

Electrochemical Synthesis and characterization of P(Py) -P(NMP)/PVS, P(Py) -P(NMP)/pTS and P(Py) -P(NMP)/-DBS composite films

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ABSTRACT

In the present investigation, we have studied the influence of large anion size dopants PVS, pTS and DBS on the synthesis of polypyrrole (Ppy)- poly(n-methylpyrrole) (PNMP) composite film. The composite film was synthesized on the platinum substrate by electrochemical polymerization with different dopants such as PVS, pTS and DBS under galvanostatic condition over a wide range of pH of the reaction medium and applied current density. The synthesized composite films were characterized using galvanostatic electrochemical technique, electrical conductivity, UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). This study reveals that Ppy-PNMP-pTS composite film provide a polymer matrix with very good porosity, mechanical and environmental stability, uniform surface morphology and higher conductivity, which is suitable for the immobilization of bio-component.

Keywords: polypyrrole, poly (n-methylpyrrole), large anion size dopant, electrochemical polymerization, galvanostatic technique.

INTRODUCTION

Polypyrrole and its family e.g. Poly (*N*-methylpyrrole) is an important member of intrinsically conducting polymers which can be synthesized by electrochemical or chemical methods. It is reported to be a stable polymer that has excellent retention of its electrical, chemical, thermal, and mechanical properties^{1,5}. The Ppy and P(NMP) has a nodular, cauliflower-like surface morphology,

the roughness of which depends on the electrochemical synthesis conditions⁶. Smoother films with improved surface morphology can be synthesized by careful choice of synthesis parameters, such as pH⁷, synthesis temperature, deposition time, type of dopant and concentrations⁶. The Ppy and P(NMP) can be synthesized with an electrical conductivity ranging from 10^{-4} to 10^2 S/cm. The remarkable switching capability of these electroactive materials (conducting polymers)

between the conducting oxidized (doped) and the insulating-reduced (undoped) state is the basis of many applications. Among others, the poly-conjugated conducting polymers have been recently proposed for biosensing applications because of a number of favorable characteristics, such as (1) direct and easy deposition on sensor electrode by electrochemical oxidation of monomer, (2) control of thickness and (3) redox conductivity. Various conducting polymers viz polyacetylene, polythiophene, polypyrrole, polyindole and polyaniline have been extensively used for immobilization of enzymes. Among the conducting polymers, polypyrrole has been widely studied because it can be easily polymerized, with ease of membrane formation, high conductivity and chemical stability⁸⁻¹⁰. However, synthesis of Ppy-P(NMP) composite film has been studied by very few researchers¹¹⁻¹⁴. The Ppy and P(NMP) can be easily synthesized by electrochemical oxidation of the monomer with suitable doping. The electrochemical synthesis of Ppy and P(NMP) films are dependent on many parameters viz. current density, monomer type, monomer concentration, electrolyte type, electrolyte concentration, pH of the reaction medium and the reaction time etc.¹¹⁻¹⁷. The stability of polymer matrix depends on anions. The anions play an important role during electrosynthesis. The anions are divided into three groups: (a) small inorganic anions, such as NO₃; (b) medium sized anions (mainly organics), such as dodecylsulphonate, p-toulenesulphonate, and (c) large polymeric anions, such as polyvinylsulphonate¹⁸. Advantages of aqueous electropolymerization include: (1) the aqueous solutions used are environmentally favorable. The use of aqueous solutions also greatly lowers the costs for materials and waste

disposal. (2) This technique combines the formation. In general, the mobility of anions in Ppy and P(NMP) films depends on the size of the anions; small anions have good mobility, medium anions have average or bad mobility, and large polyanions are not able to leave the Ppy and P(NMP) film at all. The ion exchange properties and stability of polypyrrole (Ppy) - polyvinylpyrrolidone (PVP), polypyrrole (Ppy)-polyvinyl alcohol (PVA), and polypyrrole (Ppy)-polystyrene sulphonate (PSS) composites have been studied by some authors¹⁹⁻²⁰. However, it is still important to find high-quality polymers and effective dopants showing their desirable properties.

In the present investigation, we have taken the monomer pyrrole (Py) and n-methyl pyrrole (NMP) and synthesized composite conducting polymer [P(Py)/P(NMP)] with dopants PVS, pTS and DBS by electrochemical polymerization using galvanostatic method.

EXPERIMENTAL SECTION

The pyrrole (Ppy) monomer (Alfa Aesar, 98+ %) and n-methyl pyrrole P(NMP) monomer (Acros Organics, 98%) were double distilled prior to synthesis. PVS, pTS and DBS were used as supporting electrolytes. All the reagents were obtained from Rankem, INDIA.

An Aqueous solution (20 ml) of Ppy, PNMP and various dopants were prepared in double deionized (DID) water for each synthesis process. Different concentration ratios of Ppy, PNMP and supporting electrolytes were considered. The electropolymerization were carried out by chronoamperometric technique with CHI 660C electrochemical workstation. Standard three electrode set-up was employed in one compartment electrochemical cell. Planar platinum sheet (20 × 10 × 0.25 mm) was used

as a working electrode and another platinum sheet ($20 \times 40 \times 0.25$ mm) was used as a counter electrode. The reference electrode was an Ag/AgCl electrode. We have varied supporting electrolyte, monomer concentration, supporting electrolyte concentration, current density, pH of the reaction medium and deposition time. All depositions were carried away at 27°C . After each experiment polymer coated platinum substrate was rinsed with DID water and dried in ambient atmosphere.

