Synthesis and Fabrication of Polythiophene/Zinc Oxide Nanocomposites Thin film and Characterizations

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ABSTRACT

Nanocomposites of polythiophene (PTh) and zinc oxide (ZnO) nanoparticles (NPs) were prepared by oxidative polymerization monomer of thiophene with iron (III) chloride as a catalyst in the presence of ZnO particles. After polymerisation, polythiophene in oxidized form was reduced by the extraction in methanol solution. The composite material was dissolved into M-Pyrrol, N-Methyl-2- pyrrlidinone (NMP) to produce a composite solution of PTh/ZnO Nanocomposites. The composites solutions were deposited onto glass substrates using a spin-coating technique to fabricate PTh/ZnO nano composite thin film. PTh/ZnO nanocomposites thin film were characterised by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) studies and structural properties of XRD.

Key words: Conjugated polymer; Polythiophene; Nanocomposites; Zinc oxide; Spin coating; Thin films.

1. INTRODUCTION

Organic, inorganic polymer composite materials have a wide variety of attractive potentialities to introduce novel structural design in material sciences and to novel functions for device applications\(^1\)\(^-\)\(^6\). In particular a composite structure based on conducting polymer/metal oxide semiconductors is one of the most advantageous combinations for photoelectronic devices. As organic materials, conducting polymers possess distinctive properties such as economical viability, light and easy processability and high suitability for various types of electronic devices, like display devices\(^7\), laser\(^8\), FETs\(^9\), and photovoltaic devices\(^10\). In contrast metal oxide such as zinc oxide, tin oxide and titanium dioxide are
environmentally viable with excellent chemical and physical properties like stability, that’s having been studied and used for transparent electrodes\textsuperscript{11}, electrochromism\textsuperscript{12}, photocatalysis\textsuperscript{13}, and solar cell\textsuperscript{14}. By combination of these materials with nanometer size control, an efficient electron-transfer reaction or energy transfer reaction can be derived and introducing novel functional attractive properties\textsuperscript{6,15-17}. The application of conducting polymer/metal oxide nanocomposites are used in photovoltaic devices are last several years studied as a characteristics of light absorption, charge separation, and charge transportation can be achieved\textsuperscript{16,18-24}. The fabrication of polymer/metal oxide nanocomposite generally has been accomplished by using the blend method or penetration method. In the blend method conducting polymer and metal oxide nanoparticles are mixed in solution and subsequently. For the penetration method metal oxide nanostructured films were first prepared, and then the conducting polymer solution was placed on top of the metal oxide film\textsuperscript{16,21,22}. This blend method is attractive owing to the simple process and can be introduced to diversified applications. The conducting polymer penetrates into the porous of the film until the polymer solution evaporates\textsuperscript{17,19,23,24}.

In this present work focusing on preparation of PTh/ZnO nanocomposite thin film. the PTh/ZnO nanocomposite material were prepared by through direct conducting polymer synthesis process. The synthesis of PTh conducting polymer by chemical oxidative polymerization method due to this addition to mixing of ZnO nano particle through polymerization bath metal oxide penetrate into polymer material. After the synthesised PTh/ZnO nanocomposite material were used for preparation of PTh/ZnO nanocomposite thin film by using spin coating method. The prepared nanocomposite thin film were characterized by functional group study of FTIR, structural characterization of X-ray diffraction (XRD) and surface morphological characterization of SEM.

2. EXPERIMENTAL

2.1 Materials

All chemical are used were in analytical purity. The thiophene(C\textsubscript{4}H\textsubscript{4}S) was obtained from Sigma-Aldrich distilled prior to use, chloroform, iron (III) chloride catalyst, Znonano powderand organic solvent M-Pyrol, N-Methyl-2- pyrrlidinone (NMP) all are purchased Merck Specialities Mumbai India.

2.2 Preparation of PTh/ZnO nanocomposite material

The polythiophene was synthesised by chemical oxidative polymerization through mixing of ZnO nano particles. The 0.3M of thiophene was dissolved in 25 ml of methanol with 1 ml of CTAB surfactant and addition to that ZnO nano particles per determined quantity. The monomer, surfactant and metal oxide of ZnO nano particles fully dispersed by the stirrering solution at magnetic stirrer for one hour. Then 0.5 M of lithium perchlorate was added as a supporting electrolyte to increase the bath conductivity and also added 0.2 M of ferrie chloride as an oxidant to above stirred solution. And again stirred the monomer metal oxide and oxidant mixture solution for 2 hours and kept several hours for complete
polymerization. The completed polymerization products of dark brown with black coloured precipitates were collected to reaction bath. These PTh/ZnO nanocomposite material were washed thoroughly with acetonitrile to remove any residual ferric chloride. These nanocomposite product were dried in a vacuum oven for 80°C for 10 hours to get powder form of nanocomposite PTh/ZnO material.

