Synthesis and characterization of polypyrrole-zinc oxide nano composites by ex- situ technique and study of their thermal &Electrical properties.

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Abstract :

In the present work ZnO nano particles are prepared at different calcinations temperature by sol gel process and polypyrrole by chemical emulsion. Inherently conducting PPY-ZnO nano composites were synthesized with varying amount of ZnO via ex-situ polymerization. These composites were characterized by FT-IR, UV- visible, NMR, XRD, TGA, and DSC. The FT-IR results show broadening and shifts of peaks towards lower wave number in all composite samples suggesting better conjugation and some chemical interaction between polypyrrole and zinc oxide nano particles. DSC and TGA data suggest that PPY- ZnO nano composites have high thermal stability due to better conformation and compactness and reduction of grain boundary volume with the loading of zinc oxide nano particles, that increase the conductivity of composites.. The X-RD analysis demonstrated the amorphous nature of polypyrrole and its composites with nano particles of ZnO as well no indication of crystalline peaks.

Keywords- PPY, TEA, FTIR, XRD, TGA & DSC

1.INTRODUCTION:

Nowadays the conducting polymers offers a great technological application potential in several areas [1-3]. Intrinsically conducting polymers have emerged as important class of electronic material because of their potential and wide applications in energy storage system [4,5], optoelectronic devices [6,7] , sensors [8] and as synthetic metals. They can substitute for metals and semiconductors in great Varity of electrical and electronic devices and retain the mechanical properties of conventional polymers [9] . The features of conducting polymers such as high thermal stability ,electrochemical properties, significant electrical conductivity, reversibility, bio-compatibility and switching capability between conducting oxidized and insulating reduced state is the basis of tremendous technological, bio-sensing and commercial applications.[10, 11] The prospects of "plastic metals" has inspired much interest in these materials for technological applications such as antistatic coating and electromagnetic interference shielding and in other areas where light weight, flexibility and high conductivity materials are required. However intrinsically conducting polymers (ICPs) face some limitations as they are brittle, insoluble and infusible material and suffers from poor processibility because of their highly rigid conjugated back bone structure [12,13,14], poor mechanical strength of such polymers restrict their applications in various field. Research in the field of such polymers aims mainly at some suitable modifications of existing polymers so that their applicability can be improved. Some of these modifications involve preparing hybrid materials in which ICPs are used as organic materials and inorganic oxides or salts of different metals combine in some special fashion with the conducting polymers to give rise to the composites. These composite have lead to outstanding thermal stability, retention of charge and dramatic increase in the conductivity of conjugated polymers with attractive mechanical and physical characteristics.

Among conjugated polymers polypyrrole has attracted great interest due to its high conductivity, good thermal and

environmental stability and ease of synthesis. However, it is an infusible, inprocessible polymer having relatively poor mechanical properties. In metal- polymer composites, conductivity depends on various factors such as oxidant to monomer ratio, particle loading concentration, filler morphology, size, compactness and interfacial interactions between filler molecule and host matrix [16]. SnO_2, ZnO, CeO_2, V_2O_5, TiO_2, fly ash composites, Fe_3O_4, ZrO_2 [17-20] among such transition metal oxides ZnO has received considerable interest in the fabrication of PPy hybrid materials because of its variety of applications in optoelectronic devices. ZnO has high refractive index and thermal stability, UV- protection, good transparency, high electron mobility and wide band gap. In this study, the synergistic assemblage of polypyrrole with zinc oxide is investigated. The aims of this study are synthesis of polypyrrole nano particles via micro-emulsion polymerization and preparation of PPy/ ZnO nano composites by ex-situ chemical oxidative polymerization. In the present work ,ex-situ polymerization of pyrrole was carried out in the presence of Zinc Oxide nano particles to synthesize Polypyrrole-Zinc oxide(PPY/ZnO) nano composites with varying amount of Zinc oxide nano particle. These composites have shown excellent thermal stability, gas sensing properties , compact morphology and high conductivity.

