Preparation, Characterization and Hall Effect Study of Conducting Polyaniline and Polyaniline-ZnO Nano Composite

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Abstract—In our present work an attempt has been made to investigate as to how the variation in the filler(ZnO NPs) concentration affects the electrical and thermal properties of the polymer nanocomposite. The morphology of PANI and PANI-ZnO nanocomposite was analysed using SEM and TEM.. SEM analysis of ZnO showed a size distribution of 50-70 nm. Thermogravimetric analysis shows the change in decomposition temperature of the polymer. Hall effect study shows the decrease in carrier concentration in composite as compared to pure PANI. The hall voltages have been found to be negative indicating that the dopant polyaniline behave like a n-type semiconductor. The Hall coefficient(RH) and carrier concentration(n) have been determined from Hall measurements. Main objective of the present work is Hall effect studies on polymer nanocomposites and their heterostructure.

Index Terms—PANI, nanocomposite, TGA, Hall voltage.

I. Introduction

The intriguing optic and electronic properties of $\square$-conjugated backbone conducting polymers have captivated much interest in the scientific community. Organic conducting polymers are of particular interest in that they offer many electronic benefits including control of Fermi levels by doping, ease of manufacture, inexpensive production and material flexibility. PANI is one of the most promising conducting polymers due to its excellent chemical stability combined with high level of conductivity. Since the discovery of conductance in conjugated polymers, polymeric materials have been extensively explored as alternative to metals or inorganic semiconductors in fabrication of electronics devices [1-6].

Nanostructured materials have received much attention because of their novel properties, which differ from those of bulk materials [7], [8]. By varying the size, shape and morphology of the material, the optical and electronic properties of functional devices made up of nanostructured material can be changed [9]. Zinc oxide, a versatile semiconductor material, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions [10]. ZnO is a direct wide bandgap semiconductor (Eg = 3.4eV and con = 5x10-5 S/cm) with large exciton binding energy (60meV) suggesting

that it is a promising candidate for room temperature luminescent and lasing device. ZnO is one of the few oxides that show quantum confinement effects in an experimentally accessible size range [11], [12]. ZnO particles with a variety of particle shape from spheres and ellipsoids to hexagons and star like particles have a narrow particle size distribution typically from 20nm to 100nm and specific surface area (SSA) in the range of 5-60 m2/g. Moreover the wide range of morphological diversity in the nano regime has made this material a promising candidate in the field of nanotechnology and opened up new possibilities for the fabrication of high performance devices based on these nanostructures [13-15].

There is a great attention in processing polymer nanocomposites, both from the point of view of fundamental properties determination and the development of new applications. Synthesis of the nanocomposites of Polymer with inorganic nanoparticles is potential route to improve the performance of polymer, aiming to attain the materials with synergetic or complementary behaviour between polymer and the inorganic NPs. Some polymer-nanoparticle composites have already been reported in the literatures [16-18]. Our work focuses on the synthesis of ZnO nanoparticles, synthesis of ZnO NP incorporated in PANI matrix and characterisation of these synthesized materials. Also, our aim is to study the hall effect of polymer composite semiconductor.

II. Sample Preparation and Experimental Technique:

Aniline (E. Merck, India) was purified by distillation. The polymerisation of aniline was performed in an aqueous solution where aniline was rapidly polymerised in 1 M HCl acid by the quick addition of oxidant (ammonium peroxidisulphate (NH4)2S2O8). The ratio of aniline to oxidant is 4: 1 and the aniline concentration is 0.5M.

We prepared the ZnO nanoparticles by sonochemical method. 0.5 gm starch was dissolved in 10 ml of double distilled water. 0.1 M aqueous solution of zinc acetate was added in starch solution, ammonia (0.2 M) then added drop wise and the reaction was allowed to proceed for 2 hours. The solution containing beaker was then kept in sonication bath (40 KHz, 350 W) at room temperature for half an hour. Then the solution was allowed to settle for over night and supernatant solution was then discarded carefully. The white precipitate formed was collected by centrifugation and then thoroughly washed many times using distilled water followed by alcohol to remove traces of starch and other impurities and dried at 80oC for overnight. During drying

complete conversion of Zn (OH)2 into ZnO takes place.

To prepare PANI-ZnO nanocomposite, during polymerisation, ZnO nanoparticles (50% by wt of aniline) were dispersed in the solution. The reaction mixture was kept under constant stirring for 4 hours at room temperature for synthesising the composite. Precipitated polymer was filtered and washed with distilled water. Finally polymer was dried in an oven at 700C for 12 hours. PANI and PANI-ZnO Composite was crushed finely and pelletts of the composite were prepared using a steel die in a hydraulic press under a pressure of 5 tons/cm2.

Thermal degradation studies were performed using Shimadzu DT-30 at a linear heating rate of 10 0C/min from room temperature upto 10000C.

Hall voltages of pure PANI and the composites were measured at room temperature. The Hall coefficient and carrier concentration were calculated from the measurements.