2.3 Preparation of PTh/ZnO nanocomposite Thin film

The nanocomposite thin film were prepared by using sol-gel spin coating method on glass substrate. The spinning solution was prepared by using a organic solvent of NMP. The determined quantity of PPh/ZnO nano composite material dissolved in organic solvent. The Composite material dissolved solution were filtered and then using a thin film preparation. The well cleaned substrate were kept in the spinner, the spinner rotating at constant speed of 3000 rpm, before spin coating solution draped over the substrate and rotating at constant rotations of spinner for 45 seconds. The evenly coated thin film taken in out to the spinner base then drying at oven at 70°C for two hour. The prepared PPh/ZnO nanocomposite thin film was using a characterization studies.

2.4 Characterization of PPh/ZnO Nano composite Thin film

The vibrational properties of the PPh/ZnO thin film were analyzed by Fourier transform infrared spectroscopy (FTIR) Perkin Elmer make model spectrum RXI spectroscopy in the wave number range of 400-2000 Cm⁻¹. The crystalline structural study of PPh/ZnO thin film were determined using Rigaku X-ray diffractometer (XRD) [2θ = 10-60°, Cu-Kα = 40 kV, 15 mA]. The top view surface morphology of PPh/ZnO thin film structure were analyzed by VEGA3 TESCAN (SEM HV: 5.0 kV) scanning electron microscope (SEM).

3. RESULTS AND DISCUSSIONS

3.1 FTIR spectroscopy Analysis

The FTIR spectrum of PTh/ZnO nanocomposite thin film as shown in figure 1. The expected spectrum of PTh/ZnO nanocomposite is clearly exhibits bands attributable to both PTh and ZnO nanoparticles. The peak absorbed at 647 cm⁻¹ it indicates the presence of a thiophene monomer, attributed C-S bending mode vibration, and C=C characteristic band at 1707 cm⁻¹ absorbed. In its comparison of previous report similar bands are observed between 400-4000 cm⁻¹ indicating that the main constituents of chemical structure of polymer and its nanocomposite at present in this spectrum. The peak at 1362 cm⁻¹ and 1537 cm⁻¹ corresponding to C=O and O-H bending vibrations respectively. The band 1081 cm⁻¹ to 1362 cm⁻¹ are due to deformation of C-H bending and C-H in-pane of vibrations.
3.2 XRD Spectral analysis

The typical X-ray diffraction pattern of PTh/ZnO nanocomposite thin film as shown if figure 2. The spectrum clearly indicated that amorphous nature of polymer structure presenting in this film and addition to that film containing some diffracted crystalline peaks also. The diffracted peaks represented by crystalline inorganic ZnO nano particles incorporating to the polymer materials. The crystalline sizes were calculating to use scherrers formula, the peaks position at about $2\theta = 17.56^0$, $27.02^0$, $35.46^0$, $36.74^0$ and $41.06^0$ calculated crystalline sizes are $d = 32.02$ nm, 25.5 nm, $40.43$ nm, $42.21$ nm and $19.86$ nm$^{28,29}$. 

3.3 Scanning Electron Microscope Analysis

The scanning electron microscope showing the surfaces micrograph of PTh/ZnO nanocomposite thin film as shown in figure 3. SEM image taking in to surface of the spin coated PTh/ZnO nanocomposite thin film at magnification of 2 micrometer range. The nanocomposite thin film exhibits a granular structure, while the morphology of PTh/ZnO nanocomposite thin film is characterized by the presence of large globules and some sharp needle structure at present this means the ZnO nanoparticles form this shape over the polymer phases$^{29}$. 

![Figure 1. FTIR Spectral line of PPh/ZnO nanocomposite Thin film](image1.png)

![Figure 2. XRD Spectral line of PPh/ZnO nanocomposite Thin film](image2.png)
4. CONCLUSION

The nanocomposite of PTh/ZnO material successfully synthesised and prepared by novel in-situ chemical oxidative polymerization method. The prepared nanocomposite material have used for preparation of PTh/ZnO thin film by sol-gel spin coating technique. The prepared PTh/ZnO nanocomposite thin film were characterized by functional group study of FTIR revel that main characteristics peak and band are presenting the film, structural characterization of XRD clearly showing amorphous nature of polymer and presenting ZnO nanoparticles diffractions and the morphological characterizations of SEM micrograph showing globular structure of polymer presenting some external shapes had also studied.

REFERENCES