Synthesis Characterization and electrical studies on Polyaniline/WO_3 composites

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Abstract:
Conducting polyaniline with tungsten oxide have been synthesized by in- situ polymerization method using ammonium persulphate as an oxidizing agent. The weight percentage of WO_3 is varied from 10 % to 50 wt%. The structure and properties of PANI/WO_3 composites was characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The XRD image shows a particular structure of WO_3 which is well dispersed in the polyaniline matrix. The DC conductivity of Pure PANI and its composites have been measured in the temperature range from 30°C to 160°C. The DC & AC electrical study of PANI /WO_3 composite clearly indicates that the WO_3 particles increase the electrical conductivity of polyaniline composites as compared to pure polyaniline.

Key words: PANI, electrical conductivity, SEM, XRD.

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1. INTRODUCTION

Conducting polymers are conjugated chain of organic compounds that display high electrical conductivity similar to metals because of the presence of large carrier concentrations of extended π-electrons, known as polarons, which allow charge mobility along the backbone of the polymer chain. Their electrical conductivities are comparable with metals but polymers have many advantages, such as being light-weight, resistance to corrosion, flexibility, and low cost. Conducting polymers are finding numerous applications in television sets, cellular telephones, displays, light emitting diodes, solar cells, batteries, actuators, sensors, electromagnetic shielding, and microelectronic devices [1–3]. Hence PANI is useful in wide area of application such as solar energy conversion, rechargeable batteries, electro chromic displays, electrochemical sensors, capacitors and active corrosion protector [4].Due to the ease of synthesis, processing environmental stability and low synthetic cost, polyaniline is probably the most important industrial conducting polymer today [4-5].The use of conducting polymers for photovoltaic applications has been reported [6]. PANI is combined with inorganic nanoparticles such as silver, gold, Copper, CeO_2 and TiO_2 to form PANI/metal nanoparticle nanocomposites in order to improve physical, mechanical, and electrical properties. The obtained nanocomposites have characteristic advantages between their single component counterparts [7] and can have potential applications in new device. In particular, transition metal nanoparticles dispersed within a polymer matrix offer attractive routes for combining properties stemming from metal nanoparticles and from that of polymers [8]. The incorporation of metal nanoparticles could effectively improve the optical and dielectric properties of the PANI composites. The nanoparticles could act as conductive junctions between the PANI chains that resulted in an increase of the electrical conductivity of the composites [9]. The composites of PANI with magnetic metal nanoparticles are also promising candidates, based on the fact that the small sized particles enhances the physical properties while the conducting polymer matrix present electrical host-guest interaction to occur in a new magneto-electric phenomenon at the same time, allowing coupling between magnetic and electric properties for future

devices[10]. In the present paper, authors report the synthesis, characterizations, and effects of WO_3 particles in Polyaniline/ composites on Electrical properties,

2 EXPERIMENTAL PROCEDURES:

2.1 CHEMICAL SYNTHESIS OF POLYANILINE.

The synthesis was based on mixing aqueous solution of aniline hydrochloride and ammonium persulphate at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volume of aniline and hydrochloride acid) was dissolved in distilled water in a volumetric flask to 100 ml of solution. Ammoniumpersulphate (0.25M) was dissolved in water and also to 100ml of solution. Both solutions were kept for 1 hour at room temperature, then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 0.2 M HCL, and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then in vacuum at 60^{o}C for 24 hours. Polyaniline prepared under these reaction and processing conditions are further referred to as "standard" samples.

2.2 PREPARATION OF POLYANILINE/ WO3 COMPOSITES

Synthesis of the PANI-WO_3 composites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1 M HCl and stirred for 15 min to form aniline hydrochloride. WO_3 particles were added in the mass fraction to the above solution with vigorous stirring in order to keep the WO_3 homogeneously suspended in the solution. To this solution , 0.1 M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 5˚C for 4 h to completely polymerize. The precipitate was filtered, washed with deionized water, Acetone, and finally dried in an oven for 24 h to achieve a constant mass. In these way, PANI– WO_3 composites containing various weight percentage of WO_3 (10 %, 20 %, 30 %, 40 %, and 50 %) in PANI were synthesized.

