Galvanostatic Study of Polypyrrole/ZnO Film Synthesized with Various Dopants: A Comparative Study

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Abstract: ***The Electrochemical (galvanostatic) study of polypyrrole/Zinc oxide film synthesized with various dopant like potassium chromate (K_2CrO_4), potassium dichromate ($K_2Cr_2O_7$)And potassium permanganate ($KMnO_4$) has been carried out. The electrochemically synthesized (Ppy/ZnO) films were characterized by electro- chemical technique, UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and four probe technique for conductivity measurement. This comparative Study observed that as compare to (PPy/ZnO/K_2CrO_4), (PPy/ZnO/$K_2Cr_2O_7$) And (PPy/ZnO/$KMnO_4$) film but the (PPy/ZnO/$KMnO_4$) film provide a polymer matrix having a good porosity, high conductivity, uniform surface morphology and good mechanical and environmental stability. This is suitable for Immobilizations of biocomponant.***

Keywords: Polypyrrole, dopant, galvanastatic, electrochemical synthesis

1. Introduction

Organic conducting polymers have recently emerged as a new class of electro active materials and are interesting subjects for research and development (Chen and Cho 1996; Delccuw et al 1997; Kaneto et al 1998; Skotheim et al 1998; Shirale et al 2006). The remarkable switching capability of these electroactive materials 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 favourable characteristics such as (i) direct and easy deposition on sensor electrode by electrochemical oxidation of monomer, (ii) control of thickness and (iii) redox conductivity. Typical π-conjugated conducting polymers include polyaniline (PANI), polypyrrole (PPy) and polythiophene. Polypyrrole is the polymerization product of the monomer pyrrole consists of the repeating unit of pyrrole ($C4H_5N$). It is a heterocyclic aromatic compound i.e. it possesses a heterogeneous ring–like structure in which electrons can move around. Among all conducting polymers, PPy is extensively studied by many research groups because of ease of preparation, good stability and high conductivity. Because of these fascinating properties of PPy, it is widely used in many applications such as gas sensors [1-3], supercapacitors [4, 5], corrosion prevention [6], solar cells [7, 8], biosensors [9] and pH sensor [10]. The conducting polymers can be synthesized by chemical or electrochemical route. Electrochemical polymerization occurs when a suitable potential or current is applied to the electrode that has been immersed in the electrolyte containing monomers of polymer. In chemical synthesis rapid precipitation occurs, when PPy monomer reacts with oxidant. The oxidizing agent used in chemical polymerization initiates polymerization by oxidizing the PPy monomer and also provides dopant anions to neutralise the positive charge of the polymer in the oxidized state. Resulting radical cation reacts with another PPy monomer molecule to form dimer. Dimer further gets oxidized to form a chain of polypyrrole. Many reports are available on synthesis of PPy by different oxidizing agents [11-14]. Generally used oxidizing agents for the polymerization of PPy are the salts of transition metal ions, such as Cu2+, Mn7+, Fe3+, Ru3+ etc. The major disadvantage of chemical method is the bulk precipitation in the solution. Deposits on the substrate are very less as compared to the precipitation in the solution. Another method for chemical synthesis of PPy is to directly deposit the PPy thin film onto a stainless steel substrate using vapours of PPy monomers. Vapour phase polymerization involves applying the oxidant to the surface using a solvent coating process and then exposing the coated surface to the vapour of the monomer. There are earlier reports on the synthesis of PPy by vapour phase polymerization [15-17].

Electrochemical polymerization provides a number of advantages over chemical polymerization. The advantages offered are: 1) the reaction product is an electro active film attached to the electrode surface and having high conductivity, 2) the yield in charge terms is almost 100% which provides a possibility of controlling the mass and thickness of the film, and 3) the properties of the film produced can be controlled directly by varying the preparative conditions. Electrochemical polymerization of pyrrole is achieved when an anodic potential or current is applied to a conducting substrate that has been immersed in a suitable electrolyte containing the monomer and the desired doping salt. Different modes of electrodeposition have been used for the electrochemical synthesis of PPy. Zhang et al [18] deposited PPy thin film by pulse galvanastatic method for supercapacitor application. Dubal et al [19] deposited PPy by potentiostatic mode of electrodeposition. Potentiodynamically deposited PPy was reported by Sharifirad et al [20]. This chapter deals with synthesis of PPy thin films by electrodeposition method using all three modes i.e. galvanastatic, potentiostatic and potentiodynamic. Out of these three methods, galvanostatically deposited PPy thin films were uniform, well adherent and compact in nature and are used for further study.

