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Morphological, structural, functional effect and Comparative study of PPy with PPy/TiO_2, and PPy/ZnO composite films by Nebulizer Spray coating Technique

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Abstract

Soluble polypyrrole, PPy/TiO_2, and PPy/ZnO composite has been synthesized by chemical method in aqueous solution of pyrrole monomer. The prepared composite sample was dissolved in m-cresol solvent. The solution was coated on glass substrate by NSP technique at 150°C for 5 minutes. The sprayed films are characterized by SEM, EDAX, XRD, and FT-IR. SEM graph reveals globular morphology and the presence of functional acid on PPy film surface. SEM study shows that oxide nanoparticles have a strong effect on the morphology of composite films. The presence of elemental constituents is confirmed of Ti. Zn, and O from energy dispersive X-ray analysis. XRD study reveals TiO_2 peaks represent the tetragonal specimen lines and ZnO peaks represent the hexagonal structure. The presence of functional groups of organic and inorganic compounds is indicated in FT-IR studies. The investigation of nanocomposites confirmed their morphological effect, hybrid composite, and suitability for optoelectronics devices

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Keywords: NSP technique; Scanning electron microscopy; X-ray diffraction; FT-IR

1. Introduction

Polypyrrole (PPy) is one of the most investigated intrinsically conductive polymers (ICPs), due to its interesting physicochemical properties such as electrical conductivity, deep black color, ion-exchange capacity, and hydrophobic nature, strong adsorption capacity towards molecular and macromolecular species. PPy can be prepared in various forms including thin films, powders, colloidal particles, hollow particles, nanotubes, micrometer-sized composites and nanocomposites[1-4].

Now a day, the development of polymer/inorganic hybrid nanocomposites has been receiving significant attention due to their wide range of applications in various fields. Transparent conducting oxides (TCO) like ITO, SnO_2, CdO, TiO_2, ZnO, $ZnSnO_4$, NiO, etc., have been widely studied due to their interesting optical and electrical properties. Among these transparent conducting materials, zinc oxide (ZnO), titanium dioxide (TiO_2) is the most attractive because of its non-toxicity, low cost, chemical stability and facility to doping with a wide variety of ions [5].

In the present work aim to attempt the soluble polypyrrole, PPy/TiO_2, and PPy/ZnO composite was prepared by chemical polymerization method at room temperature. Composite solution was coated on glass substrate maintained at 150°C for 5 minutes by spray pyrolysis (NSP) technique dissolved in m-cresol and softer. The spray pyrolysis technique is used successfully in our laboratory to elaborate a variety of inorganic materials. The composite films were polypyrrole (PPy), PPy/TiO_2, PPy/ZnO thin films prepared by a facile spray pyrolysis technique. The prepared samples were characterized by SEM with EDAX, XRD, FT-IR.

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2. Experimental technique

Materials

Pyrrole and Dodecylbenzene sulfonic acid (DBSA) (Sigma Aldrich, India) were purified by distillation plant before use. Ammonium persulphate (Loba chemical, India), Titanium dioxide, zinc oxide (Sigma Aldrich, India), methanol, and acetones (Merck, India) were purchased for the synthesis.

Polypyrrole preparation

0.15 mol of dodecyl benzene sulfonic acid (DBSA) and 0.3 mol of pyrrole were dissolved in 500 ml of de-ionized water. After 10 minutes 0.06 mol of Ammonium persulphate solution was prepared in 100 ml of de-ionized water and added drop wise into solution mixtures .Above solution was stirred for 16 hours in room temperature constantly. The solution became dark brown color. Excess of methanol was added to stop the reaction. The precipitate was collected and washed with de-ionized water, methanol and acetone. Then sample was dried at 60˚ C for 12 hours in vacuum oven.

Composite solution preparation

20 mg polypyrrole powder and same quantity of TiO_2 and ZnO was added in 15 ml of m-cresol solvent. It was stirred for 5 hours. The obtained composite solution was prepared.