The P(Py)/P(NMP) with dopants PVS, pTS and DBS composite films were subjected to in-situ electrochemical characterization carried out during synthesis by CHI 660C electrochemical workstation. DC conductivity and scanning electron microscopy were studied. DC conductivity was measured by standard four probe technique with an indigenously designed computer controlled I-V characterization unit. FTIR spectrum was recorded, using Testscan Shimadzu FTIR-8000 series, using KBr pellets in the region between 400 and 4000 cm^{-1} . Scanning electron micrographs were recorded at various magnifications using JEOL JSM-6360 A Analytical Scanning Electron Microscope.

RESULTS AND DISCUSSION

Electrochemical Synthesis of P(Py)/P(NMP) Composite Films :

Galvanostatic deposition of P(Py)/P(NMP) composite films were carried out by varying supporting electrolyte, monomer concentration, supporting electrolyte concentration, current density, deposition time, pH of the reaction medium and respective chronopotentiograms were studied for lowest polymerization potential since films with low polymerization potential are reported to exhibit higher conductivity and uniform surface morphology²¹⁻²³. The values of conductivity

obtained from chronopotentiograms have been compared with the values of conductivity measured using Four Probe techniques and we observed comparable results. The composite films were synthesized for various deposition time and we obtained uniform film with good adhesivity for 900 seconds (15 minutes)

Optimization of Monomer Concentration:

The concentration of monomer and electrolyte significantly affects the surface morphology and conductivity of P(Py)/P(NMP) composite film. Therefore, P(Py)/P(NMP) composite films were synthesized for various monomer concentrations. We observed significant changes in the surface morphology and conductivity of the synthesized films for various monomer concentrations. The chronopotentiograms recorded during synthesis of composite film for various monomer concentrations and 0.1 M concentration of dopant, 1 mA/cm^2 current density, 3 pH (non optimized) is shown in figure 1. Our interest lied on synthesis of films with lower conductivity because this criterion facilitates sensing mechanism. We have observed lower polymerization potential for 0.1:0.1 M monomer concentrations (pyrrole: n-methyl pyrrole) as compared with other concentrations. This shows higher conductivity²³. The conductivity of each film was measured by Four Probe method. The synthesized film shows very good surface uniformity and adhesively.

Optimization of Dopant (Supporting Electrolyte) Type:

The dopant plays important role in the synthesis of conducting polymer films. We have studied the effect of dopant on the synthesis of P(Py)/P(NMP) composite film. The P(Py)/P(NMP) composite films were synthesized for various dopants (viz. PVS,

pTS and DBS). We have observed strong dependence of polymerization potential on anion present in the electrolyte. We have also observed lowest polymerization potential and consequently higher conductivity for pTS as supporting electrolyte. The chronopotentiograms recorded during electrochemical polymerization of P(Py)/P(NMP) composite film with various dopants PVS, pTS and DBS, 0.1: 0.1 M concentrations of monomers (optimized), 0.1 M concentration of dopant, and 1 mA/cm² current density at 3.0 pH is as shown in Figure 2. The synthesized film shows very good surface uniformity and adhesiveness.

Optimization of Dopant (Supporting Electrolyte) Concentration:

The impact of dopant concentration on the synthesis of P(Py)/P(NMP) composite film has also been studied in the present investigation. The P(Py)/P(NMP) composite films with various concentration of pTS were synthesized. The chronopotentiograms with various concentrations of dopant and 0.1 :0.1 M concentration of monomer (optimized), 1 mA / cm² current density, 3.0 pH (non optimized) is as shown in figure 3. We observed lowest polymerization potential for 0.1 M concentration of pTS as compared with other concentrations of dopant. The synthesized film shows high conductivity and very good surface uniformity and adhesiveness.

Optimization of Applied Current Density:

The applied current density is reported to have greater impact of the synthesis of conducting polymers²³. In order to study the impact of applied current density on the synthesis of P(Py)/P(NMP) composite film, the same experiment was repeated for various applied current density. The chronopoten-

tiograms with various applied current density and 0.1 :0.1 M concentration of monomer, 0.1 M concentration of dopant (optimized) , 3.0 pH (non optimized) is as shown in figure 4. The lowest polymerization potential was recorded for 1 mA/cm² current density. It has been observed that, increasing applied current density, results in increase in polymerization potential. However, at 1 mA/cm² the uniform deposition of P(Py)/ P (NMP) film was observed. It has also been observed that, the thickness of the deposited P(Py)/P(NMP) film increases with increase in the applied current density.

Optimization of pH of the Reaction Medium (Electrolyte):

The pH of the reaction medium is another crucial electrochemical process parameter, which need to be optimized. We have also studied the impact of this parameter on the synthesis of P(Py)/P(NMP) composite film. The chronopotentiograms for various pH of the reaction medium and 0.1:0.1 M concentration of monomer, 0.1 M concentration of dopant, 1.0 mA / cm² current density (optimized) is as shown in figure 5. We have observed lowest polymerization potential for 2.0 pH of the reaction medium indicating higher current density. We have also observed very good surface uniformity and adhesiveness of the synthesized composite film at this value of pH. The figure 5 exhibit that, the polymerization potential increases with increase in the pH value which is in agreement with our earlier reported results [16]. The over all optimized parameters are listed in the following bracket (0.1 :0.1 M concentration of monomer, 0.1 M concentration of dopant (pTS), 1.0 mA / cm² current density, 2.0 pH of the reaction medium and 900 second deposition time)