III. RESULTS AND DISCUSSION:

1) Fig. 1 shows diffraction pattern of ZnO nanoparticles synthesized in presence of ultrasonic irradiation with starch. The sharp and well defined peaks indicate the good crystallinity of synthesised material. And all of the diffraction peaks can be indexed with hexagonal phase. (JCPDS No. 80-0075). No characteristic peaks of impurities such as Zn, Starch are observed. This confirms that the obtained product contains pure ZnO nanoparticles.
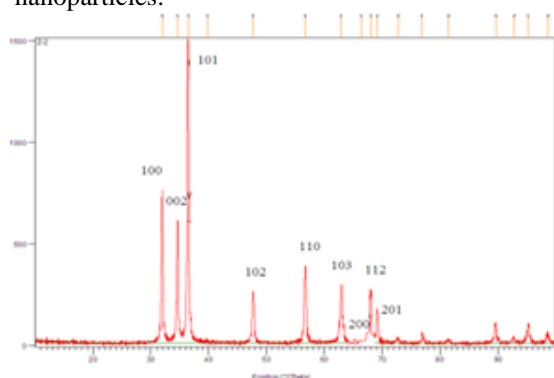

Fig. 1. X-ray diffraction spectra of ZnO nanoparticle synthesized by starch assisted sonochemical method.

The X ray diffraction pattern of the composite revealed that the degree of crystallinity of PANI-ZnO composite was higher than that of the PANI but lower than ZnO showing that the amorphous nature of PANI may inhibit crystallisation of ZnO.
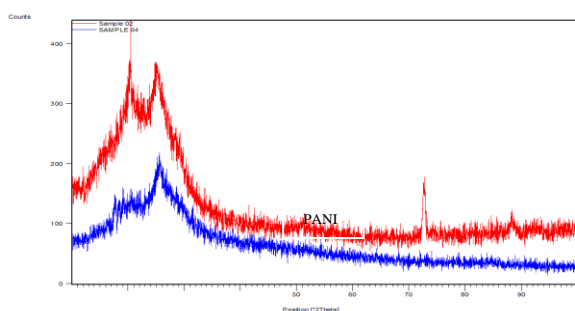

Fig. 2. X-ray diffraction spectra of PANI and PANI-ZnO nanocomposite.

2) The morphology of PANI and PANI-ZnO nanocomposite was analysed using SEM SEM analysis of ZnO showed a particle size distribution of about 50-70 nm.

Surface tailoring of the ZnO NPs is performed using starch, to improve the dispersion in aqueous medium and stability. Starch can cap around the ZnO, providing steric hindrance between ZnO NPs due to their bulkiness. In addition, the free hydroxyl group present on starch interact with the aqueous medium and enhance the solubility. Cavitation which occurs during ultrasonication plays key role in sonochemical synthesis of materials. During ultrasonic caviation very high temperature (5000K) and pressure of about (1800 atm) are reached followed by release of large amount of energy due to collapse of micro-bubbles. These conditions favour simultaneous gelatinisation of starch and formation of ZnO nanoparticles with gelatinized starch granules directing the growth of nanoparticles by binding on its surface. The advantage of using starch is that it avoids agglomeration of nanostructures in addition to that the prepared nanostructures are pure and water soluble and there are lots of hydroxyl groups attached to nanostructures surface for further functionalization.
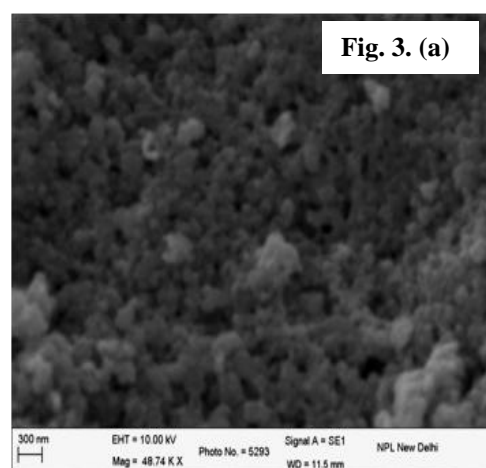

Fig. 3. (a) SEM image of ZnO nanoparticles synthesized by sonochemical method using starch.
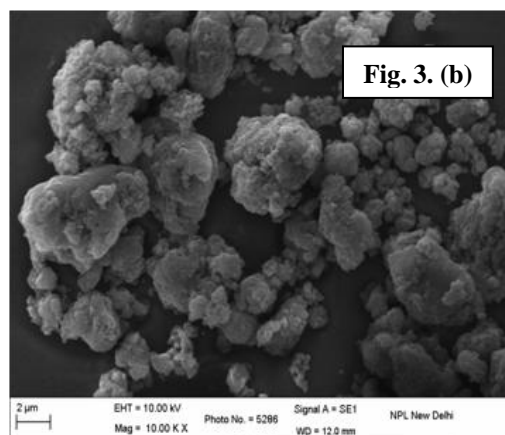

Fig. 3. (b) SEM image of PANI-ZnO nanocomposite.

From the SEM image of composite, it is observed that ZnO particles are surrounded by polyaniline matrix and hence it appears as agglomerated macromolecules.

