

Synthesis and Studies on Nanocomposites of polypyrrole-Al-doped zinc oxide Nanoparticles

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Abstract- In the present work ZnO nanoparticles are prepared by sol gel process and doped with 6 % Aluminium. Inherently conducting PPY-ZnO (Al doped) nanocomposites were synthesized with varying amount of Al-doped ZnO via in-situ polymerization. These composites were characterized by FT-IR, 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 nanoparticles. DSC and TGA data suggest that PPY-ZnO (Al-doped) nano composites have high thermal stability due to better conformation and compactness and reduction of grain boundary volume with the loading of Al-doped zinc oxide nanoparticles, that increase the conductivity of composites. The XRD analysis demonstrated the amorphous nature of polypyrrole and its composites with Al-doped nanoparticles of ZnO as well no indication of crystalline peaks.

Index Terms- PPY, TEA, FTIR, XRD, TGA & DSC

I. INTRODUCTION

The composites of polymers and inorganic materials were first prepared by Blumstein in 1960s by polymerizing methyl methacrylate in presence of inorganic material like clay and found unusual properties in the composites. His report encouraged the research in the field of polymer nanocomposites as reported by Zhang et.al [1]. There are different ways to prepare polymer – inorganic nanocomposites including direct mixing of two or more components in a common solvent, *in-situ* polymerization of monomer in presence of inorganic nanoparticles, *ex-situ* mixing of polymer with inorganic nanoparticles and melt mixing of polymer with inorganic nanoparticles.[2, 3]..

Among the conjugated polymers polypyrrole [PPY] is one of the most studies intrinsically conducting polymer. PPY obtained high value in scientific community owing to its easy preparation, better environmental stability, tunable electrical conductivity, easy doping / dedoping behavior. 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 [4]. SnO₂, ZnO, CeO₂, V₂O₅, TiO₂, fly ash, Fe₃O₄, ZrO₂ composites [5-8] 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. The zinc oxide nanoparticles has received great attention because of its unique

catalytic, electrical, electronic, and optical properties, as well as its low cost and extensive applications in diverse areas as discussed by Y. He [9]. By doping Zinc oxide with 6 % Al its electrical and optical properties were found improved. Thus in this work zinc oxide nanoparticles were prepared by doping 6% Al. The incorporation of ZnO nanoparticles doped with Al in PPy may result in new material with useful properties.

In this work, the effect of dopants on microstructure, electrical properties and thermo-mechanical properties of composites were investigated by FTIR, XRD, SEM & TGA.

II. EXPERIMENTAL

The precursors used in the synthesis of ZnO & Al doped ZnO by sol-gel process are Zinc acetate dehydrate having purity 99% is a starting material and Aluminium acetate was used as adoping material. 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 [10]. All the chemicals were supplied Merck. Pyrrole monomer and FeCl₃.6H₂O functioned as the oxidant and dopant were purchased from Aldrich chemicals. Ethanol, used in washing process, purchased from Merck.

2.1 Synthesis of PPy

Polymerization of pyrrole monomer was carried out in chemical oxidative environment. About 0.2 mole of pyrrole was inserted drop wise in 0.6M aqueous solution of ferric chloride under constant stirring and nitrogen flow at 8 °C. for 1 h. The resulting black precipitates were filtered under vacuum and washed several times with distilled water followed by ethanol until the washing were cleared. PPy so obtained was dried by keeping in oven at 60 °C.

2.2 Synthesis of Al-doped Zinc oxide nanoparticles

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 distilled water and filtered. The residue obtained is put for drying in oven at a temperature of about 95°C for 8 hrs. The yellowish white powder obtained is subjected to calcinations at room temperature 700°C for 4 hrs. The growth of ZnO from zinc acetate dihydrate precursor using sol-gel process generally undergoes four stages, such as salivation, hydrolysis, polymerization and transformation into ZnO. The nanoparticles obtained are doped with 6% Al. for preparation of PPy- ZnO nanocomposites by addition of Aluminium acetate with similar procedure.