2. Experimental

The Pyrrole was distilled before use. We have used the dopant, like potassium chromate, potassium dichromate ,potassium permanganate etc and chemically synthesized zinc oxide nano particles .We were freshly prepared 0.1N an aqueous solution Pyrrole (99%) in double distilled water , Also we prepared an aqueous solution of 0.1N potassium chromate (K_2CrO_4) , 0.1N potassium dichromate ($K_2Cr_2O_7$) And 0.1 N potassium permanganate ($KMnO_4$) dopant in double distilled water and powdered of ZnO nanoparticle are used. The pH of mixture are maintain by using buffer solution. The electrochemical polymerization of pyrrole was carried out by galvanastatic method in one compartment electro- chemical cell [25-27]. Graphite was used as a counter electrode (cathode) and another Indium Titanium Oxide glass (20mm*0.5mm) was used as a working electrode (anode). The reference electrode was silver–silver chloride (Ag/AgCl). All three electrodes were placed vertically in an electrochemical cell. An 50 ml solution was used for each reaction. The pH of the electrolyte was measured by calibrated ELICO LI120 pH meter. The electrochemical characterization was carried out by galvanostatic technique, which maintains a constant current throughout reaction. The optical absorption study was carried out in Analytic Jena specord 210 plus (Wavelength 200nm-800nm) UV- visible spectrophotometer. The conductivity was measured by using four-probe technique (S.E.S. Instrument Pvt. Ltd. Roorkee). The JEOL JSM-7500F is an ultra-high resolution field emission scanning electron microscope (FE-SEM) equipped with a high brightness conical FE gun and a low aberration conical objective lens). The improved overall stability of the JSM-7500F enables you to readily observe your specimen at magnifications up to 1,000,000xwith the guaranteed resolution of 1 nm. The energy filter (r-filter) makes it possible to observe the fine surface morphology of nanostructures [28-31].

3. Results and Discussion

Electrochemically synthesis of PPy/ZnO established that the different supporting dopant nature and concentration used to synthesize a conducting polymer affecting its morphology and some of its properties. The previous reported work electrochemical synthesis of pyrrole on Pt substrate by Otero et al. [32] However, once the pyrrole oxidation is initiated, this process is much faster for increased polyelectrolyte concentration [33] investigated the effects of various synthesis parameters (electrosynthesis method, monomer concentration, and electrolyte) on electro polymerization of pyrrole. The Synthesis of PPy/ZnO NPs composite film galavanostatically in a solution of 0.1N of pyrrole in of 0.1N potassium chromate (K_2CrO_4) , 0.1N potassium dichromate ($K_2Cr_2O_7$) And 0.1 N potassium permanganate ($KMnO_4$) dopant with ZnO NPs dispersed into the electrolyte solution at current 0.5amp.are constant.

3.1 Galvanostatic Study

A computer controlled Potentiostat/Galvanostat, indigenously designed and fabricated in the Materials Research Laboratory, Department of physics, Shri Anand College, Pathardi, Dist. Ahmednagar. (MS) India was employed for the electrochemical synthesis PPY/ZnO film by using potentiometric (Galvanostatic) method. arrangement is also especially useful for quick measurement on different samples or sampling different parts of the same sample. Below figure shows by passing constant current in 50ml solution of 0.1N pyrrole and 50ml solution of 0.1N $K_2Cr_2O_7$ $KMnO_4$, K_2CrO_4 respectively on a ITO substrate electrode. While, figure.1 shows which were recorded during 50ml solution of 0.1N pyrrole and 50ml solution of 0.1 N $K_2Cr_2O_7$, $KMnO_4$, K_2CrO_4 respectively on an ITO substrate electrode in the presence of ZnO NPs, dispersed in electrolyte solution. Here it is important to mention that addition of ZnO into electrolyte solution affects the electropolymerization process. For this reason, a certain quantity of ZnO (100 mg) was dispersed in the electrolyte solution (50 ml). Fig.1 shows the comparative voltammograms of (PPY/ZnO/K_2CrO_4), (PPY/ZnO/$K_2Cr_2O_7$) and (PPY/ZnO/$KMnO_4$) during the formation on ITO substrate, indicates that the addition of ZnO NPs significantly increase the recorded voltage at the same applied potentials. So, the higher polymerization process takes place in the presence of $KMnO_4$. Fig.1 also shows conductivity of PPY/ZnO films with different dopants, along which $KMnO_4$ shows highest conductivity 1.62 S/cm at potential 670 mv for current density 0.5A/2cm2 at pH 4 it can be concluded that electropolymerization on the PPy/ZnO/$KMnO_4$ composite initial layers is easier than the PPy/ZnO/K_2CrO_4 & PPy/ZnO/$K_2Cr_2O_7$ initial layers. So, the film can be presents a large surface area. As is well known, properties of a broad range of materials and performance of different devices depend strongly on their surface characteristics. It clearly shows porous morphology of PPy/ZnO Film. This nature helpful for the biosensor application of the film.

