DEVELOPMENT OF P(Py-2FPy)/ ZnO COMPOSITE FILMS AND INVESTIGATION OF THEIR ELECTRICAL PROPERTIES

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Abstract

Poly (pyrrole-2formyl pyrrole) /zinc oxide, P(Py-2FPy)/ZnO composite film has been developed in this work. The inorganic ZnO nanoparticles were synthesized by room temperature solution method. While the pure copolymer P(Py-2FPy) film was prepared by spin coating through copolymerization, the copolymer composited with ZnO, (P(Py-2FPy)/ZnO) films, were prepared by novel *ex-situ* copolymerization method. The volumes of ZnO in the copolymer matrices were varied from 0.1, 0.2, 0.3, 0.4 and 0.5 mL. ZnO nanoparticles and the composite film formation were characterized by Ultraviolet visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) analysis. The important parameters of films including dissipation factor and capacitance depending on AC (alternating current) frequencies in the range from 1MHz to10 MHz were measured by LCR meter. The electrical conductivities of pure copolymer film and organic-inorganic composite films were investigated based on their measurements of electrical parameters. It was found out that the composite films were conductive and AC conductivities of composite films increase with increasing the volume of ZnO nanoparticles.

Keywords: copolymer, ZnO, composite film, conductivity, polymerization, *ex-situ*, spin coating.

Introduction

Polymeric nanocomposites are materials by combining of one or more inorganic nanoparticles with a polymer to obtain unique properties of such composite materials. They possess novel characteristics such as tunable conductivity, structural flexibility, enhanced thermal, mechanical and chemical stabilities. Organic polymers are considered to be good hosting matrices for composite materials since they can easily be tailored to yield a variety of bulk physical properties. Conductive polymer films can be used in many applications in light emitting diode, transistor, electrochromic device, actuator, electrochemical capacitor, photovoltaic cell and sensor.

The enhanced conductivities of these composite films depended on density and mobility of charge carries along the polymer chains. The concentration of charge carriers can be greatly increased by doping of inorganic nanoparticles in organic polymer matrix. Doping mechanism became oxidation/reduction process which in turn created the polarons and bipolarons in the polymer. They serve as the charge carriers in both degenerate and non- degenerate systems of polypyrrole (PPy). While the p-type doping in polymer create the oxidation process, n type doping became reduction one.

Inorganic nanoparticles possess outstanding optical, catalytic, electronic and magnetic properties which are significantly different their bulk states. As the result, by combining the attractive functionalities of both components, nanocomposites derived from organic polymers

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and inorganic nanoparticles, are expected to display synergistically improved the electrical properties of composite films. Therefore, polymer-based inorganic nanoparticle composites films will be interesting in several applications as new conductive polymeric materials.

ZnO is a n-type, direct band gap, II–VI semiconductor material with a wide band gap (3.37 eV) and a large exciton binding energy (~60 MeV at room temperature).Compared with other synthetic techniques, room-temperature solution process has been generally applied due to its simplicity and ease of fabrication with polymer. While polymers have flexibility, low-dielectric constant and processability, the properties of inorganic component have rigidity, durability and thermal stability. The mixing of organic polymers and inorganic nanoparticles is opening pathways for engineering flexible composites materials that show a better magnetic, electrical, optical, or mechanical property.

In this work, inorganic ZnO nanoparticles in organic Py-2FPy copolymer were composited. The composite P(Py-2FPy)/ZnO film was prepared in order to study the electrical properties of films. The conductivities of composite films depending on various volumes of inorganic ZnO are investigated by using LCR meter. The physical properties are characterized by UV-Vis and FT-IR. This work focuses on investigation the enhancement of electrical conductivity from the development of organic-inorganic composite films.

Experimental Details

Preparation of P(Py-2FPy)/ZnO composite film

Pure copolymer films was prepared by two monomers (Py and FPy), chloroform and trifluoroacetic acid (TFA). 207 μL of Py and 286 mg of FPy were dissolved in 2 mL of chloroform ($CHCl_3$). The monomer solution was stirred at room temperature for 30 min. Then, 1 mL of TFA acid in 2 mL of $CHCl_3$ was added to the monomer solution. Then, the mixed solution was spin-coated onto the 9 cm diameter Petri dish at 20 rpm by using a homemade spin coater. The polymerization was carried out for 40 min at room temperature, and finally the metallic greenish black copolymer film was formed in a Petri dish.

