical measurements. The result shows variations in the polymeric morphology and electrochemical behavior as a function of the mode of electropolymerization. The TPB-doped PPY is sensitive to zinc ion whereas PTS-doped PPY-modified electrode is sensitive to pH.

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