



SURFACE AND STRUCTURAL MODIFICATION OF SPRAYED (PPy)/ZnO NANOPARTICLES COMPOSITE FILMS AND THE FEASIBILITY STUDY OF HYBRID SOLAR CELLS

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Abstract

Accepted Date:

19/09/2012

Publish Date:

27/10/2012

Keywords

Polypyrrole (PPy)

Spray composite films

Surface modification

Contact angle

XRD

Photoluminescence

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DBSA doped soluble polypyrrole was prepared by insitu chemical polymerization. (PPy)/ZnO composite films were coated at different temperatures 150°C, 200°C and 300°C by spray pyrolysis technique with various weight ratio of ZnO (1:1), (1:2) and (1:3). It was found that (PPy)/ZnO films coated at 300°C were found to be good. The atomic percentage of the films was analyzed by EDAX spectrum. The changes manifested on the polymer surface and in the mechanical properties were studied with respect to surface wettability. The PPy doped ZnO composite film was formed to have a change from super hydrophobic to a hydrophilic state. The SEM study shows cracks and gaps in the surface of (PPy)/ZnO films. A hexagonal structure (PPy)/ZnO composite film was confirmed by X-ray diffraction pattern. FTIR spectrum reveals that the intensity of polypyrrole decreases with the addition of ZnO content. The absorption of PPy and (PPy)/ZnO composite film at 360 nm and 380 nm was confirmed by UV spectroscopy. Photoluminescence study shows that the direct band gap energies of the PPy and (PPy)/ZnO composite films with different weight ratios are found to be 2.8eV and 3.29eV, 3.28eV and 3.27eV. It was found that the (PPy)/ZnO composite films had a (p-n) hybrid solar cells behavior was studied by I-V and conductivity measurements.

INTRODUCTION

Conducting polymer nanomaterial with various morphology have attracted considerable interest in the fabrication of various of electronic devices¹ such as batteries², capacitors and Diodes³ because of their various structures and metal-like conductivity. The most widely studied conducting polymers include polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh)⁴. Among them, PPy has attracted much attention owing to its unique electrical conductivity, redox property, excellent environment stability, as well as the virtue of easy preparation by both chemical and electrochemical approaches⁵. The electrochemical polymerization of pyrrole has been extensively studied as it is easily obtained in the form of free standing films and composite films with has good environmental stability and conductivity and to tune the deposition conditions to produce superhydrophobic PPy films. The most common strategy for creating superhydrophobic PPy films is the dopes of film with low-surface energy sulfonic⁶. It is well known that a rough surface will amplify the inherent hydrophobicity or

hydrophilicity of a surface by increasing the surface area with which a droplet interacts⁷.

Zinc oxide (ZnO), a versatile semiconductor material, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions ZnO and is a wurtzite-type semiconductor with band gap energy of 3.37 eV. It has very large excitation binding energy (60 meV) at room temperature. Special attention has been devoted to the morphology, as ZnO can form different nanostructures based on its semiconductor properties. Interest in the development of new inorganic: organic hybrid materials with composition modulated on the nanometer scale has grown exponentially in recent years due to a wide range of potential applications in microelectronics, display technologies, catalysis, sensors⁸. As a special case this work focuses on the development of p-n diodes and LEDs.

In this study, PPy and PPy /ZnO nano particle composites were prepared by spray coating technique at on optimized temperature 320°C. Optical, structural,

morphological and surface roughness were studied and discussed.

MATERIALS & METHODS

Synthesis of DBSA doped soluble Polypyrrole

Pyrrole and dodecylbenzene sulfonic acid (DBSA) (Sigma-Aldrich, India) were purified in distillation plant before use. Ammonium persulfate (APS) was obtained from Loba chemical, (India) and methanol and acetones of Merck brand were purchased.

0.15 mol of dodecylbenzene sulfonic acid (DBSA) and 0.3 mol Pyrrole were dissolved in 500 ml of de-ionized water. After 10 minutes 0.06 mol of ammonium persulfate (APS) was prepared in 100 ml de-ionized water and added drop wise into solution mixtures. Above solution was stirred for 24 hours with ice bath at 20°C constantly. Excess of methanol was poured to stop the reaction. The precipitate was collected and washed with de-ionized water, methanol and acetone. Then the sample was dried at 30 °C for 12 hours in a vacuum oven.

Polypyrrole film by spray pyrolysis technique

200 mg Polypyrrole powder was taken in 5 ml m-cresol solvent. The solution was stirred for 6 hours. The obtained solution was poured into 50 ml burette. Commercial glass substrate was cleaned, with acetone and iso-propyl alcohol properly. Then the prepared Polypyrrole was solution sprayed with in air pressure of 5 psi on glass substrate kept at 200°C and the film formed on substrate was retained at the temperature for 5 minutes. It was dried in air for 10 minutes. Polypyrrole film was formed on glass substrate. The Optical, structural and morphological studies were carried out for the prepared film samples.

The mechanical mixture (blending method)of (PPy)/ZnO

A series of (PPy)/ZnO hybrid materials with different ZnO weight percent of 1:1,1:2 and 1:3 were prepared by mechanical mixture using PPy and ZnO. (purchased from Sigma-Aldrich, India, the particle size was about <100nm). 200 mg of Polypyrrole powder and 200 mg of TiO₂ powder was taken in the equal ratio of (1:1). After that PPy is constant, but TiO₂ is varied (1:2) and 1:3).

Synthesis of (PPy)/ZnO composite film Solution

The mechanical mixtures of (PPy)/ZnO (1:1),(1:2) and (1:3) ratio in m-cresol (200 mg of 5 ml) solvent were stirred for 5 hrs and filtered with a whatman filter paper. The obtained solution was poured into 50 ml burette. Commercial glass substrate was cleaned with acetone, isopropyl alcohol properly. Then the prepared (PPy)/ZnO solution was sprayed with an air pressure 5 psi on glass substrate kept at different temperature in 150°C, 200°C, 300°C and the film formed on substrate was retained at the temperature for 5 minutes. It was dried at air for 10 minutes. (PPy)/ZnO nano composite were prepared by spray coating technique at on optimized temperature 300°C and various characterization techniques.