ZnO nanoparticles were synthesized by room temperature solution method. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and ethanolamine ($NH_2CH_2CH_2OH$) and 2-methoxyethanol were used as a starting precursor, a solution stabilizer and a solvent. 1g of $Zn(CH_3COO)_2.2H_2O$ and 0.28 mL of ethanolamine in 10 mL of 2-methoxyethanol were vigorously stirring for 12 h for the hydrolysis reaction in air.

The composite films were prepared by ex-situ copolymerization method through spin coating. The different volumes 0.1, 0.2, 0.3, 0.4 and 0.5 mL of as-synthesized ZnO nanoparticles was added to a fixed weight 486 mg of monomer solution. The composite solution was continuously stirred until ZnO were well dissolved in polymer solution. Then, the solution containing 1 mL of trifluoroacetic acid (TFA) and 2 mL of $CHCl_3$ was additionally put to composite solution at room temperature. After that, the mixed solution was spin-coated onto the Petri dish at 20 rpm using a spin coater until the complete formation of copolymerization was formed. After that, the film was successively washed by excess distilled water and acetone and they were kept in a desiccator for 24 h. Before measuring the electrical conductivity, chemical doping was performed on the films. For the doping process, a small amount of iodine (I_2) 215 mg was put in a closed vessel containing composite films and the vessels were kept for 24 h. The

electrical conductivity of the I_2 doped film was measured by LCR meter. The schematic diagram of *ex-situ* synthesis of composite film is illustrated in Fig. 1 and spin coating process and photo of composite film are shown in Fig. 2 and Fig. 3 respectively.

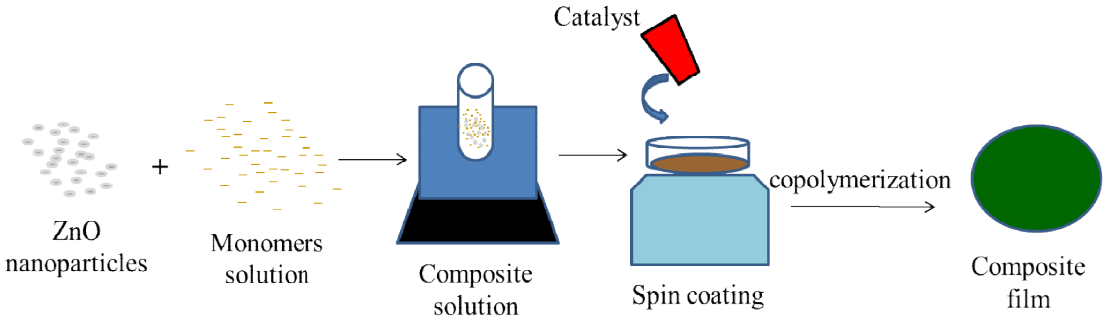

Figure 1 Schematic diagram of development of composite film by ex-situ chemical copolymerization

Figure 2 Spin coating process

Figure 3 Photo of P(Py-2FPy)/ZnO composite film casted in the Petri dish

Characterization Tools

The UV-Vis spectroscopy was performed in order to examine the absorbance values of all synthesized samples. The UV-Vis spectra were obtained by using Shimadzu UV-1800 UV-Vis spectrophotometer. The identification of functional group was investigated by FT-IR. The absorption spectra formations of ZnO, pure copolymer film and composite film were obtained by FTIR 8400 Shimadzu spectrophotometer using a KBr pallet in the mid IR radiation (4000 cm^{-1} - 400 cm^{-1}) range with a resolution of 4 cm^{-1}. The electrical properties were measured by (GW Instek LCR-8110G) LCR meter.

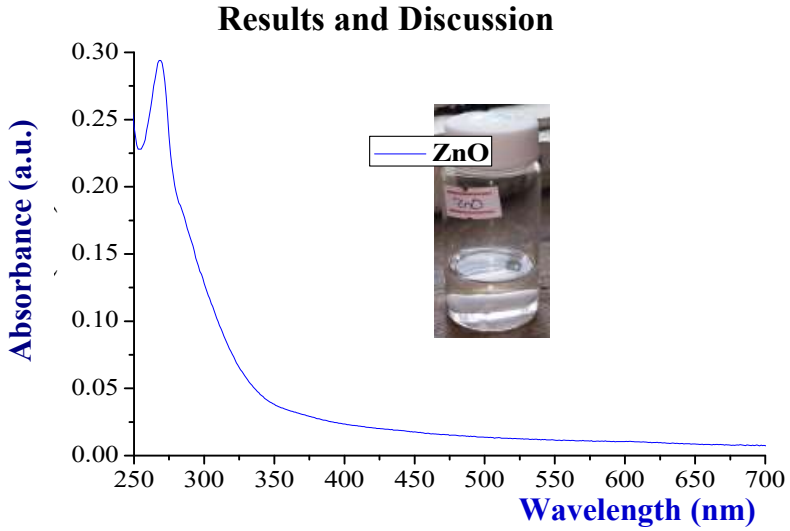

Figure 4 UV-Vis spectrum of as-synthesized ZnO nanoparticles. Inset shows ZnO nanoparticles