2.3 Synthesis of PPy- Al doped ZnO nanocomposite

The 6% Al- doped ZnO (0.05 g) was dispersed in 0.6 M aqueous solution of FeCl₃.6H₂O in distilled water and left for 30 minutes. Then 0.2 mole pyrrole solution was added drop wise in the above mixture to polymerize the pyrrole monomer and stirred for three hours to get the composite. Other samples of PPy having various weight percentage of Al- doped ZnO were prepared by adding 0.1g, 0.15g and 0.2g of Al-doped ZnO nanoparticles. The composites so obtained are dried by keeping in oven at 60 °C for a day.

III. RESULT AND DISCUSSION

3.1 FT-IR analysis

The fourier transform infrared spectra of pure and Al-doped Zinc oxide nanopowder were recorded using KBR pellets in wavelength range 4000 to 400 cm⁻¹ as shown in fig.1 (a) The broad band at 3448, 3428, 3446 cm⁻¹ can be assigned to vibration mode of chemically bonded hydroxyl groups. The band at 1627 cm⁻¹ attributed to the deformation Vibration of water molecule. The absorption band at 2345, 2348, 2337 cm⁻¹ is due to the stretching vibration of CO₂. Below 700 cm⁻¹, a single strong peak around 536 cm⁻¹ was observed in fig 2(a). Fig. 2(b) exhibits two vibration bands between 500 to 900 cm⁻¹.the spinals display stretching bands in the 500–900cm⁻¹ range, associated with the vibrations of metal– oxygen, aluminum–oxygen and metal–oxygen– aluminum [11-13]. So the doped samples show the two peaks around 500 to 900 cm⁻¹ for all the nanomaterials that is assigned to the formation of metal aluminates [14, 15]

The fig. 2 shows the FT-IR spectra of pure PPy, PPy- ZnO nanocomposite and PPy Al- doped ZnO nanoparticle composites loaded with 6 % content of Al. The spectra of bulk PPy as shown in fig.2 (a) 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. [16-18]. 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 [19]. The absorption at 1317 cm⁻¹ corresponds to C-H in- plane deformation modes [20]. 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 [20,21]. Fig.2 (b) shows FT-IR spectrum of PPy Al-doped ZnO nanoparticles composites with strong attenuation of the peak to suggest that each nano particle is coated with PPy.[22] 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 nanoparticles 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 Al-doped ZnO nanoparticles and PPy. This results into better conjugation or chain length.

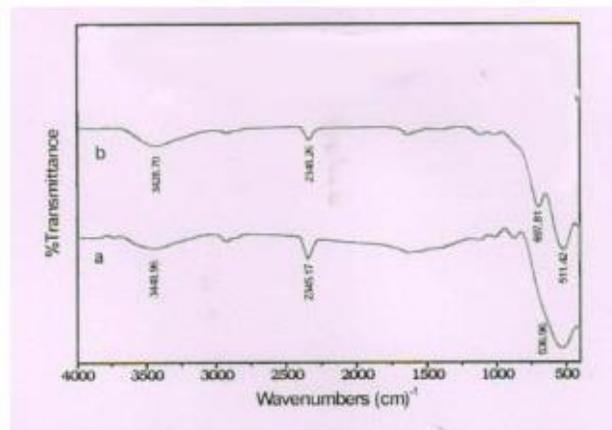


Fig.1. (a) FT-IR spectra of pure ZnO & (b) Al –doped ZnO

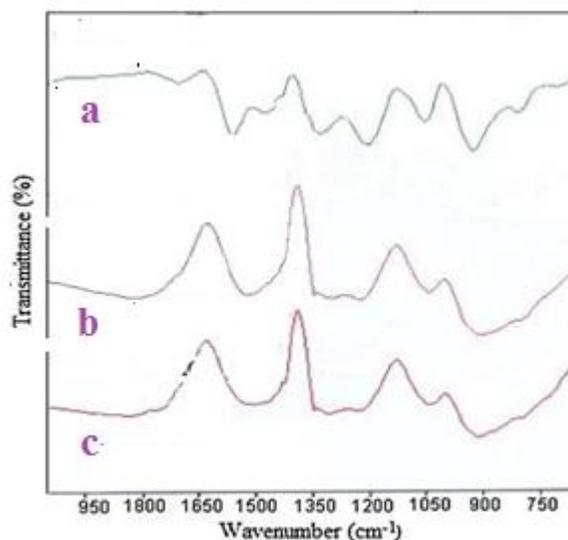


Fig.2. (a) FT-IR spectra of PPy (b) PPy-ZnO nanocomposite and (c) Al-doped PPy- ZnO nanocomposite