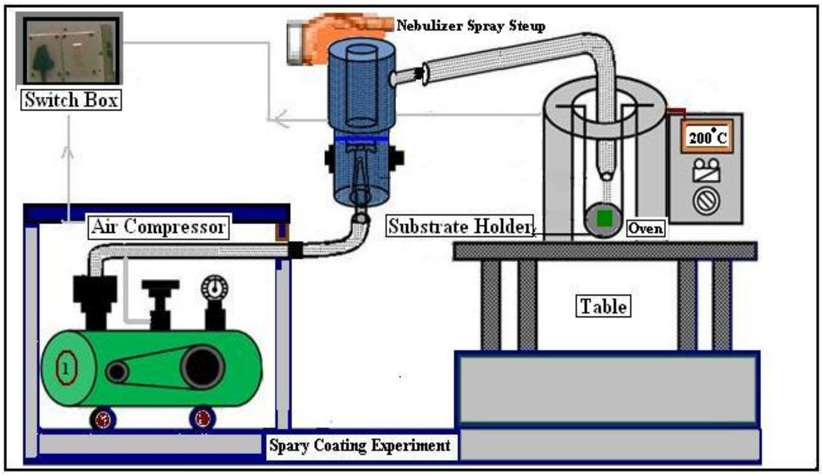


Fig. 1 Schematic diagram of Nebulizer Spray Pyrrolysis (NSP) Technique

Cleaning of the glass substrate and Spray Coating

Commercial glass substrates were cleaned with acid, detergent shop solution, running water and ultrasonic cleaner for about 20 minuties. In the second process, the substrates were cleaned with distilled water and iso-propyl alchol.

Then the prepared PPy, PPy/TiO_2, PPy/ZnO composite solution was sprayed with an air pressure of 5 psi on glass substrate at 150°C temperature. The film formed on substrate was retained at the above temperature for 5 minutes. It was dried in air for 10 minutes. In this study, the sprayed composite films prepared by NSP technique are shown in schematic diagram Fig. 1.

3. Results and Discussion

3.1 Morphological analysis of spray coated composite film

AJEOL JSM-5610 Scanning electron microscope was used to study the surface morphology of the Spray coated composite films. Fig. 2(a-c) shows the SEM image of the soluble polypyrrole, PPy/TiO_2, and PPy/ZnO composite films prepared by spray pyrolysis technique