2.EXPERIMENTAL

The precursors used in the synthesis of ZnO by sol-gel process are Zinc acetate dehydrate having purity 99%. The surfactant is Triethanolamine (TEA) which also possesses 99 % purity. Ethanol and ammonium hydroxide takes care for the homogeneity and PH value of the solution and helps to make a stichiometric solution to get Zinc oxide nanoparticles [22]. All the chemicals were supplied Merck. Pyrrole monomer and $FeCl_3.6H_2O$.functioned as the oxidant and dopant were purchased from Aldrich chemicals. Sodium dodecylsulphate, used as surfactant and dispersant, was purchased from Merck. Methanol, used in washing process, purchased from Merck

2.1 Synthesis of nano particles of ZnO

Keeping the stoichiometry in mind a 2g.batch of zinc oxide is prepared. Firstly, 30 ml of water is mixed with 20 ml of TEA with constant stirring and drop wise addition of ethanol. The homogeneous solution obtained is kept for 2-3 hrs. Simultaneously, as per the molar calculation for 2gm batch of zinc oxide 5.39 gm of zinc acetate di-hydrate is mixed with 50 ml water and 0.5M of solution is prepared which is subjected to continuous stirring to get a homogeneous solution. Now the two solutions are mixed together in 500 ml beaker and drop wise ammonium

hydroxide is added with continuous heating and stirring for 20 minutes. About 10 ml of distil water is added during stirring. Then the solution is left for 30 minutes which results in the formation of white bulky solution. The solution is then washed 8-10 times with distil water and filtered. The residue obtained is put for drying in oven at a temperature of about 95^oC for 8 hrs. The yellowish white powder obtained is subjected to calcinations at two different temperatures 500^oC and 700^oC for 4 hrs. The growth of ZnO from zinc acetate dehydrate precursor using sol–gel process generally undergoes four stages, such as salvation, hydrolysis, polymerization and transformation into ZnO.

2.2 Synthesis of Polypyrrole

The surfactant (SDS), 0.86 g was added to 30 ml distilled water and stirred moderately with a magnetic stirrer. The solution was stirred for 30 minutes at room temperature until the surfactant is completely dissolved. When a clear aqueous solution of surfactant was obtained, the monomer pyrrole, 1 g was added drop wise to the solution while stirring. After obtaining a mixture of aqueous surfactant solution and the monomer, an aqueous solution of the oxidant $FeCl_3. 6H_2O$, 9.25 g in 5 ml distilled water was added drop wise to the mixture. Immediate formation of black PPy precipitate was clearly observed right after addition of the oxidant. The polymerization process was carried out for 3 hours at room temperature by moderate stirring. The black polypyrrole precipitate was filtered off and washed with water and methanol several times. The black polypyrrole powder was dried under vacuum at room temperature for 10 hours .

2.3. Synthesis of PPy/ZnO nano composites

The PPy-ZnO nano composite was prepared by ex-situ technique. In this technique PPy-ZnO composite was made by cryogenic grinding process, the PPy and ZnO nano particles were exposed to liquid nitrogen for five to ten minutes. This were then mixed physically (% of ZnO 5 to 20% in polypyrrole) and transferred in a high speed mixer and crushed.(maintaining temperature much below Tg)

3. CHARACTERIZATION :

In order to investigate various properties of the prepared sample, it has to goes under a number of characterization techniques. The results of which gives the information about the different optical and structural properties of sample.

3.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR analysis was carried out on a Model Shimadzu IRAffinity-1 FTIR Spectrophotometer. The FTIR spectrum of polypyrrole and polypyrrole Zinc oxide nano composite was obtained by preparing a thin KBr pellet containing the sample.

3.2 Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis of samples were done using DTG-60 H Shimadzu thermal gravimetric analyzer. The samples were investigated at a heating rate of 10°C/min under N_2 atmosphere

3.3 Scanning Electron Microscopy (SEM)

The morphological studies of the samples were performed by FEI Quanta 400 F Scanning Electron Microscopy. All investigations are performed using secondary detector, 3.0 probe size and 20.00 kV acceleration voltage. The fracture surfaces of the samples were coated by a thin layer of gold before investigation.

3.4 X-Ray Diffraction (XRD)

The X-ray diffraction pattern of the sample was recorded on Rigaku (Japan) X-ray diffractometer using CuK*a* (*l* = 1×5406 Å). The diffractogram was recorded in terms of 2Θ in the range 20–80°.

3.5 DSC and Thermo gravimetric analysis

DSC studies for the above samples were also carried out by using a V2 6D TA instrument model STD Q.600 .The calorimeter cell was flushed in an inert atmosphere of 100 ml /min. Initial scan was taken from 50–100°C to remove the thermal history effects, then cooled to 50°C under nitrogen atmosphere. Data collected at 10°/min, in the range of 25–1200°C showed typical sample size for pure PPy as 2 mg, and that of the composite, 5 mg. TGA analysis was performed at STD Q600. The calorimeter

3.6 D.C. Conductivity

DC electrical conductivity of PPy-ZnO nano composite was measured by standard four-probe technique at room temperature (25°C). Compressed pellets of materials were made under hydraulic pressure of 8 tones by using Apex hydraulic press and then were cut into rectangular shape of dimensions (1 cm×1 cm) with average probe spacing of 0.2 cm. AVO Meter (M 2007) was used to measure the voltage applied across circuit and corresponding current was measured from Professional Pro's Kit Multimeter.