3 PREPARATION OF PELLETS

The powders of Polyaniline, Polyaniline/WO_3 composites, so obtained from synthesis techniques discussed in early sections were crushed and finely ground in agate mortar in the presence of acetone medium. The powder is then pressed to form pellets of 10 mm diameter and thickness varying up to 2 mm by applying pressure of 90 MPa in a hydraulic pressure. For temperature dependent conductivity studies, a silver paste was coated on both sides of surface of the pellet for providing electrical contacts[].

4 RESULTS AND DISCUSSION

4.1 SEM (Scanning Electronic Micrograph)

Figure 4.1 (a) shows that Scanning Electronic Micrograph (SEM) image of pure polyaniline, which has highly agglomerated granular in shape and has amorphous nature. The grains are well interconnected with each other which indicate that they have enough binding energy to combine with neighbor grains or molecules.

Figure 4.1 (b) shows the SEM image of pure WO_3 particle. The grains are irregular in structure, some of them are elongate and some are spherical in shape. Figure 4.1(c) shows the SEM photographs of WO_3 composites. It can be seen from the figures that the connectivity of WO_3 grains is dispersed by the distribution of polymer grains, which leads to the variation of magnetic properties of the composites[4-6].

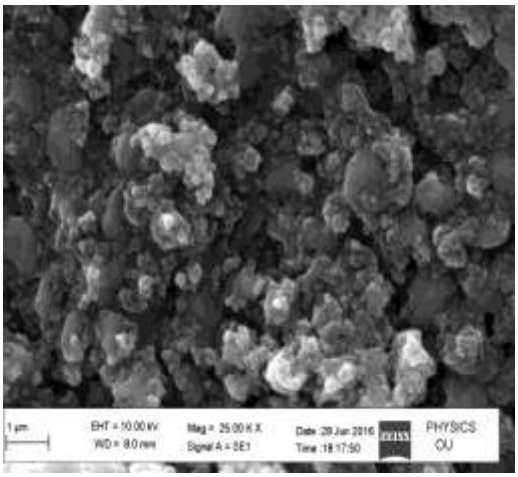


Fig 4.1a) PURE PANI

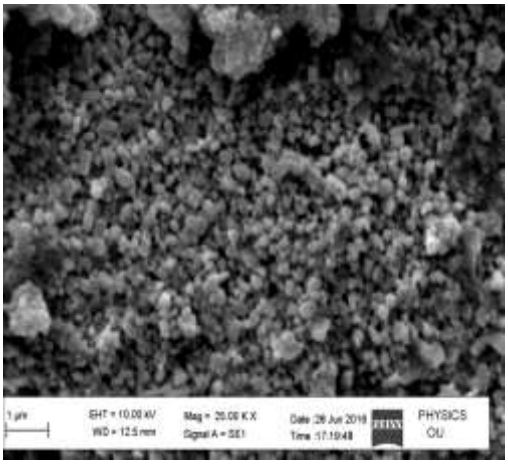


Fig 4.1b) WO_3

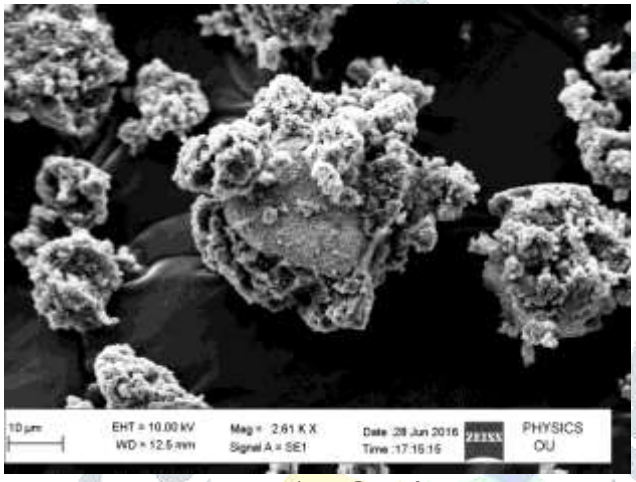


Fig 4.1c) WO_3 PANI

Figure 4.1 (a, b &c) shows that Scanning Electronic Micrograph (SEM) image of pure polyaniline, WO_3 & PANI/WO_3 composites.

