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Chemical Oxidation Method for Synthesis of Polyaniline–In_2O_3 Composites

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Abstract: *Polymer composites containing metal oxides are new class of materials shows the enhanced properties and applications. Insitu polymerization by chemical oxidation of aniline is carried out for Polyaniline (PANI) and Polyaniline-In_2O_3 (PANI- In_2O_3) composite material. Different weight percentage of InO in PANI constitutes different PANI- In_2O_3 composite materials to know detailed changes. The structural changes of prepared composite materials were carried out by X-ray diffraction (XRD) tool. Morphological study of Indium oxide, PANI and PANI-InO composites was studied by Scanning Electron Micrograph (SEM) tool. Bonding changes was observed by Infrared (IR) study. Structural, morphology and bonding variation is observed in PANI- In_2O_3 composite materials compared to pure indium oxide and PANI samples. Dielectric study of the composite materials is undertaken for its dielectric behavior. The study shows the variation of the dielectric behavior for different weight percentage composite materials.*

Key words: *Synthesis, Composites, Structure, Morphology, Polyaniline, In_2O_3*

I. Introduction

The technological importance of basic research and its development has been carried for new properties and applications [1]. Indium oxide is a materials shows good electrical and optical properties [2-3] .Various techniques have been used for the preparation of Indium oxide materials [4-6]. More recently, there has been considerable attention on the synthesis of In_2O_3 nanostructures with well-defined nanocuboids in order to endow nanomaterials with additional properties or potential applications [7-8] However, it is very difficult to obtain the In_2O_3 nanocuboids directly using solution synthesis method, in which the calcination of corresponding hydrothermal precursors. Yang prepared the In_2O_3 nanocuboids used a one-step aqueous solvo thermal process, among the above methods, it can be concluded that H_2O plays a crucial role and hydrolyzation of In3+ is absolutely necessary. Hence, how to prepare highly crystalline In_2O_3 nanocuboics using a more convenient direct synthesis route is urgent. So far, the synthesis of In_2O_3 nanocuboids in nonaqueous system is rarely reported. New approach on conducting polymer composite materials integrates the technology of conducting polymeric materials. Metal oxide inserted Polymers constitute polymer composites, which are well studied for its properties [9-11]. Conducting polymers have a variety of applications in various fields, such as in Industry, Scientific and in medical (ISM) fields. Applications like anticorrosion, static coating electromagnetic shielding etc comes under first generation. Second Generation of electric polymers have applications such as transistors, LEDs, solar cells batteries etc. Controlled conductivity, high temperature resistance, low cost and ease of bulk preparation make these materials attractive in the engineering and scientific world. Among conducting polymers, polyaniline is the most extensively studied polymer obtained by simple chemical or electrochemical route. Polymeric materials has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices [12-13]. This polyaniline has received much attention because of its high electrical conductivity and ease of preparation at low cost. The demand of high quality materials for electromagnetic compatibility is alarmingly increasing [14]. Metal oxides dispersed polymer composites have attracted a great deal of interest from researchers, because they frequently exhibit unexpected hybrid properties synergistically derived from both components. Indium oxide is one of the examples of oxide material, which is known for progressive properties and applications [15]. Composite of Indium oxide dispersed PANI with variable compositions my lead to desirable properties and new applications. These materials are especially important owing to their bridging role between the worlds of conducting polymers [16]. In this paper, we describe the synthesis of PANI and indium oxide dispersed PANI composite materials through insitu polymerisation method. As prepared PANI and its In_2O_3 composite is well characterized by various characterization techniques. Dielectric study of the as prepared PANI composite material is also well studied for its dielectric behavior.

II. Experimental

1.1. Materials and Methods

Chemicals used in the preparation PANI and PANI composites are Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl), aniline and Indium oxide (In_2O_3) are of AR grade. Double distilled water was used in the synthetic process Chemical oxidation of aniline was carried out for Polyaniline and Indium oxide composite materials.3

2.2. Synthesis of Polyaniline-In_2O_3 Composites

0.1 M aniline was dissolved in 1M HCl to form aniline hydrochloride. Indium oxide was added in the weight percent of 10, 20, 30, 40 and 50 to the above solution with vigorous stirring in order to keep the Indium oxide suspended in the solution. 0.1M of ammonium persulphate $[(NH_4)_2S_2O_8]$ as an oxidant was added slowly to the reaction mixture with continuous stirring for 4-6 hours at 0-5^OC. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. Similarly five different PANI- In_2O_3 composites with different weight of In_2O_3 (10, 20, 30, 40 and 50) in PANI have been synthesized. Pure polyaniline was prepared by chemical oxidation of aniline without adding Indium oxide [17-18].