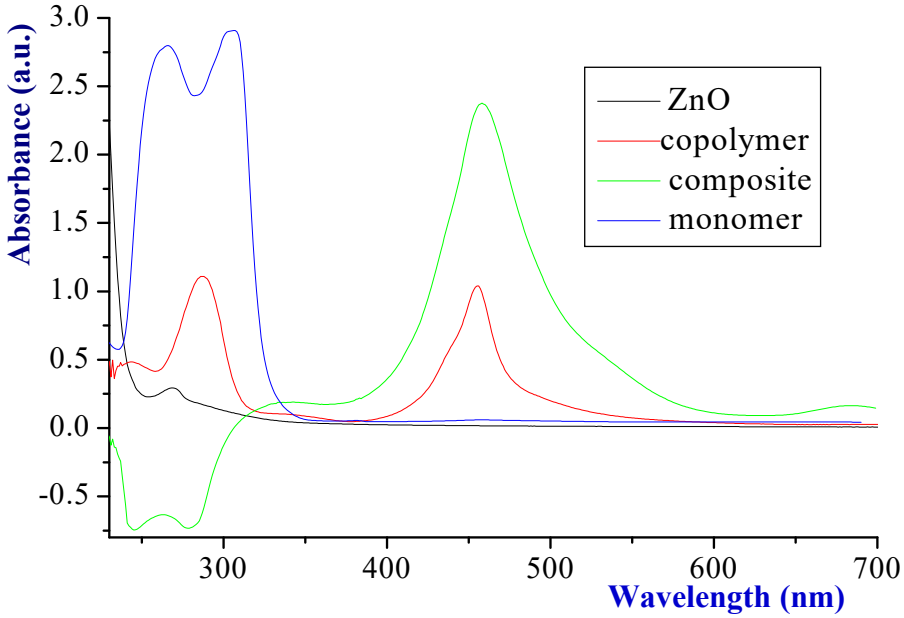

Figure 5 UV-Vis spectra of as- synthesized ZnO, copolymer and composite solutions with TFA catalyst

The UV-Vis absorption spectrum of as-synthesized ZnO nanoparticles was shown in Fig. 4. The maximum absorption wavelength was appeared at 268 nm. This shorter wavelength of ZnO nanoparticles tended to decrease in their size. Thus, room temperature solution method can be successfully obtained smaller size of ZnO particles which are very well dispersed in the solution as shown in the inset of figure 4. The optical band gap (E_g) of ZnO nanoparticles was estimated from its UV-Vis spectrum. Since the band edge wavelength was found out to be 359.78 nm, the optical band gap was about 3.4465 eV. Blue shift occurs since the wavelength of ZnO nanoparticles was decreased than the bulk ZnO due to smaller size of ZnO which is well dispersed in the solution. Thus, room temperature solution method was an excellent synthesis for

ZnO nanoparticles since the smaller size of inorganic part can combine very well in the copolymer matrix, P(Py-2FPy) to integrate the composite film.

Figure 5 shows the comparative UV-Vis spectra of ZnO, copolymer film and P(Py-2FPy/ZnO) composite films respectively. The optical absorption wavelengths of monomers, FPy and PPy, are found at 266 and 305 nm. However, the new copolymerization peak was formed at the wavelength 454 nm after TFA catalyst was added. This peak indicated that the FPy group was incorporated into the chemical structure of the conjugated polymer chains . When ZnO was present in the copolymer matrix of composite film, the absorption intensity of polymer chains was greatly increased. Besides, the weaker band was additionally appeared around 680 nm. This was due to strong interaction of ZnO with pyrrole segments to form bipolaron state which can enhance the electrical conductivity of composite films than pure copolymer film. The movement of polarons and bipolarons along the polymer backbone up lifts to enhanced conductivity of polymer film.