4.2 XRD (X-ray Diffraction)

The X-ray diffraction patterns of the samples in this present study are obtained using a Philips X-ray diffractometer with CuK_α radiation ($\lambda = 1.54060$ Å).The diffractograms were recorded in terms of 2θ in the range $20^0 - 80^0$ Å with a scanning rate of 2^0 per minute. The mean crystallite size of the powder was determined by Debye Scherrer formula Figures 4.2 (a), (b) &(c) shows the XRD pattern of synthesized pure PANI, WO_3 and PANI/WO_3 composites. The XRD diffraction peaks of WO_3 powder are shown in Figure 4.2(b) and are good agreement with monoclinic structure reported in JCPDS File Card (No01-072-0677) The intensity of diffraction peaks for PANI/WO_3 composites are lower than that for WO_3. The presence of amorphous nature of PANI reduces the percentage ratio of WO_3 and sequentially weakness the diffraction peaks of WO_3 composites[2,6,10].

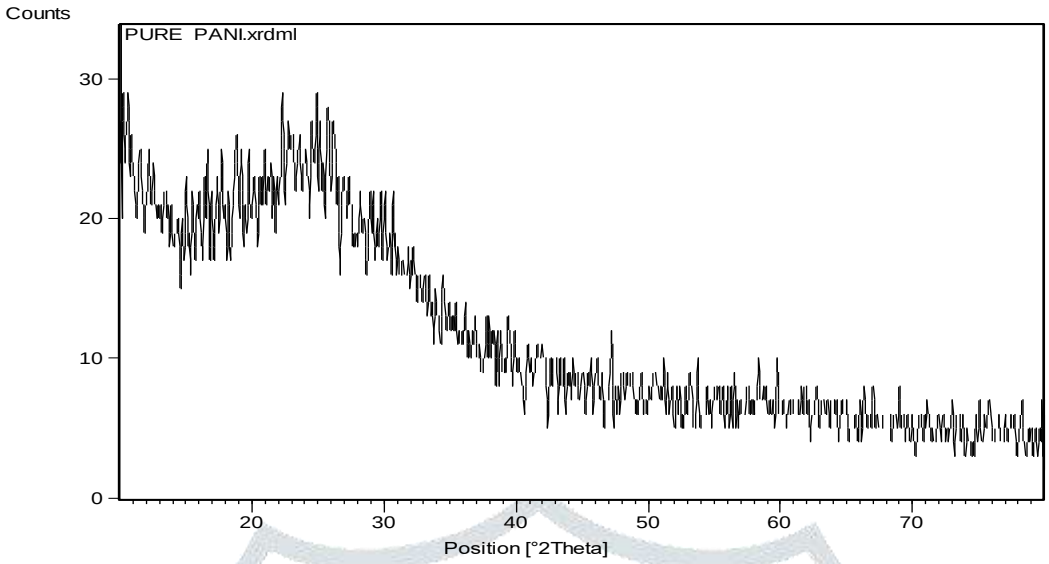


Fig 4.2 a) PURE PANI

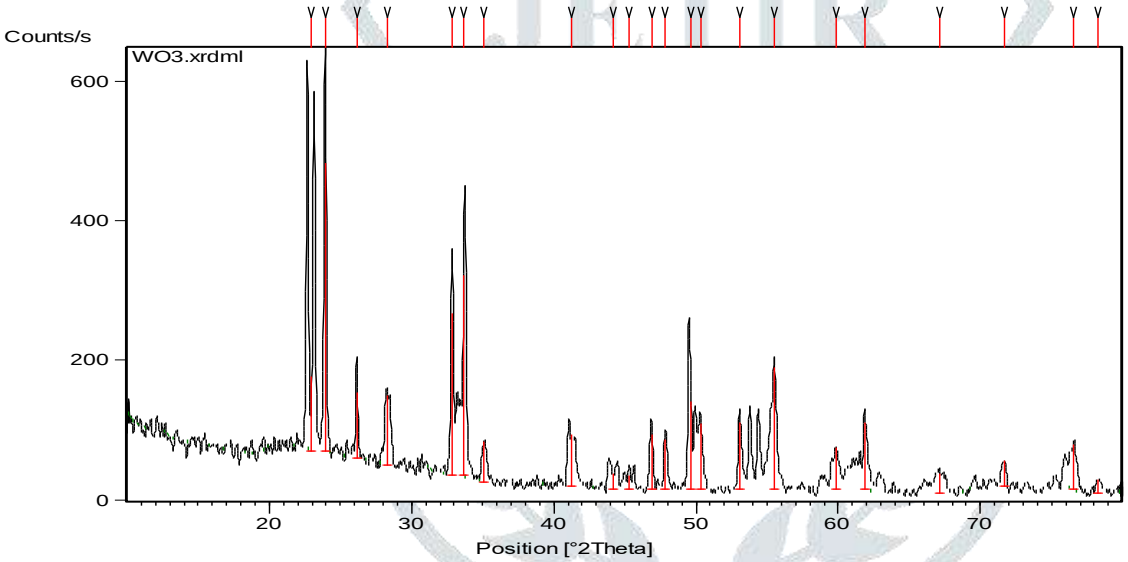
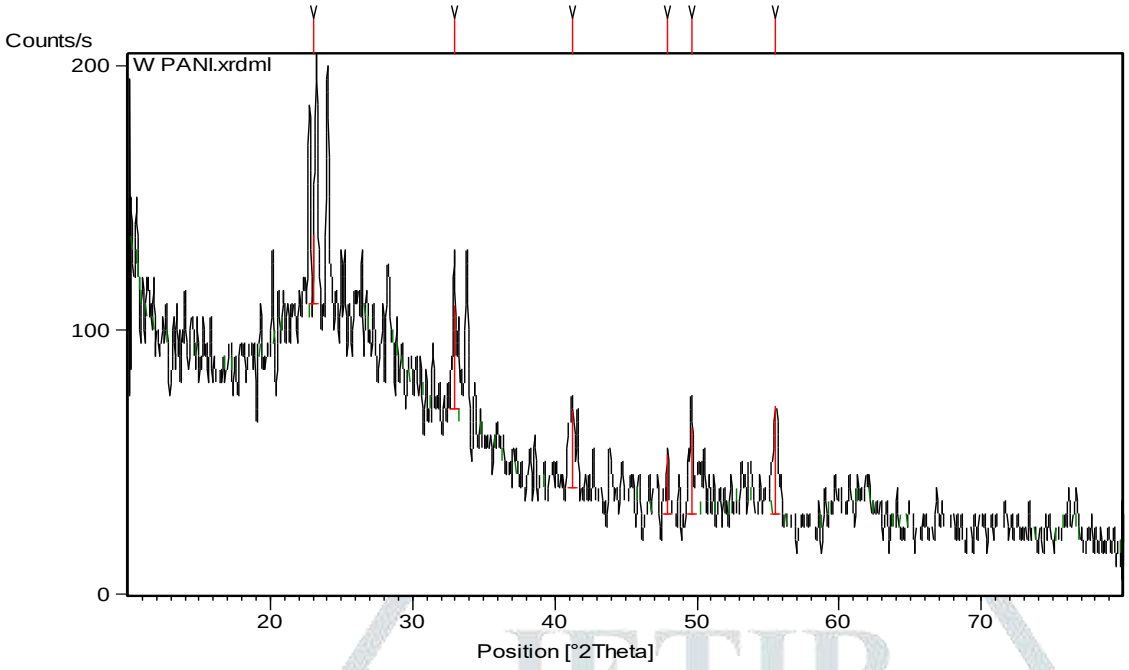