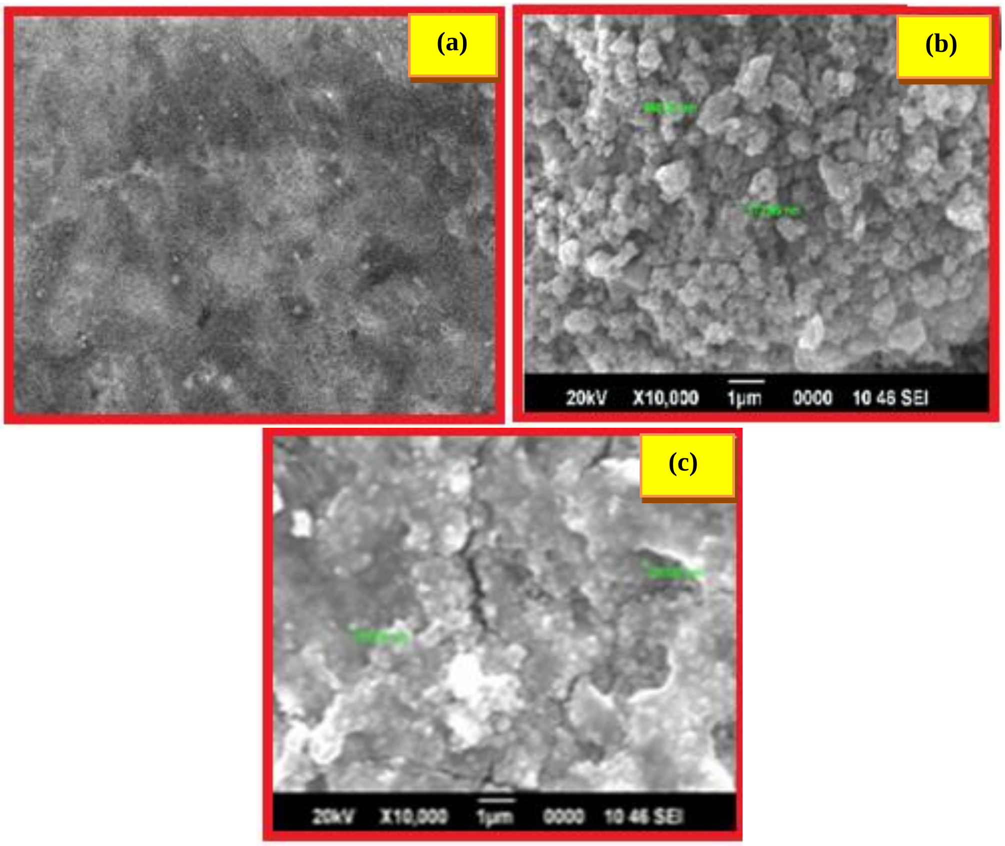


Fig. 2 SEM images of sprayed (a) PPY, (b) PPY/TiO_2, and (c) PPY/ZnO composite films

Fig. 2a shows that the no cracks and pin holes are found in the morphology of the polypyrrole film is globular [6], which is the characteristic of the functional acids used as dopants [7]. Fig. 2b shows the SEM images of composites films with the same wt. ratio of TiO_2. It can be seen that the morphology of composites at low content, are much similar to that of the Polypyrrole whereas some fibrous microstructure appears clearly PPy/TiO_2 composite film. Fig. 2c show that the cracks and gaps on the composite films. When the zinc oxide become too large, they cannot with stand the volume change and cracking occurs. It may be lead to the conductivity reduction of (PPy)/ZnO.

3.2 Elemental analysis of spray coated composite film

The composition of the films were investigated using an energy dispersive analysis by X- rays EDAX set up attached with scanning electron microscopy. The EDAX spectra of the prepared PPy/TiO_2, PPy/ZnO composite films were recorded in the binding energy 0-10 KeV as shown in Fig. 3(a, b).

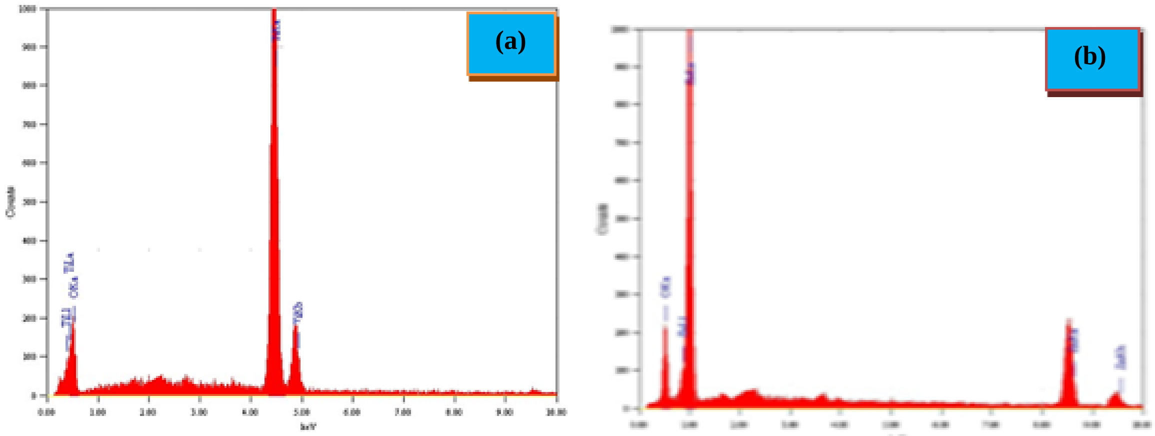


Fig. 3 EDAX Spectrum of Spray coated (a) PPy/TiO_2, PPy/ZnO composite film

The quantitative analysis result indicates the presence of carbon, titanium, copper, and oxide in the polymer composites. Also, the result confirms the formation TiO_2, ZnO nanoparticles. Elemental atomic percentage (%) of C, S, Ti, Zn, and O elements in the composite samples are shown in the Fig. 3 and listed on the Table.1.