3.2 Scanning Electron Microscopy (SEM):

To observe the surface morphology of electrodeposited polymer films, the surface was examined by SEM and FTIR techniques. Parts figure 2, figure 3 and figure 4 show the SEM images. Compare the morphology of PPy/ZnO/$KMnO_4$ grown is different than other two SEM images. This facility provided by Dept. of Physics, University of Pune, India. The JEOL JSM-7500F is an ultra-high resolution field emission scanning electron microscope (FE-SEM) equipped with a high brightness conical FE gun and a low aberration conical objective lens). he improved overall stability of the JSM-7500F enables you to readily observe your specimen at magnifications up to 1,000,000xwith the guaranteed resolution of 1 nm. The energy filter (r-filter) makes it possible to observe the fine surface morphology of nanostructures.

3.3 FTIR

The FTIR spectrum of synthesized polypyrrole/Zinc oxide film is shown in Fig.5 spectrums showed the peak at 2500-3000 cm-1 corresponds to N-H stretching. The incorporation of the counter anion in the polymer is evidenced by the peaks. Further evidence of the presence of this anion in the polymer film is revealed by peaks at 1260 and The peak at 1519 cm–1 (1581 cm–1 for PPy) attributable to C=C stretching is considered to be an overlap of two oxidized structures. These bands correspond to the characteristic bands for polypyrrole/Zinc oxide film it shows very good agreement with earlier reported work. Thus, the FTIR spectral results confirm the formation polypyrrole/Zinc oxide film.

3.4 Conductivity Measurement

The four-probe set up (S.E.S. Instrument Pvt. Ltd. Roorkee) was used for the measurement of electrical conductivity of synthesized PPY/ZnO films. The conductivity measurement was done in the Department of Physics, Garware College (MS) India. The Four Probe Method is one of the standard and most widely used methods for the measurement of resistivity of semiconductors. The experimental arrangement is illustrated. In its useful form, the our probes are collinear the error due to contact resistance, which is especially serious in the electrical measurement on semiconductors, is avoided by the use of two extra contacts (probes) between the current contacts. In this arrangement the contact resistance may all be high compare to the sample resistance, but as long as the resistance of the sample and contact resistances are small compared with the effective resistance of the voltage measuring device (potentiometer, electrometer or electronic voltmeter),the measured value will remain unaffected. Because of pressure contacts, the arrangement is also especially useful for quick measurement on different samples or sampling different parts of the same sample. Table.1 shows conductivity of PPY/ZnO films with different dopants, along which $KMnO_4$ shows highest conductivity 1.62 S/cm at potential 670 mv for current density 0.5A/2cm2 at pH 4.