Figure 6 represents the FT-IR spectra of as-dried ZnO nanoparticles (a), copolymer films (b) and composite films (c). The OH band was observed in 3300-3400 cm^{-1} in ZnO. However, this peak disappeared in the copolymer and composite films. These results meant that O-H band of TFA catalyst has been removed and the C=O group was interacted with the Py-FPy film. The peak around 3124 cm^{-1} was due to aromatic C-H stretching band. The strong peak around 1672 cm^{-1} was due to C=O stretching band. The peaks of C=N stretching at 1487 cm^{-1} were attributed to the formation of the conjugated structure in the film. The peak observed at 1258 cm^{-1} was assigned to -C=CH- stretching from methine group of the copolymer. C-H out-of-plane deformation vibration from methine group occurred at 1003 $cm^{-1}$and that peak of the aromatic C-H out-of-plane deformation vibration are appeared 829 cm^{-1}. Peaks around 563, 515 and 420 cm^{-1} are related to the C-O stretching of PPy and FPy which have been overlapped with ZnO. Thus, it clearly mentioned that ZnO nanoparticles were well incorporated in the polymer matrix through *ex-situ* polymerization method.

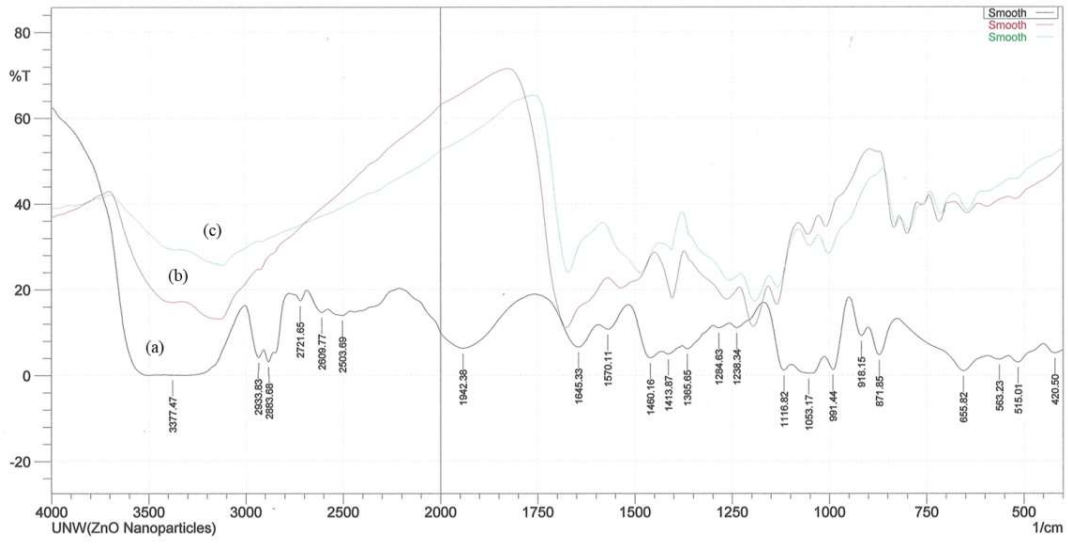

Figure 6 FTIR spectra of (a) ZnO nanoparticles (b) pure copolymer P(Py-2FPy) films without ZnO nanoparticles and (c) P(Py-2FPy) /ZnO composite films

The electrical properties of conductive films were studied by using the LCR meter. The diameter of the sample size is 9.578 mm in a circular shape for each film. The parameters

including capacitance and dielectric loss in the frequency range 1 MHz to 10 MHz are measured. Dielectric constant (κ) was calculated by using the formula:

$$\kappa = \frac{Cd}{\varepsilon_0 A} \tag{1}$$

where, κ *is* dielectric constant or relative permittivity of the medium, C is capacitance, d is the thickness of the sample, A is the cross sectional area of the sample and ε_0 is the relative permittivity of vacuum (8.854 x 10^{-14} F/cm).Then dielectric loss ($\tan\delta$) is determined by the formula:

$$\tan\delta = \frac{D}{\kappa} \tag{2}$$

where, D is the dissipation factor obtained from LCR measurement. Finally, the AC conductivity (σ_{ac}) was determined by using the relationship:

$$\sigma_{ac} = 2\pi f \tan\delta\ \varepsilon_0 \kappa \tag{3}$$

where, f is the frequency of applied field. Iodine (I_2) doping was carried out for all investigated films since it can generate the new charge carriers (electrons and holes) which can transport through the polymer chain. I_2 doping takes the form of vapor-phase. In this doping, polymers are exposed to the vapors of iodine dopant compounds. The level of doping is determined by the vapor pressure and reaction time.