Table.1 Energy dispersive analysis of the PPy/TiO_2, PPy/ZnO composite films

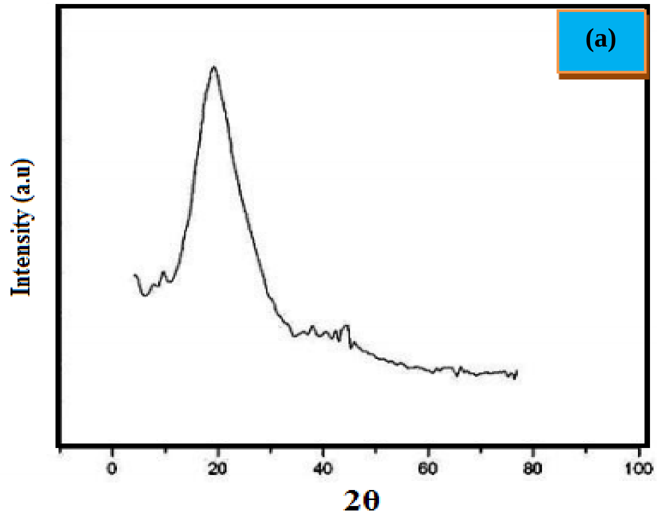
Elements	KeV	Mass %	Atom %
Ti	4.508	81.83	60.06
O	0.525	18.17	39.94
Zn	1.012	68.28	34.51
O	0.525	31.72	65.51

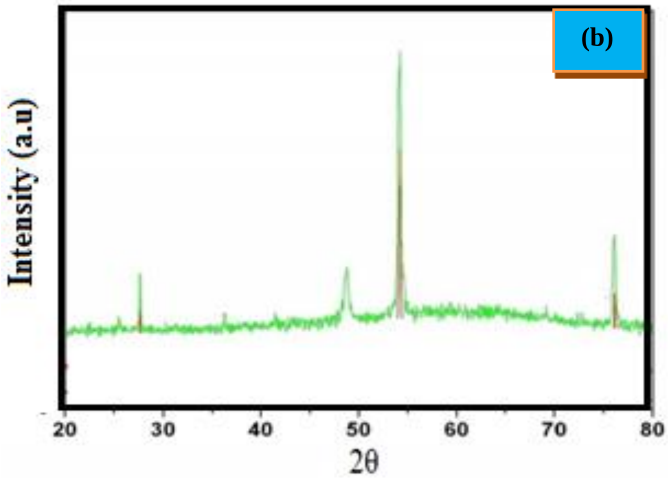
3.3 Structural analysis

X-ray diffraction patterns of PPy, PPy/TiO_2, and PPy/ZnO composite films were recorded using an X-ray diffracto meter with CuKα radiation (λ=1.54A˚). The X-ray diffraction pattern of Spray coated PPy film is shown in the Fig. 4a. The peak at 2θ= 22º reveals the semicrystalline nature of polypyrrole film. It corresponds to (1 0 1) plane value. The peak at 2θ= 22º describes the periodicity perpendicular to the polymer chain [8]. The XRD result shows that the semicrystalline nature of doped polypyrrole.

The XRD pattern of PPy/TiO_2 composite films exhibited diffraction peaks at 2θ = 25°, 36°, 41°, 54°, 62° and 69° [10]. Fig. 4b the presence of a broad, small and well distinct peak indicates the nanocrystalline nature of the TiO_2 film. The planes corresponding to (1 1 0), (1 0 1), (1 1 1), (2 1 1), (0 0 2) and (1 1 2) are in good agreement with the Joint Committee on Powder Diffraction Standard (JCPDS no. 894 920), confirming the formation of nanocrystalline TiO_2. The angle obtained from 2θ value corresponding to the (1 1 0) peak indicates the tetragonal specimen lines of TiO_2.