RESULTS AND DISCUSSION

SCANNING ELECTRON MICROSCOPE (SEM)

SEM images of spray coated PPy and (PPy)/ZnO composite films at different ratios.

AJEOL JSM - 5610 scanning electron microscope was used to study the surface morphology of the Spray coated polypyrrole film. Figure 1(a) shows the DBSA doped soluble polypyrrole film prepared by spray

pyrolysis technique. There are no cracks and pin holes in the morphology. The obtained film on glass substrate shows uniformity. The morphology of the polypyrrole film is globular⁹. Figure 1(b) shows that the composite films have no agglomeration of ZnO particles in PPy matrix and there is a uniform distribution of the ZnO particles in the PPy matrix¹⁰. Figure 1(c) and Figure 1(d) show 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. No peels off of the PPy layers were observed for all samples. The average grain size of (PPy)/ZnO composite films was found to be 120 nm.

ENERGY-DISPERSIVE X-RAY SPECTROSCOPY ANALYSIS (EDAX)

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)/ZnO composite films were recorded in the binding energy 0-10 KeV as shown in Figure 2(a), Figure 2(b) and Figure 2(c). The EDX analysis was performed with an aim to

determine atomic percentage of the (PPy)/ZnO spray coated composite films. EDX reveals composition the Zn (34.5); O (65.5) for the film deposited at 300°C with an equal ratio of (PPy)/ZnO. Zn (74.3); O (25.7) for 1:2 ratio and Zn (77.13); O (22.87) for 1:3 ratio at the same temperature of 300°C. The EDAX results reveal that the content of O decreases with the increases of Zn content. The Zinc ions have a stronger tendency to form a nano structure owing to their higher charges. For the composite films at various ratios at (1:1), (1:2) and (1:3). The average atomic percentage of Zn was presented 61.97%. Figure 3 shows the EDX spectrum of the composite films prepared by spray pyrolysis method. It is observed that the average atomic percentage of Zn was higher than O, and almost all Oxygen were evaporated¹¹.

SURFACE WETTABILITY: CONTACT ANGLE AND SURFACE ENERGY.

Wettability is important in coating and deposition process and is a measure of how a liquid spreads on a surface. If the liquid is water, the surface is termed hydrophilic or hydrophobic, depending on whether it likes water or not. Hydrophobic is a substance that has a positive Gibbs energy of

transformation from a non-polar to a polar solvent. Hydrophilic is a substance that has a positive Gibbs energy of transformation from a non-polar to a non-polar solvent. Complete wetting is extremely important as spray coating. Surface tents may be used to facilitate the process. The wettability of the surfaces and determine by contact angles of the samples. An OCA 20 video-based contact angle meter attached with a camera was used to measure the wettability. The wetting liquid used was Millipore-grade distilled water (liquid surface tension $\gamma_l=72.8\text{mJm}^{-2}$). To produce superhydrophobic surfaces, one must be able to control the micro and nanostructure of the film by spray method of producing superhydrophobic (water contact angle of 154°) Polypyrrole films¹². The surface roughness is one of the important factors of influencing the contact angle value. Wenzel et.al was the first to discover the influence of surface roughness on the contact angle. He reported that a decrease in surface roughness produces an increase in contact angle. The PPy doped ZnO composite film formed to have a change from superhydrophobic to a hydrophilic state¹³.

Figure 4 shows the contact angles of the (PPy)/ZnO samples at different ratios. The contact angles 127.56°, 115.77° and 107.00° respectively. It was decreases with higher content of ZnO nano particles. It was observed that the higher concentration of ZnO enhances the surface change in composite films. The lower contact angles value reveals the formation of 'hydrophilic groups' in the composite film surfaces.

Surface energy was calculated using the equation of state, Schultz Method-2, and Data Physics SCA20 software (Version 2.01).

The adhesion work (W_{adh}), a quantity related to surface wettability, was calculated using the following formula:

$$W_{adh} = \gamma_l (1 + \cos\theta) \text{ (mJm}^{-2}\text{)}$$

where γ_l are the surface energy of the testing liquid and contact angle.

The composite films of W_{adh} values are given in Table 2. W_{adh} was calculated from contact angle measurements with respect to water. These measurements showed that the ZnO sample values increased with time and concentration. The W_{adh} values are 28.42, 41.15 and 51.52 (mJm⁻²) respectively. The increment of W_{adh}

confirms the formation of new functional groups in composite films as show the Figure 5 1:3 ratio.

FTIR SPECTRAL ANALYSIS

The FTIR spectra of the prepared samples PPy and (PPy)/ZnO composite films were recorded and the results are reported have, FTIR spectroscopy analysis was scanned from 500 to 4000cm⁻¹ using thermo Nicolet V-200 FTIR Spectrometer. Figure 6 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 these 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 ring¹⁴. The peak 1036 cm⁻¹ confirmed that the sulfonyl group is attached to the pyrrole ring. On comparison of Figure 6 shows respectively, the presence of peak at 493 cm⁻¹ and the shifted characteristic peaks at around 1082 cm⁻¹ in (PPy)/ZnO composite films¹⁵. The presence of new peaks is shifted to 493 cm⁻¹ to 1543 cm⁻¹ in shows the Figure 6. The bond of C-H and C-C stretching mode of quinoid rings, in plane deformation vibration is situated at

493 cm^{-1} and 1543 cm^{-1} . The specific bands are observed at 1560 cm^{-1} in (PPy)/ZnO composite films is confirmed. The peak intensity decreases, when increase the ZnO content. It was observed that there is a remarkable difference of the presence of new peaks 2853 cm^{-1} in the FTIR spectra for the samples with the different contents of ZnO. It is only one peak broad band between 350 to 600 cm^{-1} . The peak was assigned to Zn-O stretching.