Conductivity (S cm−1) was measured as reported previously. [23].

4. Results and Discussion
4.1 FT-IR analysis

The fig.1and 2 shows the FT-IR spectra of pure PPy, ZnO nano particles prepared by sol-gel method and PPy/ZnO nano particle composites loaded with various content of ZnO. From spectra it is observed that ,the FTIR spectrum of ZnO nano particle synthesized from sol-gel method, which was acquired in the range of 400 – 4000 cm^{-1} the stretching mode of ZnO appears at around 876 cm-1 (fig.2) . The spectra of bulk PPy as shown in fig.1 confirmed the formation of PPy. The band at 1557 cm^{-1} and weak band at 1468 cm^{-1} are assigned to stretching vibration of C=C and C-C in the pyrrole ring. [24-26]. PPy shows characteristic C-N and C-H stretching vibration of pyrrole at 1202 cm^{-1} and 1051 cm^{-1} respectively in the IR spectrum [27]. The absorption at 1317 cm^{-1} corresponds to C-H in-plane deformation modes [28]. The band observed at 920 cm-1 and 677 cm-1 may be attributed to the out-of-plane ring deformation and to the N-H vibration in polymer [28,29]. Fig.2 shows FT-IR spectrum of PPy/ZnO nano particles composites with strong attenuation of the peak to suggest that each ZnO particle is coated with PPy. [30] The band at 1557 cm^{-1} and 1467cm^{-1} due to stretching modes of C=C and C-C has disappeared in the pyrrole ring and a broad band appeared at 1522 and 1480 cm^{-1} in 10%, and 20% content of ZnO nano particles respectively. Due to metal oxide bond the peak was observed at higher frequencies from 1317 to 1296, 1202 to 1180 and 1051 to 1043 cm^{-1} with a broad peak at 896 cm^{-1}. These significant changes are corresponding to some chemical interaction between ZnO nano particles and PPy. This results into better conjugation or chain length.
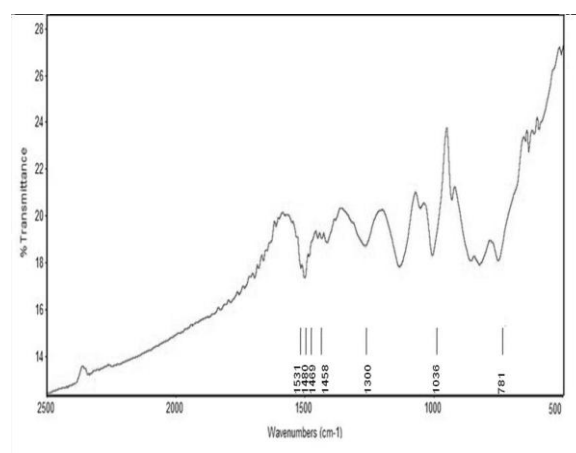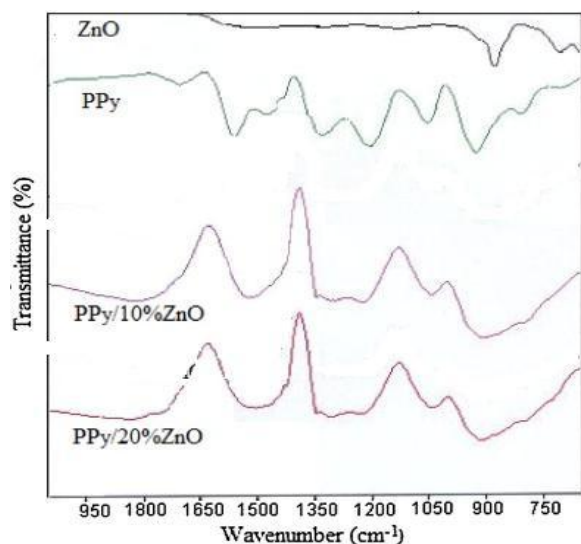