3.2 XRD analysis

Fig. 3(a-b) shows the typical X-ray diffraction patterns for the ZnO and Al doped ZnO powder samples annealed at 900 °C temperature. The observed diffraction peaks in the recorded XRD patterns correspond to those of the standard patterns of ZnO polycrystalline and correspond to hexagonal wurtzite structure. . The peak intensities of prepared powder at 36.336° (2 theta) and that of standard data were the same. No diffraction peaks of Al or other impurities phases are detected in our samples, indicating that Al ions would uniformly substitute into the Zn sites or interstitial sites in ZnO lattice. From fig 3(b), after the doping of Al , ZnO nano particles appeared in the polycrystalline structure.

Comparing the crystallization of ZnO with AZO, a large amount of Al dopants resulted in lattice disorder, which is associated with the stress generated. Besides the stress problem, the grains grew more easily when Al dopants were incorporated with ZnO.

The Fig.4 (a-c) shows the XRD curves of PPy and its composites. All patterns has broad peaks at lower diffraction angles $2\theta = 22.5^\circ$, which indicates their amorphous nature. This broadening of peaks can be ascribed to the scattering of the PPy chains at the inter planner spacing [4]

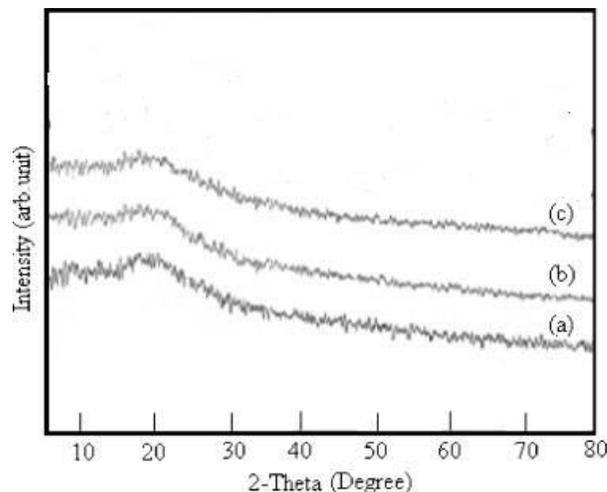


Fig.4. XRD pattern of (a) PPy (b) PPy-ZnO (c) PPy- ZnO- Al 6 %

3.3 SEM analysis

The surface morphology of material in the form of granular structure with round morphology and little agglomeration were investigated with a scanning electron microscope. Fig.5 (a-b) and Fig.6 (a-b) shows SEM of ZnO, Al doped ZnO. And PPy Al – doped ZnO nanocomposites respectively. It shows uniform distribution of pores with clusters of crystallites over the entire material indicates that ZnO nanoparticles interacts with PPy. The Al-doping did not significantly change the appearance of the particles. This PPy- ZnO (Al- doped) nanocompsite shows homogeneous, large area dense granular morphology suitable for gas sensing application and energy storage devices.