X-RAY ANALYSIS

XRD PATTERN OF PPy and (PPy)/ZnO (1:1), (1:2) and (1:3) COMPOSITE FILMS

X-ray diffraction patterns of PPy/ZnO composite films were recorded using an X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.54\text{\AA}$)

Figure 7 shows a peak around at $2\theta=20^\circ$ reveals the crystalline nature of DBSA doped Polypyrrole films. Figure 7 show the XRD patterns of PPy/ZnO composite films. From the Figure 7 the 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 films⁹. All

the peaks can be indexed to hexagonal with lattice constants: $a=b=3.253\text{\AA}$, $c=5.3213\text{\AA}$ 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 are well crystallized. The crystallite size of (1 0 0) plane decreases for 1:3 and also increases (0 0 2) and (1 0 1) planes. (1 0 1) plane is strong peak of ZnO. The equal ratio of (PPy)/ZnO shows weak peaks. It was observed that the ZnO particle interacts on polypyrrole surface¹². The crystallite size for the 1:1, 1:2 and 1:3 samples are found to be 24.8 nm, 34.3 nm and 51.1 nm.

Using FWHM data and Debye-Scherrer formula, the crystallite size of the films was calculated.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where,

'k' is proportionality constant approximately equal to unity,

' β ' the FWHM of the peak in radians (theoretically corrected from the instrumental broadening),

' λ ' is the wavelength of X-rays (1.5406 Å for CuK α),

' θ ' is the Bragg's angle.

Dislocation density

The dislocation density (δ) can be evaluated from Williamson and Smallman's formula,

$$\delta = \frac{1}{D^2} \text{ lines/m}^2$$

The variation of crystallite size and strain and dislocation for with different ratios are shown in Figure 8 and 9 As the weight percentage of ZnO increases the crystallite size increase and the intensity of Zn ion with reduces in resistivity.

PHOTOLUMINESCENCE SPECTRUM

Photoluminescence spectrum of PPy and PPy/ZnO

The PL property of the soluble polypyrrole film was studied using FP-6500 Spectrofluorometer- 67 at room temperature at 30°C.

Photoluminescence spectrum of soluble DBSA doped PPy film coated by spray pyrolysis technique is shown in Figure 10 (a). The PL intensity of DBSA doped PPy is found to have higher luminescence than DMSO,

Chloroform and THF in m-cresol solvent. The broad emission wavelength of the PPy film is found at 380nm.

The direct band gap of the film was calculated by using this formula,

$$(E_g = hc/\lambda)$$

where,

'h' is a constant,

'c' is velocity of light,

' λ ' is emission wavelength in Photoluminescence spectrum.

The direct band gap energy of the PPy film is found as 2.8eV. The PPy/ZnO composite films for various weight of ZnO. Figure 10 1:1, (c) 1:2 and (d) 1:3) reveal strong peaks at 377 nm, 378 nm and 379 nm¹⁶. In the case of (PPy)/ZnO composite films intensity is found to be decreased for higher ZnO content. The direct band gap energies of the PPy/ZnO composite films of different ratios are found as 3.29eV, 3.28eV and 3.27eV. The band gap is decreased due to content increase of ZnO nano particles.

UV-VIS Absorption Spectrum

The UV-visible spectrum of PPy and (PPy)/ZnO film sample was recorded employing Jasco V-530 dual beam spectrometer. PPy and (PPy)/ZnO composite films are shown in Figure 11. The absorption peak at 360 nm reveals electron transition in the benzenoid rings of DBSA. A broad band at 380 nm is the characteristic band of the hexagonal pure ZnO. (PPy)/ZnO composite film and PPy have the peaks of same shape, but some shifting in the bands is noticed. Furthermore, the increased relative intensity of the peak for (PPy)/ZnO composite film is attributed to the interaction between ZnO nanoparticles and Ppy molecules. It is confirmed that the strong guest-host interactions in organic/inorganic composites are occurred due to the presence of hydrogen bonding.

The interaction between ZnO and PPy composite film contributes to the decrease in the degree of orbital overlap between the π electrons of the phenyl rings with the lone pair of the nitrogen atom in the PPy molecules. It forms strong hydrogen bonding between them. Consequently, the extent of conjugation of PPy, thus resulting in the increased intensity of the peak in (PPy)/ZnO composite film substrate shifted

to peaks for 380 nm respectively and are ascribed $\pi \rightarrow \pi^*$ transitions¹⁵.

I-V characteristics and conductivity

I-V characteristics and conductivity of Polypyrrole and (PPy)/ZnO were done by Kiethly 210061/2 electrometer using Four Probe –Setup (DFP.2 model). The current I was kept constant and the room temperature at 35°C. The voltage values were recorded with varies percentage of 1:1, 1:2 and 1:3 ratios.

The resistivity at different percentage was calculated using the relations.

$$\rho = \frac{4.5324 \times V \times d}{I} \times F \quad \text{And}$$
$$F = \frac{d}{s}$$

Where, I-Current, V-Voltage, d-thickness of the Pellet (2.434mm) F- Correction factor and S- distance between two probes. Distance of the probe is 2 mm.

The conductivity was calculated using the relation.

$$\sigma = 1/\rho$$

ρ is resistivity; the correction factor depends on the sample geometry, thickness, borders and location of points in the sample. I-V characteristics of the

Polypyrrole and (PPy)/ZnO composites are shown in the Figure 12(a). The resistivity of the pellet with a thickness 2.231mm was obtained for different currents 0 to 0.8 μ A.

Figure 13(b) shows the various weight (%) versus conductivity PPy and (PPy)/ ZnO. The conductivity of the polypyrrole pellet was more than value at room temperature. The conductivity of Polypyrrole and variation of σ_{dc} with weight percent of Zinc Oxide were analyzed up to 8 μ A. It is observed that the higher content of Zinc Oxide increases the conductivity. The result of the conductivity shows a strong dependence on the various weight ratio of ZnO in Polypyrrole. The charge transformation of the composite was confirmed by photo luminescence spectroscopy. This possibility may suitable for hybrid solar cell applications.