Fig. 1. FTIR of PPy nano particles

Fig. 2. FTIR of Pure PPy, ZnO and their
nano composites

4.2 Thermal gravimetric analysis

The thermograms of pure ZnO nano particles, PPy and their composites corresponding to 10, and 20 wt% of Zinc oxide particles in PPy/ZnO composites shown in Fig.3. These thermogams show fleet degradation at temperature ranging from 28 to 1100 ^{0}C. The initial mass loss between 50 to 110 ^{0}C is due mainly to release of moisture in the polymer. The weight loss at temperature higher than 210 ^{0}C is due to degradation of PPy [31] and was found to 19.80 ^{0}C at 260 ^{0}C, the decomposition initiate from this temperature resulting into weight loss of 74.08% up to 1100 ^{0}C. This is mainly due to release of C, H, and N moieties of PPy [32] .The weight left at 1100 ^{0}C is due to carbon residue. The thermal stability of PPy at high temperature is because of great extent of π- electron over the heterocyclic ring. The thermal stability increases sharply with the increase of ZnO nano particle % in PPy. Which are due to the barrier effect of Zinc oxide. The continuous increase of thermal stability with the increase of particle loading also indicates the uniform coating of PPy on zinc oxide particles surface [21]. The TGA result also indicates that the existence of forgoing coordination bond interaction between zinc oxide particles and PPy coatings improve the thermal stability of PPy backbone.
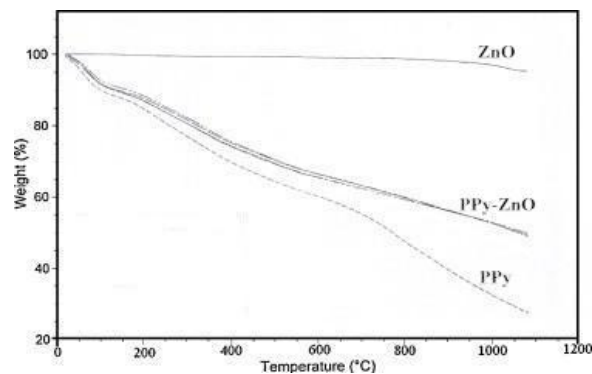

Fig. 3. TGA of PPy, ZnO and their nano composites

4.3 Differential scanning calorimeter analysis

The resulting curves obtained by differential scanning calorimeter analysis of PPy and its composites with zinc oxide nano particles obtained at calcinations temperature 500 ^{0}C (a) and 700 ^{0}C (b) in nitrogen environment are shown in Fig.4. The broad endothermic dip about 74^{0}C is corresponding to the glass transition temperature of PPy. The Addition of zinc oxide nano particles significantly affects the glass transition temperature of PPy in composites. The glass transition temperature shifts towards higher temperature in case of PPy- ZnO nano composites (a) and (b).In fig 4 (a and b) it is observed that the particle size of ZnO also affect the glass transition temperature of PPy. It is mainly due to the thermal stability and better conjugation induced by the addition of ZnO nano particles in PPy consistent with XRD, TGA and FTIR analysis.
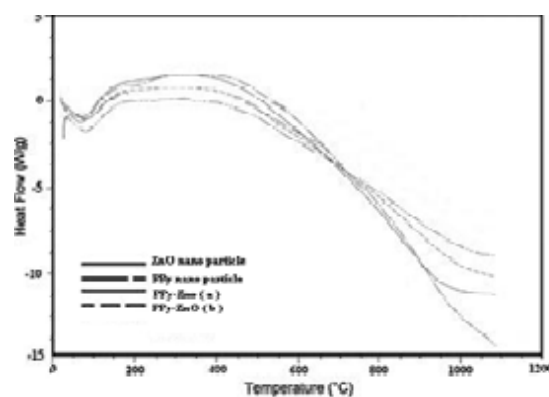

Fig. 4 DSC of PPy, ZnO and PPy-ZnO nano composites.

4.4 X-ray diffraction analysis

Figure.5 gives the X-ray diffraction pattern for sample -1and sample-2 calcined at 500^{0}C and 700^{0}C respectively. Study of standard data JCPDS 76-0704

confirmed that the synthesized materials are hexagonal ZnO phase with increasing calcinations temperature from 500^0C to 700^0C peak height increases and FWHM decreases as result diffraction peaks become stronger and sharper, thereby indicating that the crystal quality has been improved and the size of particles become bigger. The table below shows the variation of peak height and FWHM with different annealing temperature. The result has been shown for only high intensity peak.