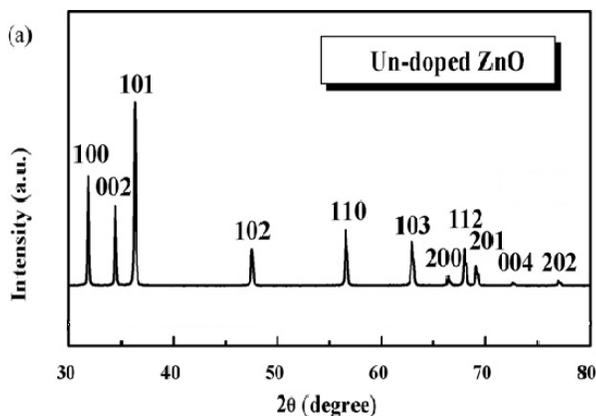


Fig. 3. (a) XRD patterns of un-doped ZnO powders sintered

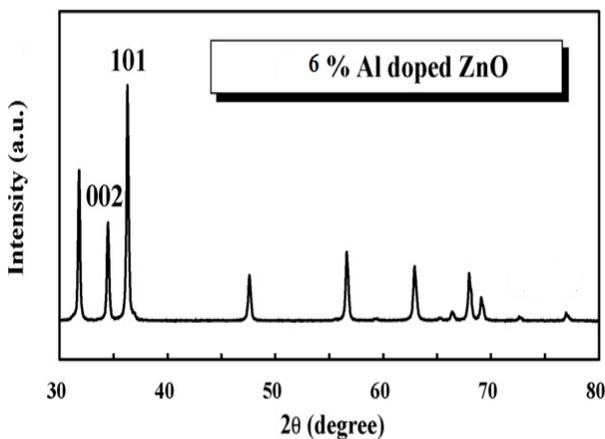


Fig 3. (b) XRD patterns of 6 at.% AZO powders sintered

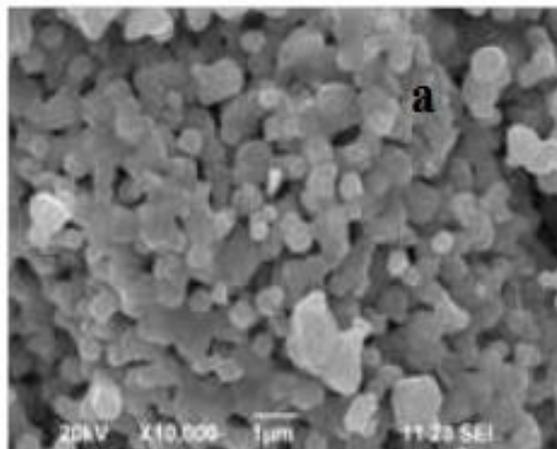


Fig.5. (a) & (b) SEM images of ZnO & Al-doped ZnO nanoparticles

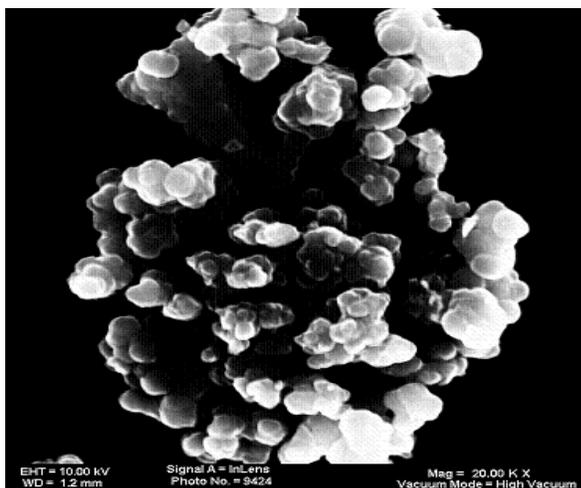


Fig. 6 (a) SEM image of PPy- Al- doped ZnO nanocomposite

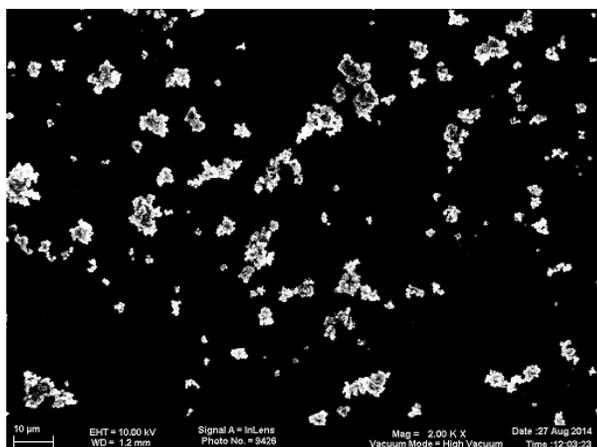


Fig. 6 (b) SEM image of PPy- Al- doped ZnO nanocomposite

3.4 TGA and DSC analysis

To investigate the crystalline conditions, differential scanning calorimetry (DSC) and TGA of ZnO nanoparticles were carried out. The specimens were heated from room temperature to 900 °C with an increment of 10 °C/min in air. Fig. 6 (a) shows a combined plot of DSC and TGA. Notably, the TGA data plots the weight loss of the nanoparticles which is found to take place till 520 °C. For the DSC curve (room temperature), an exothermic peak and two endothermic peaks are found at 270, 147 and 317 °C, respectively. These peaks are attributed to the evaporation of water and organics. A large exothermic peak is exhibited at 490 °C, due to the crystallization of ZnO. Therefore, the crystallization of ZnO nanoparticles occurred at temperatures over 520 °C. For this reason, this study selected 700 and 800 °C to estimate the crystallization of AZO nanoparticles. The TGA analysis of PPy Al-doped ZnO nanocomposite were studied. The runs were performed from room temperature to 1000 with heating rate 10 per minutes. The weight loss of 10.65 % is observed at temperature 110 due to expulsion of moisture. The thermal stability of composite at higher temperature is because of loading of Al doped ZnO in PPy. as shown in fig. 6 (b) .