CONCLUSION

PPy and (PPy)/ZnO composite films were prepared by spray pyrolysis technique. PPy Film shows the globular morphology and (PPy)/ZnO films at 1:2 and 1:3 ratios show the cracks and gaps on the morphology. EDAX analysis reveals Zinc ions have a stronger tendency to incorporate into a nano structure, probably because of their

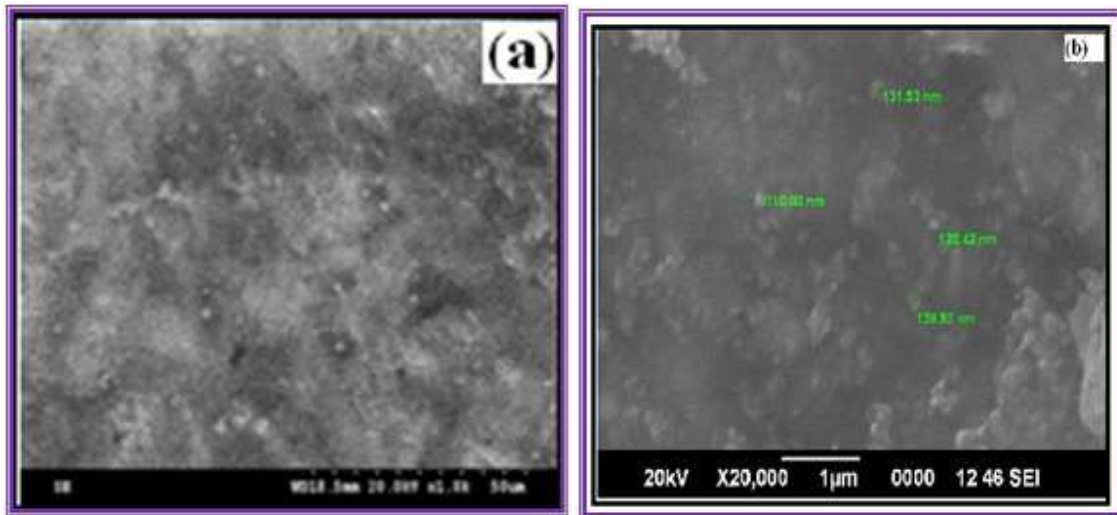
higher charges. (PPy)/ZnO composite film is finding to the changed from a super hydrophobic to hydrophilic state. FTIR analysis confirms the attachment of sulfonyl group with to the pyrrole ring. The peak intensity decreases, with the increase of ZnO content. It is observed that there is a remarkable difference in the FTIR spectra of ZnO variation. (PPy)/ZnO composite films can be indexed to hexagonal with lattice constants. The strong and sharp diffraction peaks indicate that the (PPy)/ZnO are well crystallized. The grain sizes of the composite films are found as 24.8nm, 34.3nm and 51.1nm respectively. PL spectrum of (PPy)/ZnO composite shows an increase of intensity with increase of ZnO content. The increased intensity of the peak in (PPy)/ZnO composite film is found to be shifted to 380 nm due to the $\pi \rightarrow \pi^*$ transition. The result of the conductivity shows a strong dependence on the various weight ratio of ZnO in Polypyrrole.

ACKNOWLEDGEMENTS

The authors are grateful to Sophisticated Test and Instrumentation Center, Cochin (Kerala), Birla Institute of Technology,

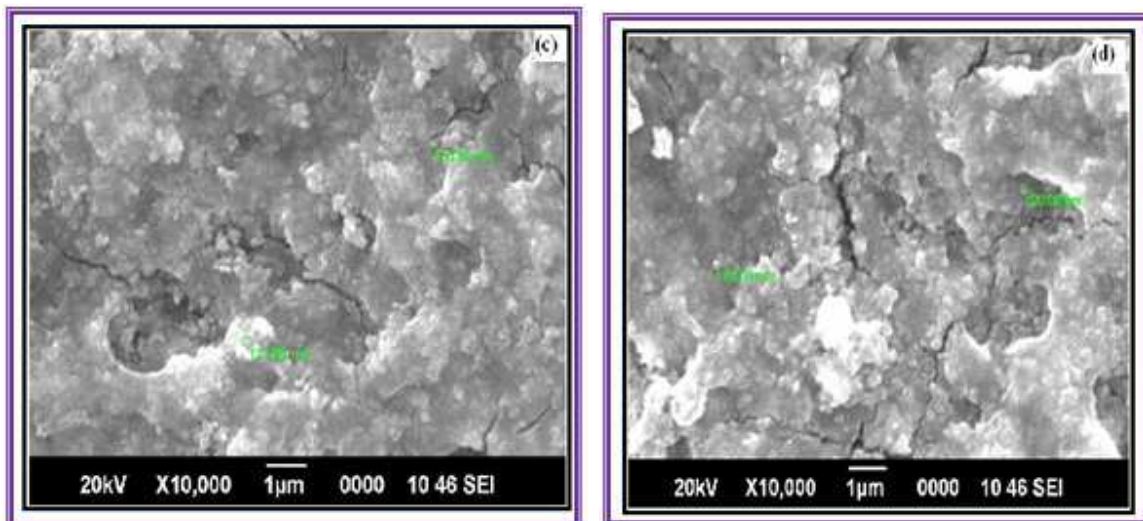
Mesra (Ranchi) and financial assistance given my parents.