2.3. Preparation of Pellets

Varied concentrations of prepared composites were pressed under pressure for its pellet form. The test samples to be used were prepared in pellet form of diameter 10mm and thickness 3mm by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides [19].

2.4. Characterization

The structures of as prepared polymer composite were studied by X–ray diffraction using Phillips X–ray diffractometer (PW3710) with Cu Kα as source of radiation. Morphology and bonding of the above polymer composites were studied by Phillips XL 30 ESEM and Perkin–Elmer 1600 spectrophotometer in KBr medium tools respectively. Dielectric measurements were carried out at room temperature over the frequency range 10^2-10^7Hz using the Hiokie LCR Q meter.

III. Results And Discussion

3.4. X-ray diffraction

Figure-.1 shows indexed XRD pattern of pure PANI. The pattern shows the characteristics peak at 2Theta = 25^o confirms the formation of pure PANI. It shows the partial crystallinity. Figure-2 shows XRD pattern of PANI- In_2O_3 at 50% weight composition. Presence of Indium oxide reflections are observed in the composite pattern and are identified on comparison with Indium oxide JCPDS file 76-0152. This oxide peaks in the composite pattern confirms the formation of Indium oxide dispersed polyaniline composite.

3.5. Scanning Electron Microscopy (SEM)

Figure-3 shows SEM image of Indium oxide sample. This image shows the irregular spherical particles are compressed each other. Most of the particles form globular arrangement with compact structure indicates the crystalline structure of the sample. Figure-4 shows SEM image of pure PANI obtained by chemical oxidation route. This image also shows the irregular particles are in micro range and particles are spherical agglomeration without uniform packing. Figure-5 shows the SEM image of PANI- In_2O_3 at 50% weight percentage. The image shows the fine flecks of In_2O_3 particles in the PANI matrix forms cluster morphology. Some smooth solid blocks are due to the presence of oxide particles, which increases the crystallinity of the composite materials. Figure 6 shows a representative energy-dispersive X ray (EDX) spectrum of as prepared Indium oxide. The pattern shows the presence of In metal peaks, which again confirms the presence of In metal in polyaniline.

3.6. Infrared Study

The bonding nature in pure PANI and PANI- In_2O_3 composite was well studied by infrared tool. This study is to ascertain the metal- oxygen (M-O) bond and shift in frequency in the PANI and metal oxide inserted PANI composite sample. Metal oxides generally give absorption bands below 1000cm^{-1} arising from inter-atomic vibrations [20]. Figure-7 shows FTIR spectrum of pure PANI obtained by chemical route. The peak at 1103cm-1 is due to the B-NH+ = Q vibration, indicating that the PANI is conductive and is in the form of emeraldine salt. The absorption peak at 925 cm-1 is due the C-H bonding of the aromatic ring. The peak 666 is attributed to the out of plane deformation of C-H aromatic ring. Additional peaks at 2322, 2089, 1537 and 1280cm-1 are may be due to overtones. Figure-8 shows the FTIR spectrum of as prepared PANI- In_2O_3 composite. The spectrum shows some peaks below 1000cm-1clearly shows presence of Indium oxide. Some additional peaks and shift in vibrational frequency were also observed on comparison with pure PANI and In_2O_3 spectrum. This confirms the formation PANI- In_2O_3 composite.

3.7. Dielectric Study

Figure-9 represents the variation of ε' as a function of frequency for polianiline- In_2O_3 composites (Different wt%). In all the composites it is observed that, the dielectric const is high at low frequency and decreases with increase in frequency. The observed behavior may be due to the Debay's relaxation mechanism taking place in materials. It is also found that, the dielectric constant increases for 20wt%, &decreases 30wt % and there after increases 40wt% which is a characteristic of Debye relaxation mechanism. From the above studies, it is confirmed that at lower frequencies PANI composites behave as dielectric materials

IV. Conclusion

The chemical oxidation method was used for preparation of PANI and its composites. This method may be used for the preparation of PANI composites with various metal oxide materials. Structural changes of pure PANI and pure metal oxide is taken place due to the presence of oxide material in the PANI is observed by XRD pattern. Similarly, morphology and bonding changes is observed in composite material compared to pure PANI and pure metal oxide.