In Fig. 7, the AC conductivity of the pure copolymer film, that is there is no ZnO nanoparticles in the composite film, showed the lowest conductivity values while the conductivity of composite films improved with the increasing volume of ZnO. It was found out that the highest conductivity was obtained for the film composited with 0.5 mL of ZnO nanoparticles among the investigated volume limits of ZnO nanoparticles. The electrical conductivity measurement shows that the enhanced conductivity of the conducting P(Py-2FPy/ZnO) polymer films due to the presence of ZnO nanoparticles in the composite films. Figure 8 shows the summarized graph for the average AC conductivity of the films versus different volumes of ZnO nanoparticles. The conductivities are increased with an increasing volume of ZnO.

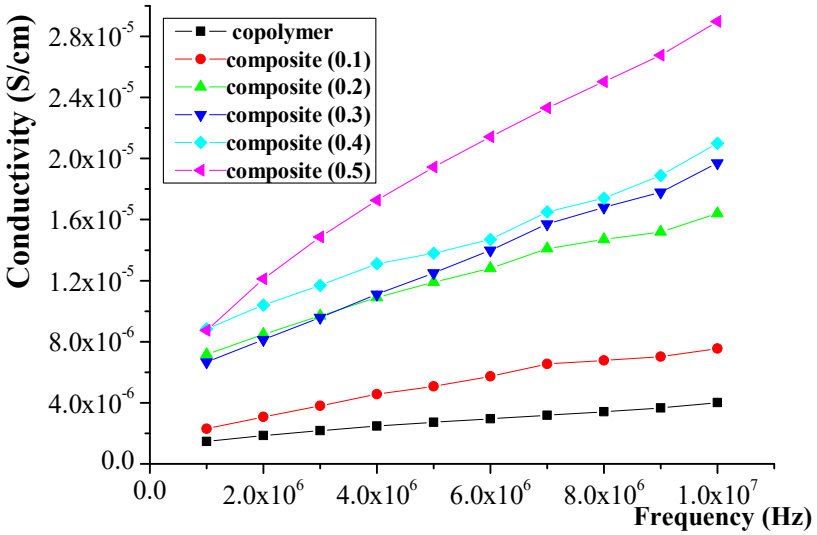

Figure 7 Electrical conductivities of composite films at different ac frequencies

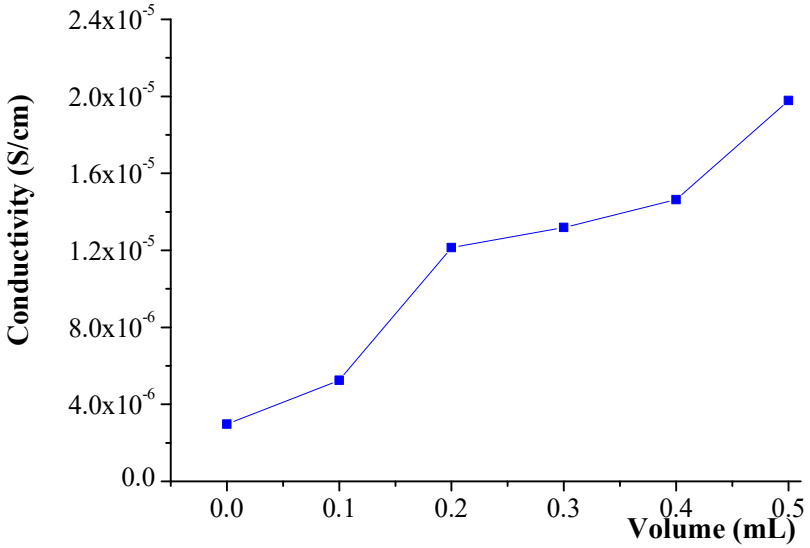

Figure 8 Average electrical conductivities of composite films depending on different volumes of ZnO nanoparticles

Conclusions

To sum up, the enhancement of conductivity of P(Py-2FPy)/ZnO composite film has been studied. The electrical conduction properties of copolymer-ZnO composite films with different volumes of ZnO are investigated for frequencies range from 1MHz to 10 MHz.

The conductivities of composite films are better than pure copolymer film. The composite film for highest volume of ZnO shows the greatest electrical conductivity. It can be explained that ZnO nanoparticles are strongly interacted with pyrrole segments which are intended to form bipolaron state. The movement of such bipolarons by excitation of AC frequencies along the polymer backbone up lifts to enhanced conductivity of composite films. The novel formation of composite film was identified and characterized by UV- Vis and FT-IR. The resulted films show that the inorganic ZnO nanoparticles can be successfully incorporated into the organic copolymer matrix and also scalable. The composite polymer films can be applied in the electrochemical devices technology.

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