Fig 4.2 b) WO_3



4.2 c) PANI/WO_3

Figure 4.2 (a,b &c) shows that XRD image of pure polyaniline,WO_3 & PANI/WO_3 composites

5 DC-CONDUCTIVITY

The temperature dependence of dc-conductivity for PANI/WO_3 composites in a temperature range between 30^0C and 160^0C is illustrated in Fig 5. It is clear from the figures, the conductivity values of investigated composites are higher than that found for each of pure PANI. The conductivity increases steadily with temperature showing semiconductor behavior up to a transition temperature T_t. The figure shows also that at temperature higher than T_t, Figure also shows that the conductivity increases with increasing WO_3 particle content to attain an almost constant value at higher concentrations of Wo_3 Among all the composites, 40 wt% shows higher conductivity and it clearly shows that the conductivity is not only the motion of ions but also hopping of charge carriers and also because when PANI mixed with 40 wt% WO_3 gives more feasibility of matrix's for fast mobility of ions through it easily. The conductivity varies directly with the temperature, obeying an expression of the following form:

$$\sigma(T) = \sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right]$$

Where: σ is the conductivity, T is the temperature and $\sigma_0$is the conductivity at characteristic temperature T_0[14].

Though the composite having 40wt% of PANI/ WO_3 shows the higher conductivity than pure PANI such enhancement of DC conductivity values can be attributed to the uncoiling of polymeric chains due to strong interfacial interaction between WO_3 with PANI caused by their composition indicating that they have enough binding energy to combine with neighbors grains or molecules. The electrical properties in WO_3 can be explained on the basis of exchange of electrons between ions of the same element that are present in more than one valence state distributed randomly over equivalent crystallographic lattice sites[11-14].

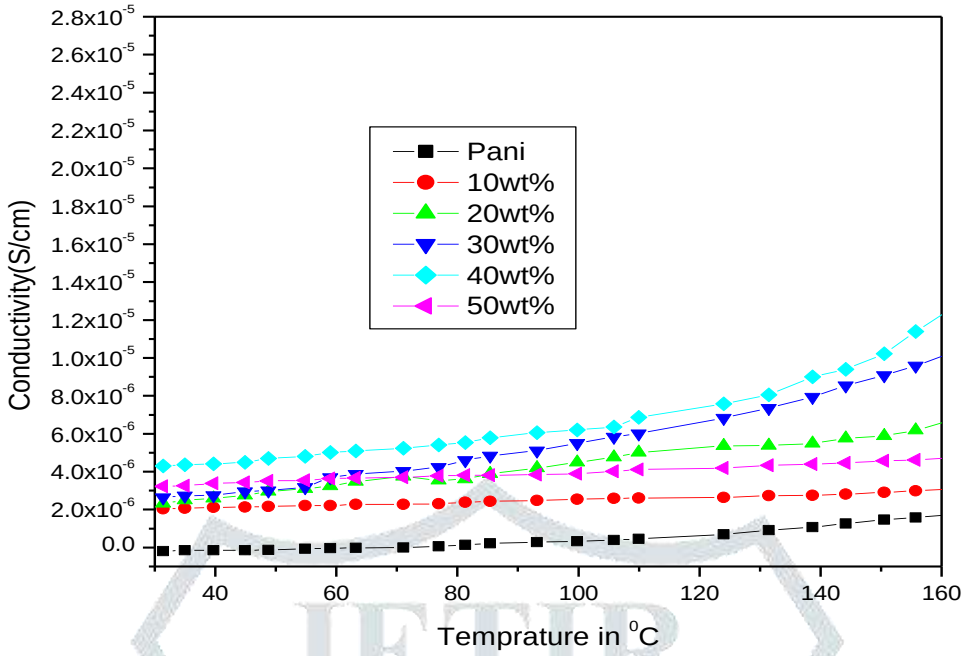


Figure 5 shows DC conductivity of Polyaniline nanocomposites.