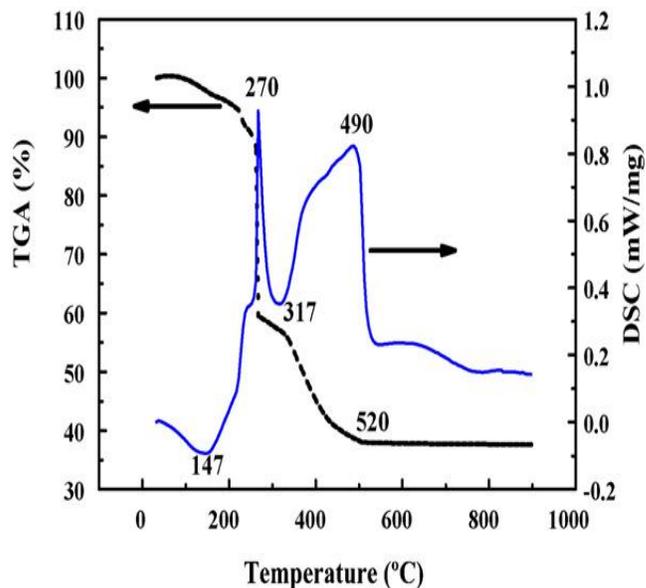


Fig. 6 (a) TGA & DSC of Al-doped ZnO nanoparticles.

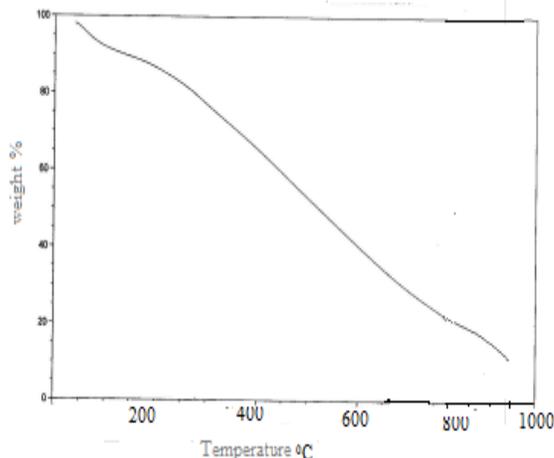


Fig 6 (b) TGA of PPy- Al-doped ZnO Nanocomposite.

IV. CONCLUSION

The sintered precursors yielded nanocrystalline ZnO and Al doped ZnO were synthesized successfully by a sol-gel process. The nanocomposite of conducting polymer PPy with Al-doped ZnO were also synthesized by chemical oxidative polymerization. The composite obtained was analyzed for structure, thermal stability, surface morphology and optical and electrical properties using various analytical techniques. The structural, morphological and optical properties were examined. The prepared samples have hexagonal wurtzite structure when characterized by XRD and the evaluated average particle sizes are 124.72 nm, 48.51 nm and 80.69 nm respectively. SEM images of the samples show the formation of granular structure and agglomeration. The Energy dispersive X-ray analysis shows the presence of Zn, Al, and O. FT-IR revealed the presence of

metal–oxygen, aluminum–oxygen and metal–oxygen–aluminum bands indicating the formation of ZnO and Al doped ZnO phase. The shift from 1558cm^{-1} to 1524cm^{-1} of PPy in the composites indicating some interaction between C-C in the pyrrole ring and metal oxide nanoparticles, it was also confirmed by XRD analysis. The thermal stability of composite increased by doping of Al- doped ZnO as compared to the PPy- ZnO composite.

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