3) TGA of the composite was performed to determine the degradation temperature, absorbed moisture content of

materials, decomposition points solvent residues etc. Thermal degradation studies were performed at linear heating rate of 10 0C/min from room temperature upto 10100C. The thermogravimetric analysis (TGA) curve of the sample pure PANI showes weight loss(17%) due to absorbed moisture and solvent upon initial heating up to 234 0C, followed by a slow weight loss(5.4%) upto 6480C which could be attributed to the elimination of dopant. The final degradation of the polymer occurs from around 750 to 1002 0C. TGA curve of the composite shows gradual weight loss (5.3%) due to absorbed moisture and solvent upon initial heating up to around 173 0C, followed by a slow weight loss (6.16%) upto 462 0C due to elimination of dopant. The final degradation of the polymer occurs from around 700 to 1000 0C. Thus it can be concluded that HCl doped pure polyaniline can sustain thermally more as compared to the composite sample.
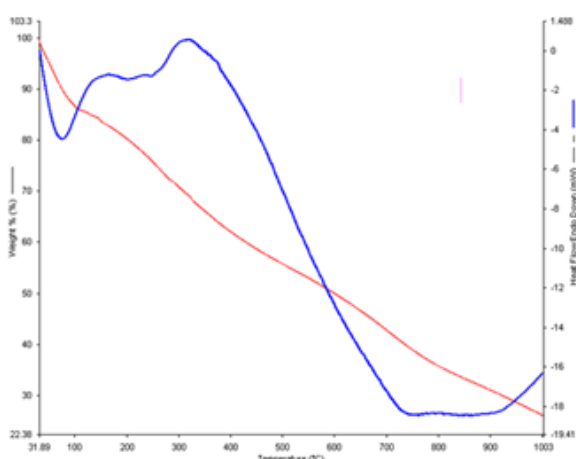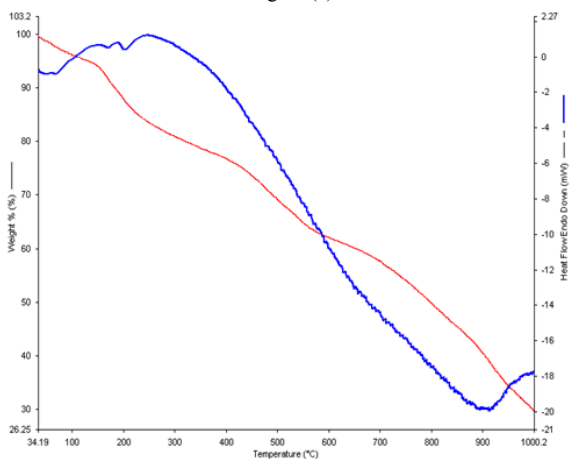

Fig. 4. (a)

Fig. 4. (b)

Fig. 4. (a) TGA of PANI. (b) TGA of Zno-PANI nanocomposite.

4) For hall effect study, specially designed hall probe was used with hall effect set up. Hall voltage was measured for various values of magnetic field by changing current through the samples at room temperature. The graph plotted between Hall voltage and sample current is shown in Fig. 5. From the graph it is observed that in composite sample, hall voltage is less than that in PANI sample. And it is supported by the dc conductivity results of composite and PANI. From the Hall effect studies, it is observed that the conductivity and carrier

mobility are linearly related while the carrier mobility are inversed of the carrier density. The hall voltages have been found to be negative indicating that the dopant polyaniline behave like a n-type semiconductor. The Hall coefficient (RH) and carrier concentration (n) have been determined from Hall voltage measurements at constant magnetic field 0.36T and the values are listed in Table I. It is observed that RH is increased and hence n is decreased in composite as compared to pure PANI, supporting the decrease in dc conductivity of the composite.

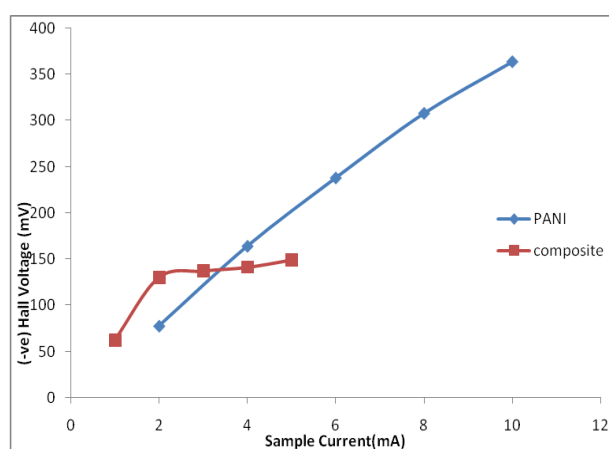| Parameters	PANI	Composite
Hall Coefficient(R_H) m^3/C	1.97×10^{-3}	4.5×10^{-3}
Carrier concentration(n)/m^3	3.17×10^{20}	1.3×10^{20}

Fig. 5. Variation of hall voltage with sample current .

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