Fig. 4c show the XRD patterns of PPy/ZnO composite films peaks at 31.7˚, 34.4˚, 36.2˚, 47.5˚, 56.6˚, 62.8˚, 67.9˚, 69˚ are assigned to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) diffraction of hexagonal PPy/ZnO composite films. All the peaks can be indexed to hexagonal with lattice constants: a=b=3.253A˚, c=5.3213A˚which is good arrangement with the values from the standard card JCPDS file. No [891-397].The strong and sharp diffraction peaks indicate that the PPy/ZnO is well crystallized.





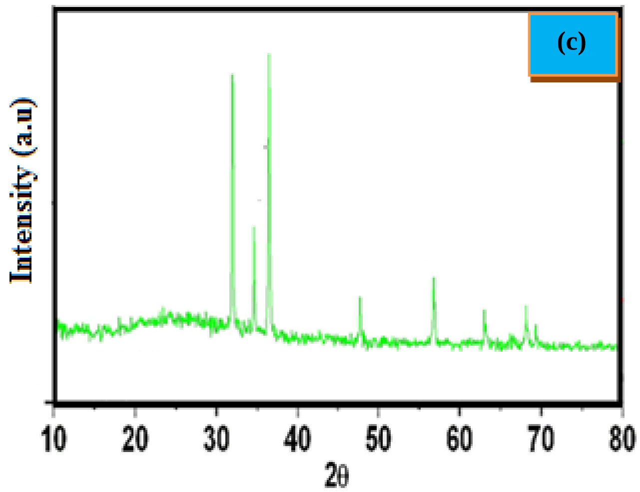


Fig. 4 XRD patterns of Spray coated (a) PPy, (b) PPy/$TiO_{2,}$ and PPy/ ZnO films at 150°C

The crystallite size of the samples was evaluated by the Debye-Scherer formula,

$$D = K\lambda/\beta \cos\theta$$

where, k is the shape factor, D is the crystallite size, y is the diffraction angle, b is the full width half maximum of diffraction angles in radians. The average crystallite size for the TiO_2, and ZnO samples to be 80 nm, and 51.1 nm respectively.

3.4 Functional group analysis

The FTIR spectra of the prepared PPy, PPy/$TiO_{2,}$ and PPy/ZnO composite films were recorded between the ranges 500 to 4000 cm^{-1} using thermo Nicolet V-200 FT-IR Spectrometer.

Fig. 5a shows FTIR spectrum of spray coated PPy film. The specific bands are observed at 3400, 1530, 1470, 1176, 1036, 900 cm^{-1}. They are close to the reported data. The stretching vibrations (3400 cm^{-1}) of N–H bond, stretching vibrations (1530 cm^{-1}) of C=C bond and bonds (1470, 1176, 1036, 900 cm^{-1}) of pyrrole ring [11] are obtained**.**

Fig. 5b shows the broad IR absorption peaks at 3450 cm^{-1} to 3550 cm^{-1} are assigned to the symmetric and asymmetric O-H mode of water coordinated Ti cations. The spectrum also shows the characteristics TiO_2 absorption at 466 cm^{-1} due to C-O and 1071 cm^{-1} at aliphatic sulfoxides S=O stretching. Fig. 5c shows the presence of a peak at 493 cm^{-1} is confirmed in the PPy/ZnO composite films [12].