SCANNING ELECTRON MICROSCOPE



(a) PPy film

(b) PPy/ZnO 1:1

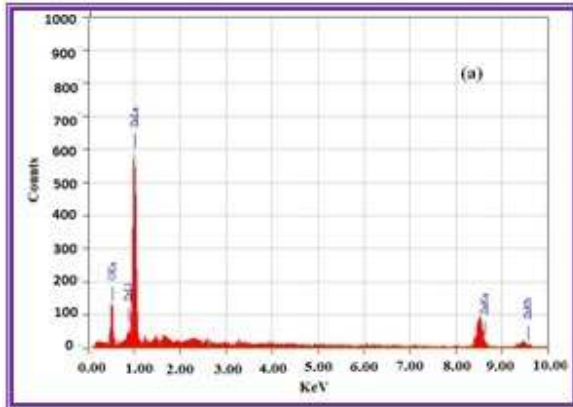


(c) PPy/ZnO 1:2

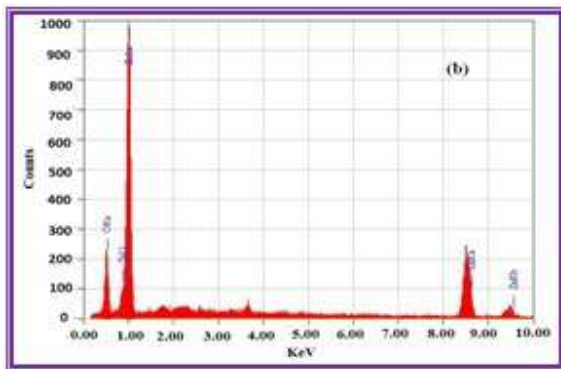
(d) PPy/ZnO 1:3

Figure 1 SEM images of spray coated (a) PPy and PPy/ZnO composite films at various ratios (b) 1:1, (c) 1:2 and (d) 1:3.

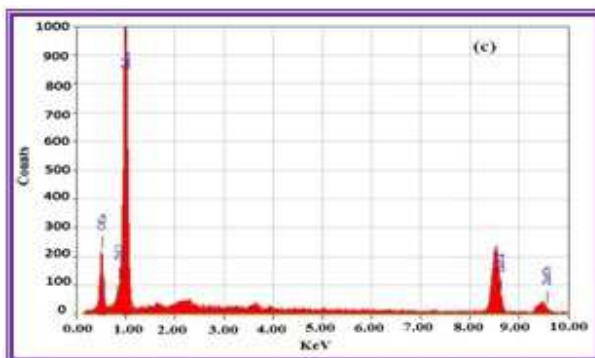
ENERGY-DISPERSIVE X-RAY SPECTRO-SCOPY ANALYSIS



PPy/ZnO (a) 1:1



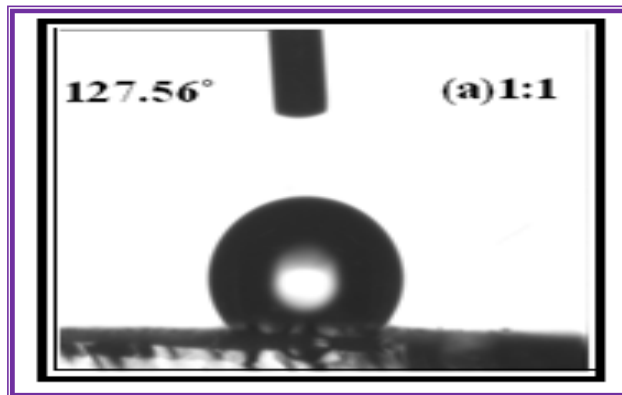
PPy/ZnO (b) 1:2



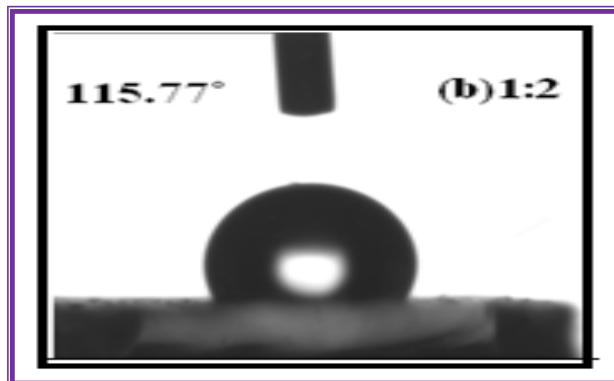
PPy/ZnO (c) 1:3

Figure 2 EDAX Spectrum of Spray coated PPy/ ZnO composite film at varies ratio

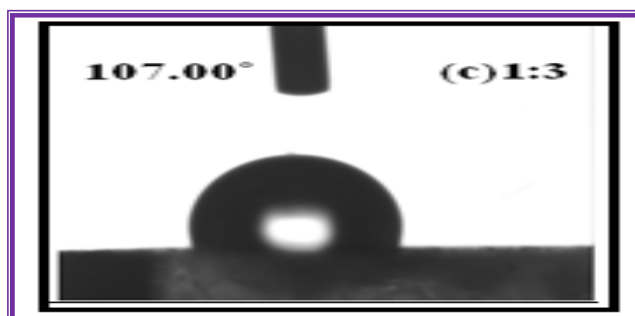
CONTACT ANGLE MEASUREMENT



PPy/ZnO (a) 1:1



PPy/ZnO (b) 1:2



PPy/ZnO (c) 1:3

Figure 3 The water contact angles of the films PPy/ZnO.

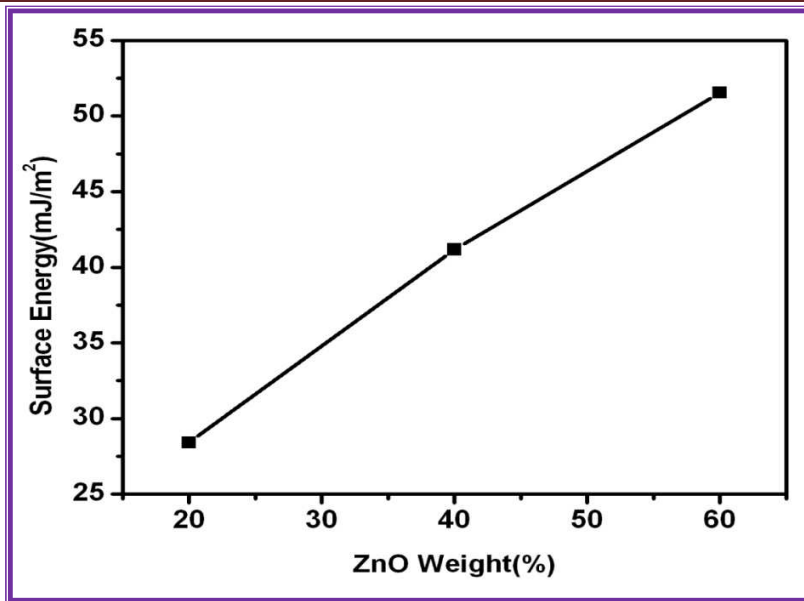


Figure 4 Surface energy with variation ZnO ratio(%)