Sample	Calcinations Temp. ^{0}C	Peak height	FWHM (0)
S-1	500	105.64	0.2681
S-2	700	164.12	0.2152

Diffraction lines of ZnO were broadened, and diffraction broadening was found dependent on Miller indices of the corresponding sets of crystal planes. For most samples the diffraction line (0 0 2) is narrower than the line (1 0 1), and (1 0 1) is narrower than the line (1 0 0). This indicated an asymmetry in the crystallite shape. The average crystallite sizes of samples 1 (500^0C) and 2 (700^0C) were determined by the Debye-Scherer formula 0.9λ/B cos (θ) and were found to be 26.74 nm and 28.93 nm respectively.
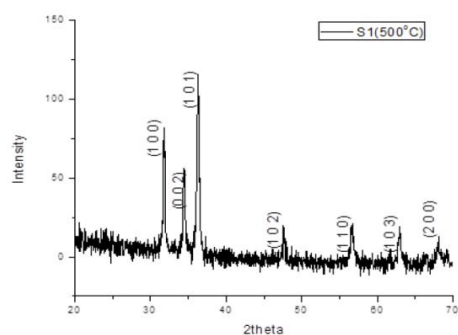

Fig. 5 X-ray diffraction patten of ZnO nano paticle (calcination temp 500^0C & 700^0C)

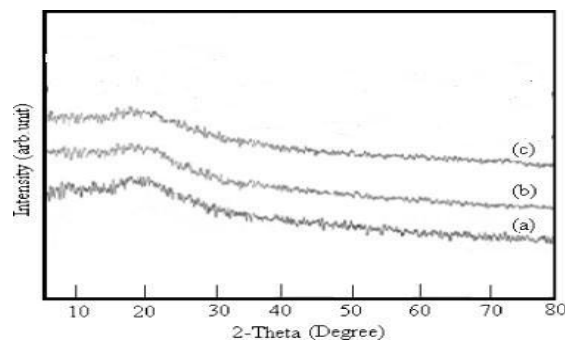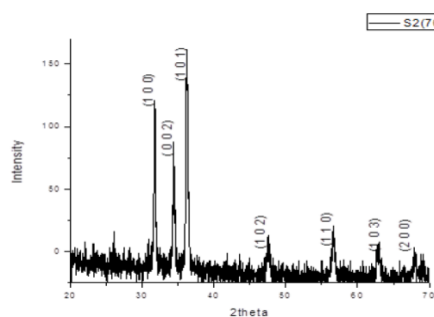Fig.6 a, b and c X-Ray Diffraction pattern of PPy-ZnO nano composite

Fig. 6 a, b, and c shows the x-ray diffraction patterns of PPy, PPy-ZnO 10 % and PPy-ZnO 20 % composite respectively. All patterns has broad peaks at lower diffraction angles (22.5 0) Which indicates their amorphous nature. This broadening of peaks can be ascribed to the scatterring of the bare PPy chains at the interplaner spacing [16].

4.6 Conductivity measurement:

The relation between conductivity and ZnO content in PPy composites is depicted in Fig. 7 The room temperature DC conductivity of PPy is 6 S cm−1 [12] while in PPy/ZnO composites it increases dramatically from 7.24 to 18.52 S cm−1 with the increase in ZnO content from 5 to 20 wt.%. The current versus voltage characteristics for each composite measured at room temperature also showed good ohmic behavior over wide range of applied current as given in Fig. 7. The appreciable linear increase in DC conductivity may be due to enhancement in the mobility of electrons owing to highly extended chain conformation to increase tunneling probability in all succeeding composites and is attributed towards the versatile semiconducting nature of ZnO [25–29] which is contrary to our and some other previous reported work in which dopant material was an insulator [12,30,31]. Low DC conductivity of pure PPy is due to the random orientation of its particles, poor link among the polymer chains through the grain boundaries and compactness. In this respect increasing semiconducting ZnO content means better conjugation, an improvement in compactness and coupling through the grain boundaries to facilitate the charge motion as inferred from FT-IR and SEM studies. In addition to the shifts of peaks in FT-IR studies, some new peaks were also observed to indicate the interfacial chemical interactions between PPy chains and ZnO particles to increase the disorderliness of composites and reduce the delocalization length with the increase of particle loading percentage of ZnO in PPy that also governs the conductive network formation to enhanced DC conductivity in all
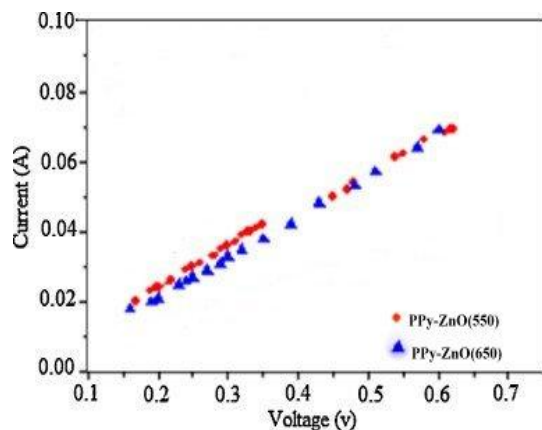
Fig.7 Current – Voltage plot of PPy-ZnO nano composites

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