4. Figures and Tables

3.5 Figures

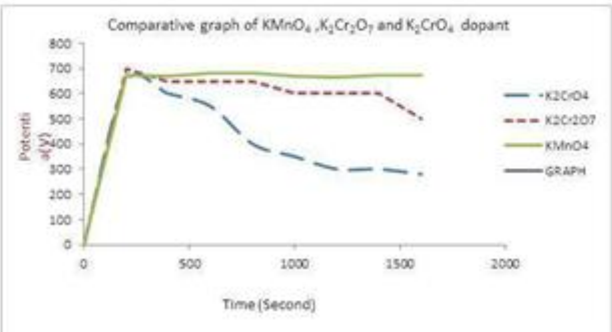

Figure 1: Comparative potentiogram with different dopants

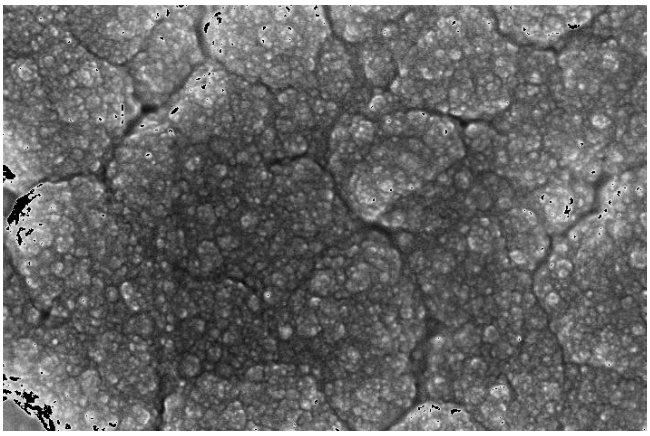

Figure 2: SEM images of PPy/ZnO NPs composite film with dopant $K_2Cr_2O_7$

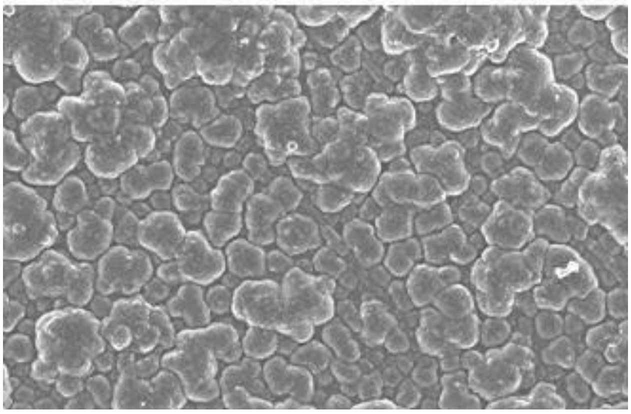

Figure 3: SEM images of PPy/ZnO NPs composite film with dopant K_2CrO_4

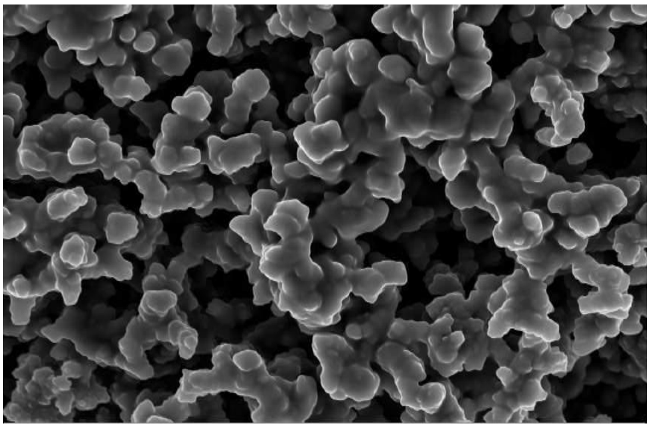

Figure 4: SEM images of PPy/ZnO NPs composite film with dopant $KMnO_4$.

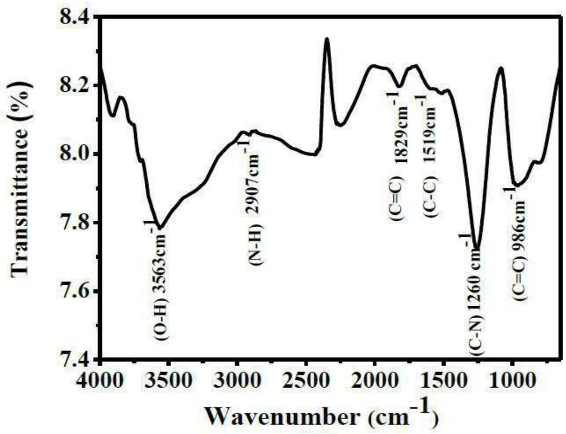

Figure 5: FT-IR spectrum of Ppy/ZnO thin film

4.2 Tables

Table 1: Conductivity measurement of Ppy film with dopant $KMnO_4$, $K_2Cr_2O_7$ & K_2CrO_4.

Sr. No.	Ppy film with dopants	Polymerization potential (mV)	Conductivity (S/cm)
1	$KMnO_4$	670	1.62
2	$K_2Cr_2O_7$	676	1.54
3	K_2CrO_4	700	1.2

5. Conclusion

The influence of electrochemical process parameter on the surface morphology and the conductivity of $PPy/ZnO/KMnO_4$ film were successfully studied. Process has been developed for the aqueous electropolymerization of $PPy/ZnO/KMnO_4$ coating on ITO substrates. The concentration ratio of 1:1 of PPy and $KMnO_4$ for the synthesis of $PPy/ZnO/KMnO_4$ film on ITO electrode is good combination for the deposition. The film shows good conductivity for current density 0.5A/2cm2 at pH 4. This is observed when ZnO acts as incorporating agent. If we vary the amount of ZnO NPS it affects the morphology of conducting polymer film. The ($PPy/ZnO/KMnO_4$) film provides a polymer matrix having a good porosity, high conductivity, uniform surface morphology and good mechanical and environmental stability.

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