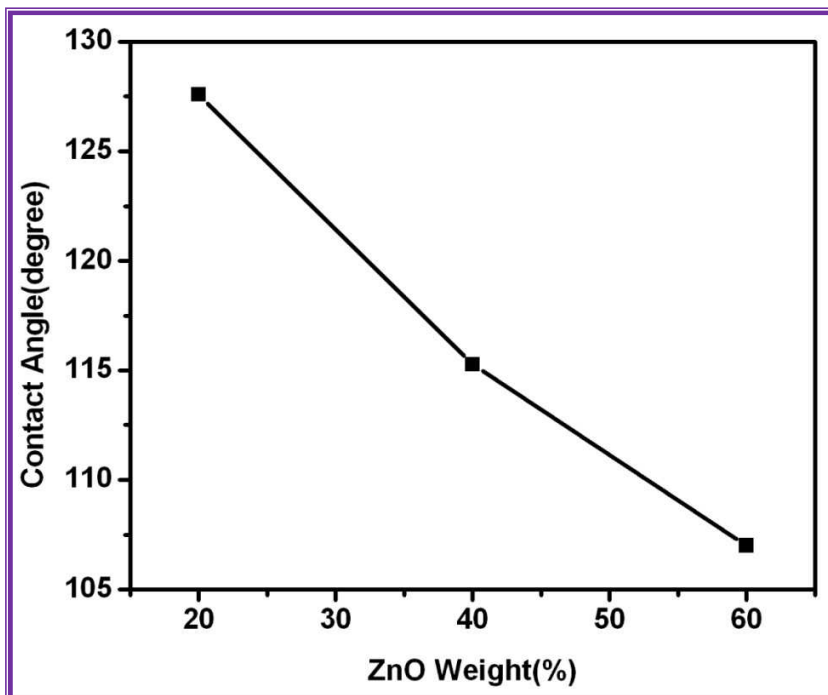
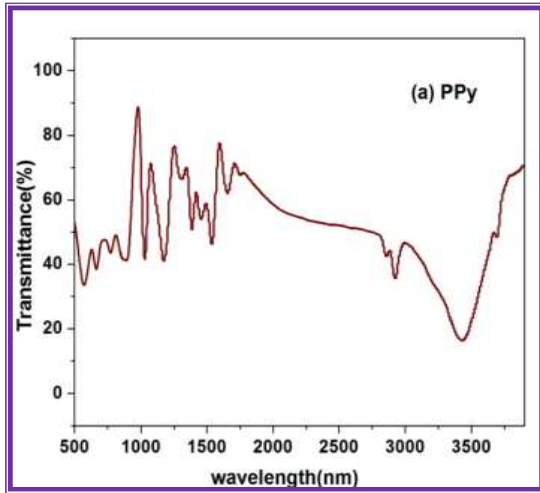
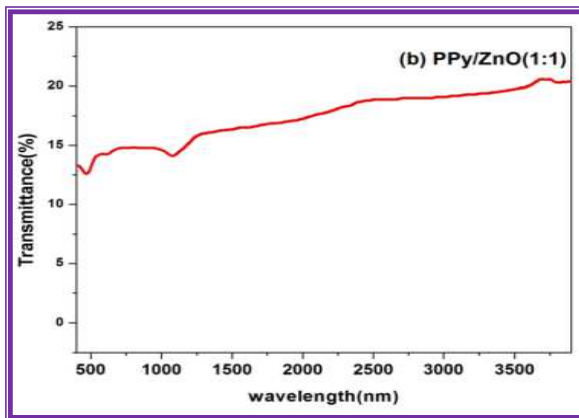


Figure 5 contact angle with variation ZnO ratio

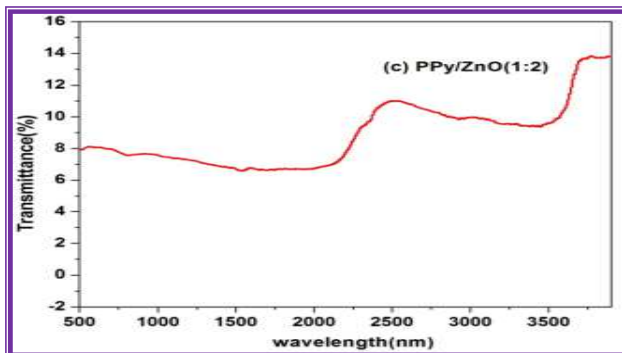
FTIR IMAGE



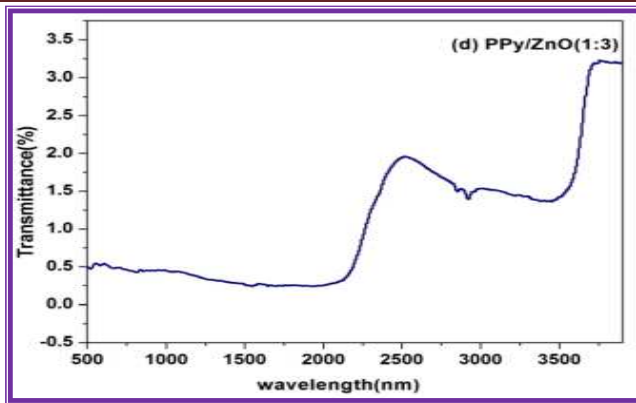
(a) PPy



(b) PPy/ZnO (1:1)



(c) PPy/ZnO (1:2)



(d) PPy/ZnO (1:3)

Figure 6 FTIR Spectrum of PPy and PPy/ZnO composite films at various ratios.