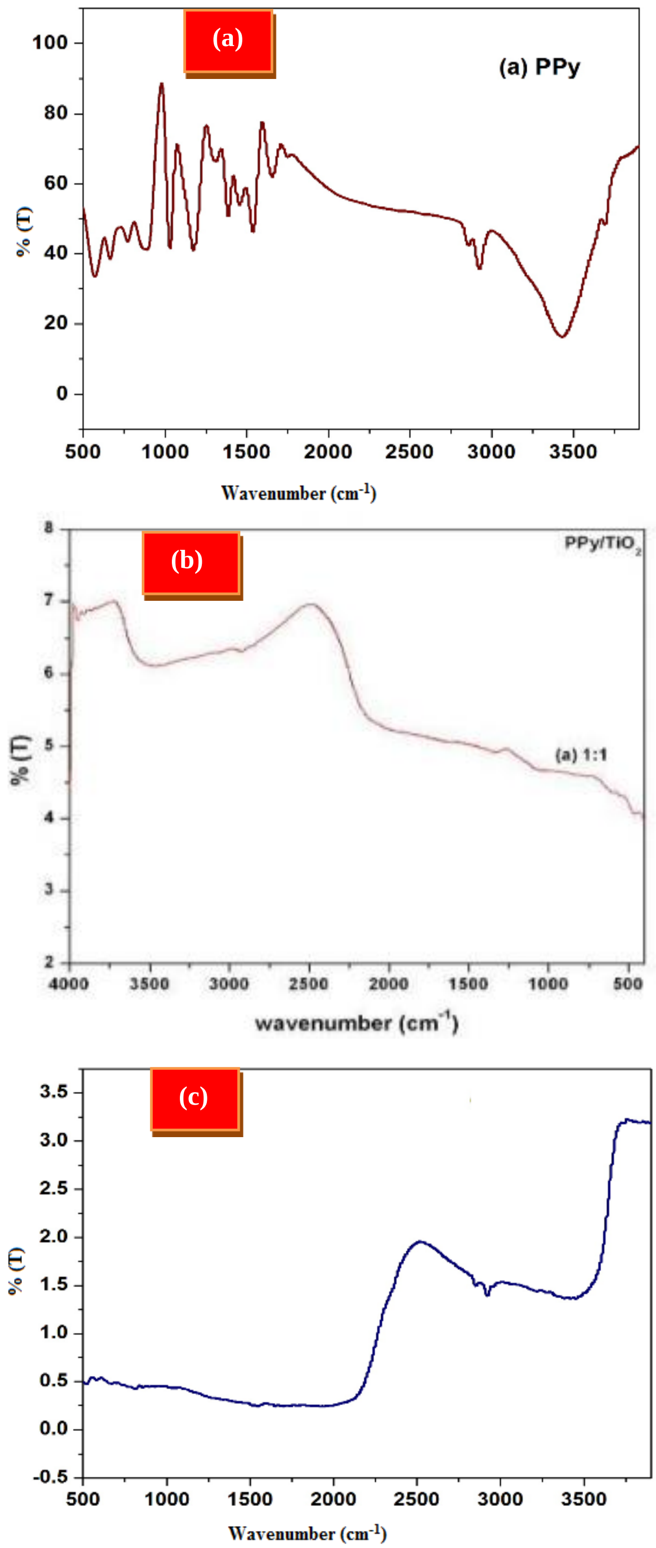


Fig. 5 FT-IR spectrum of Spray coated (a) PPy, (b) PPy/TiO_2, and PPy/ ZnO films at 150°C

4. Conclusions

Morphology and bonding changes are observed in composite films compared to PPy films and composites. Thus, depending upon the type of dopant, the morphology is found to be varied. The SEM morphology clearly reveals that various shapes are embedded in the polymer matrix. The presence of elemental constituents is confirmed from energy dispersive X-ray analysis. EDAX analysis reveals zinc ions have a stronger tendency to incorporate into a nano structure, probably because of the PPy/ZnO composite films can be indexed to hexagonal with lattice constants. The strong and sharp diffraction peaks indicate that the PPy/ZnO is well crystallized. FT-IR spectra reveal the effect of TiO_2, ZnO nanoparticles in the PPy films is confirmed. Therefore, it can be concluded that a p–n heterojunction at nano-crystalline hybrid nanocomposite interface has been created.

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