6 AC CONDUCTIVITY

Figure 6 shows the variation of ac conductivity as a function of frequency for Polyaniline –WO_3 composites for (different wt %). It is observed that in all the cases, σ_{ac} remains constant up to 10^4Hz. Among all the composites, 40wt% of polyaniline / WO_3composites shows high conductivity due to interfacial polarization. However, in case of polyaniline and other composites 10, 20, 30 and 50wt%, the conductivity value is low because of dipole polarization. This behavior of these composites may be due to the variation in the distribution of WO_3 particles in polyaniline. There is a sudden increase in the conductivity with increase in frequency which is the characteristic property of disordered materials[13].

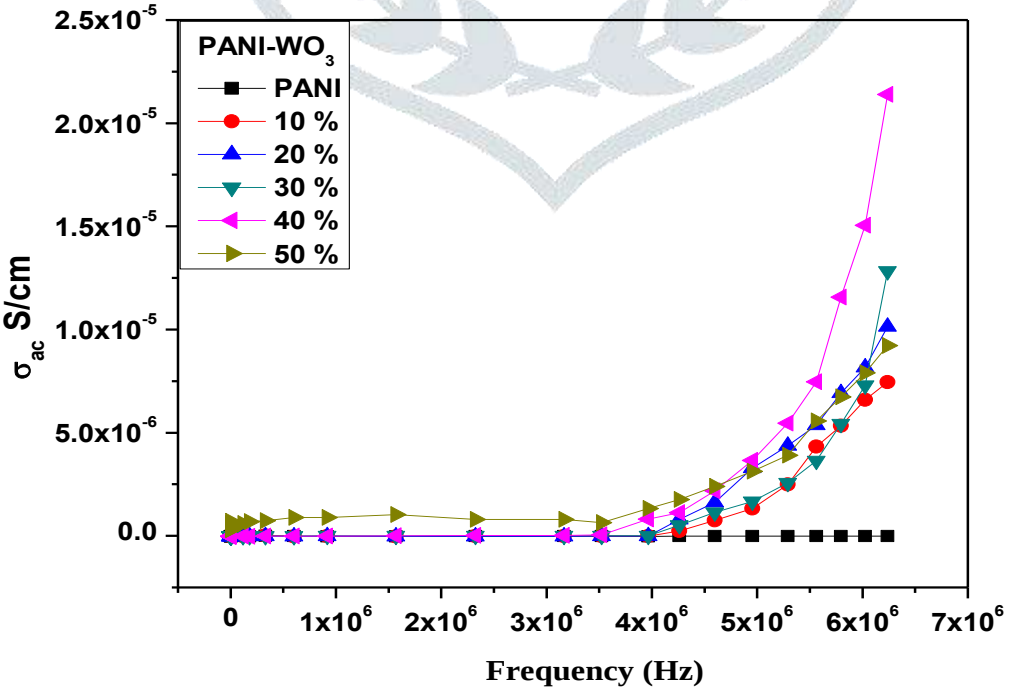


Figure 6 shows AC conductivity of Polyaniline nanocomposites

7. CONCLUSION

Polyaniline tungsten oxide composites were prepared by in-situ polymerization method.The SEM study performed on these samples indicates many aggregated particles and pores that have been reduced due to the homogeneous distribution of tungsten oxide particle in PANI composites. The presence of tungsten oxide particle in PANI nanocomposites influences electrical parameter such as conductivity of these composites. The DC &AC conductivity studies shows the prepared composites exhibits typical semiconductor behavior. Hence PANI/tugsten oxide composites is one of the promising materials for the potential applications.

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