XRD PATTERNS

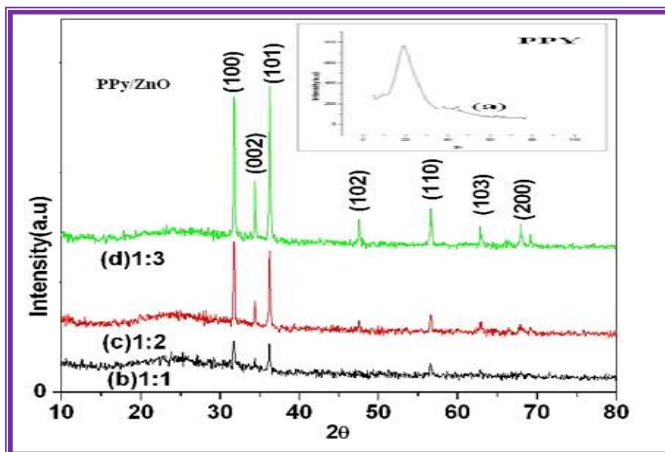


Figure 7 XRD patterns of Spray coated (a) PPy and PPy/ ZnO composite films at different ratio (b) 1:1, (c) 1:2 and (d) 1:3

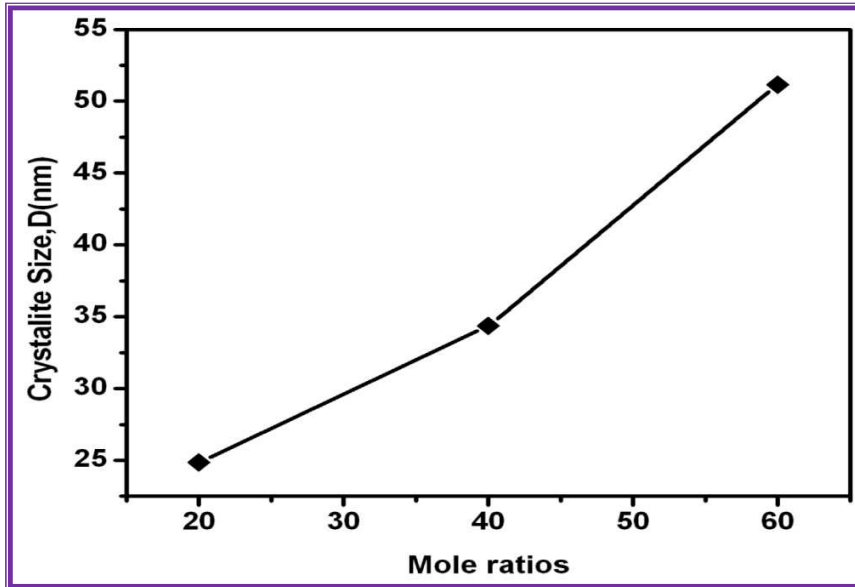


Figure 8 Various Crystallites Size with weight ratio

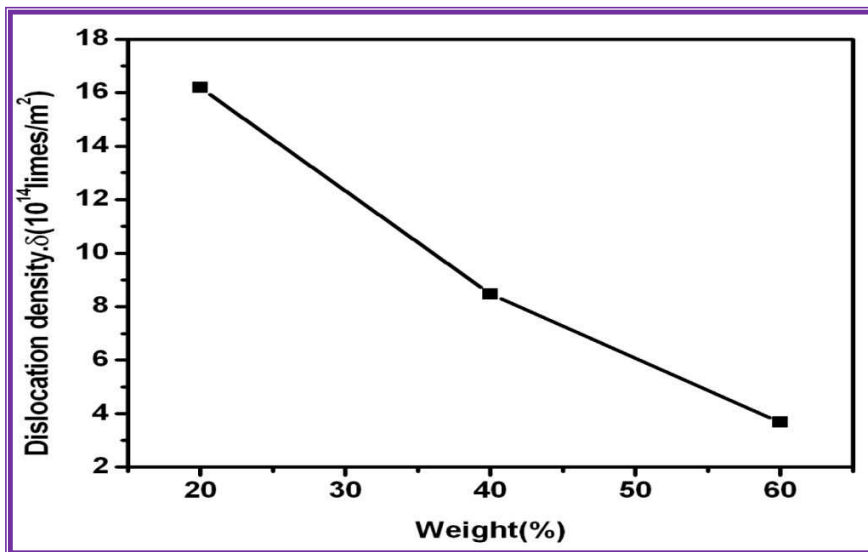


Figure 9 Dislocation densities with weight ratio

PHOTOLUMINESCENCE SPECTRUM

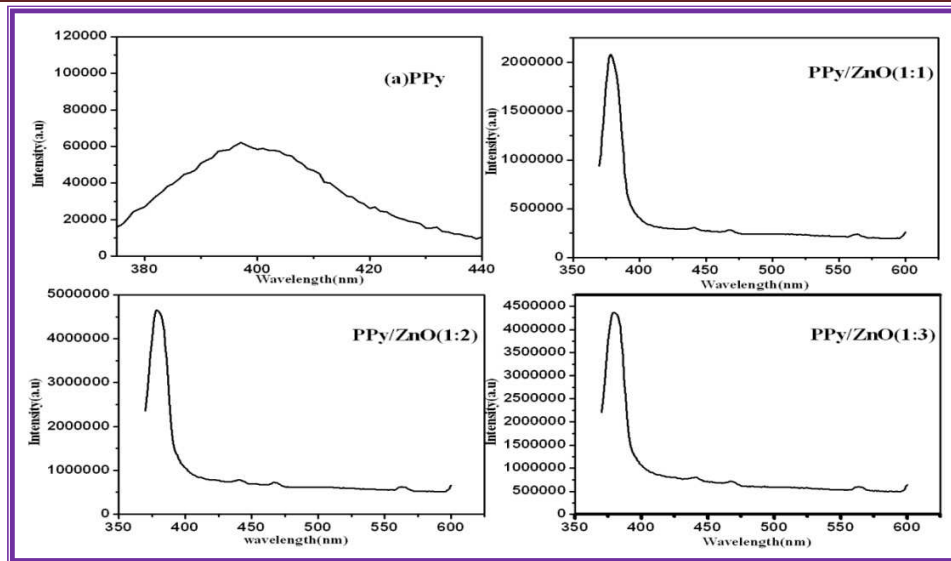


Figure 10 Photoluminescence spectrum of PPy and PPy/ZnO composite films at different ratio

3.7 UV-VIS ABSORPTION SPECTRUM

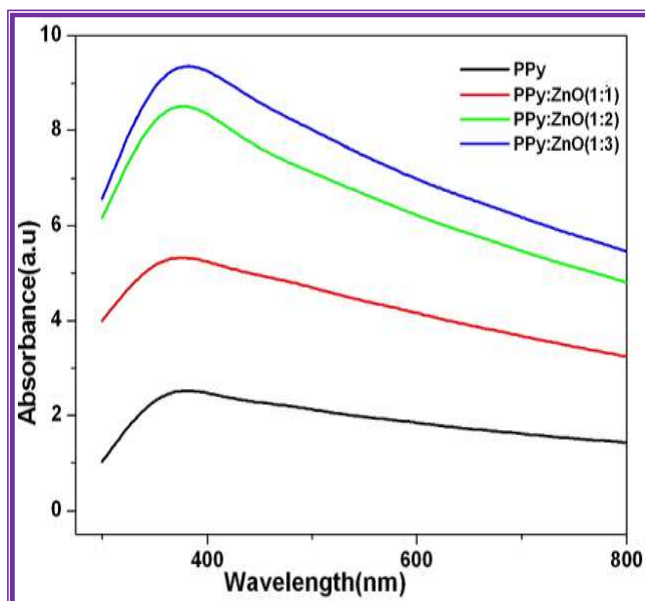


Figure 11 UV-vis absorption spectrum of PPy and PPy/ZnO composite films at different ratio

I-V characteristics and conductivity

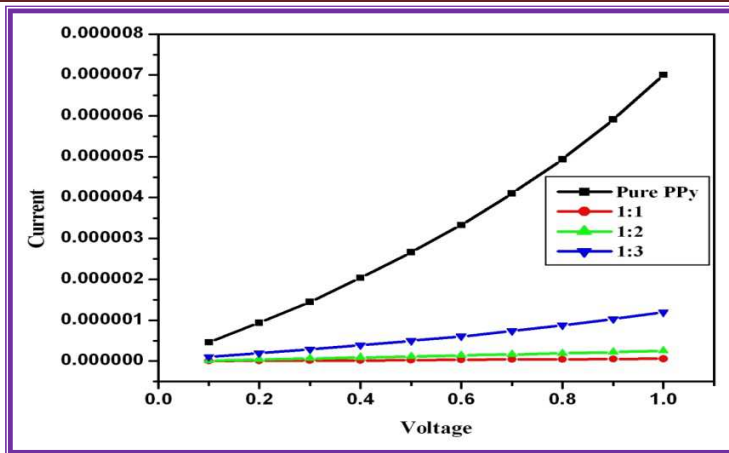


Figure 12 (a) I-V characteristic PPy and (PPy)/ZnO

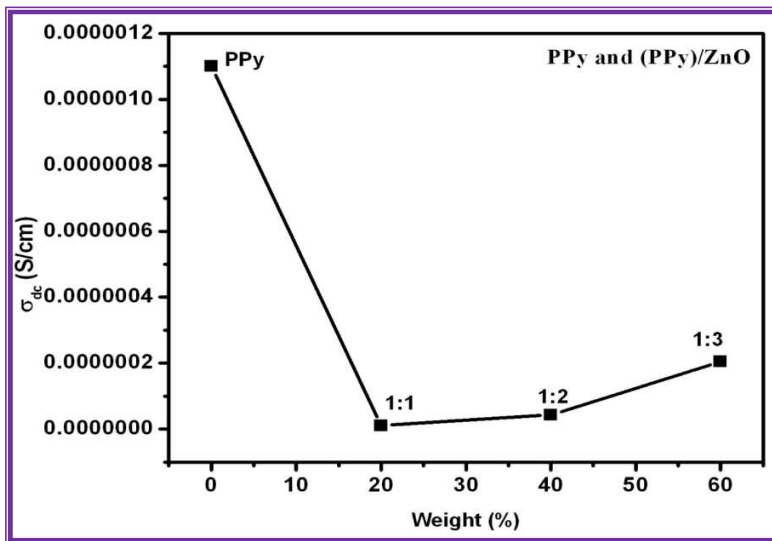


Figure 13 (b) various weight percentage versus conductivity of PPy and (PPy)/ZnO

Table.1

Presence of Elements Mass % and Atom % (PPy)/ZnO at different ratios (a) 1:1, (b) 1:2 and (c) 1:3

Weight Ratio	1:1		1:2		1:3	
Elements	O	Zn	O	Zn	O	Zn
KeV	0.525	1.012	0.525	1.012	0.525	1.010
Mass %	31.72	68.28	7.81	92.19	6.77	93.23
Atom %	65.5	34.5	25.7	74.3	22.84	77.13

Table: 2: W_{adh} values of (PPy)/ZnO at different ratio (a) 1:1, (b) 1:2 and (c) 1:3.

Samples	Theta	SFM (mN/m)	$W_{adh} = \gamma l(1+\cos\Theta)(mJm^{-2})$
1:1	127.56	7.96	28.42
1:2	115.77	13.77	41.15
1:3	107.00	18.85	51.52

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