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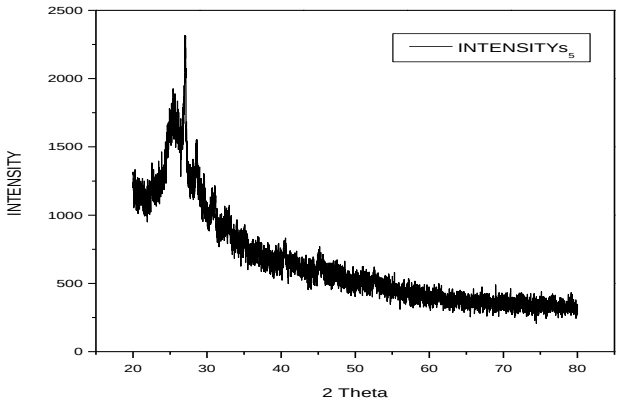

Figure 1: XRD pattern of as Pure In_2O_3 sample

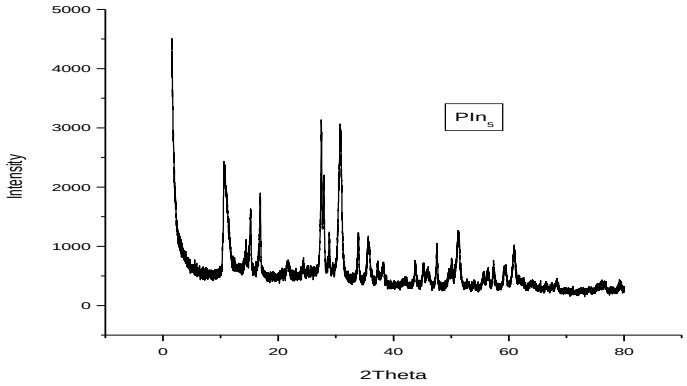

Figure 2: XRD pattern of pure PANI- In_2O_3 at 50% weight composition

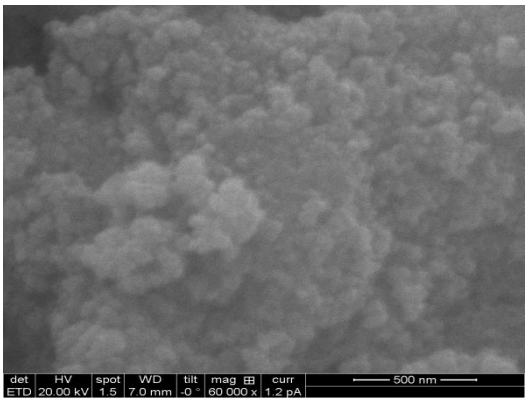

Figure 3: SEM image of In_2O_3

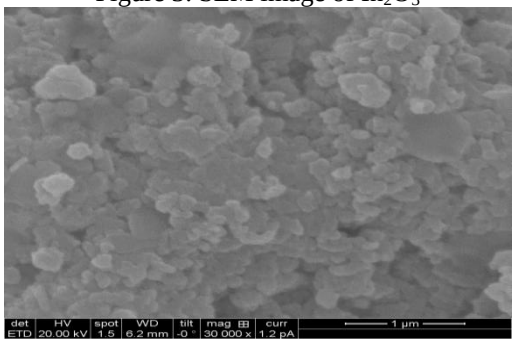

Figure 4: SEM image of pure PANI

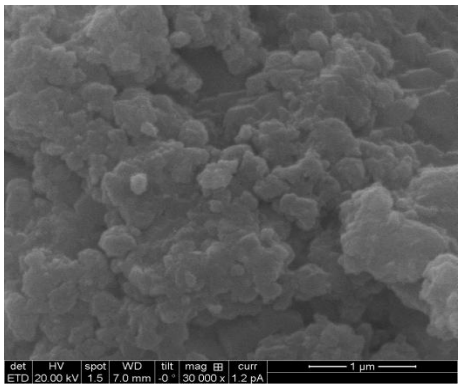

Figure 5: SEM image of PANI- In_2O_3 at 50% weight composition

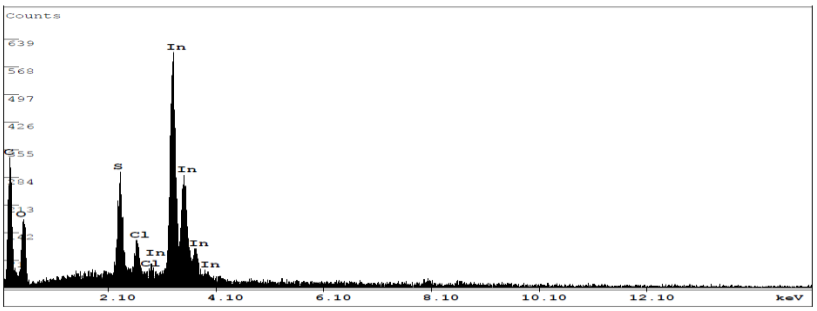

Figure 6: EDAX of PANI- In_2O_3 at 50% weight composition

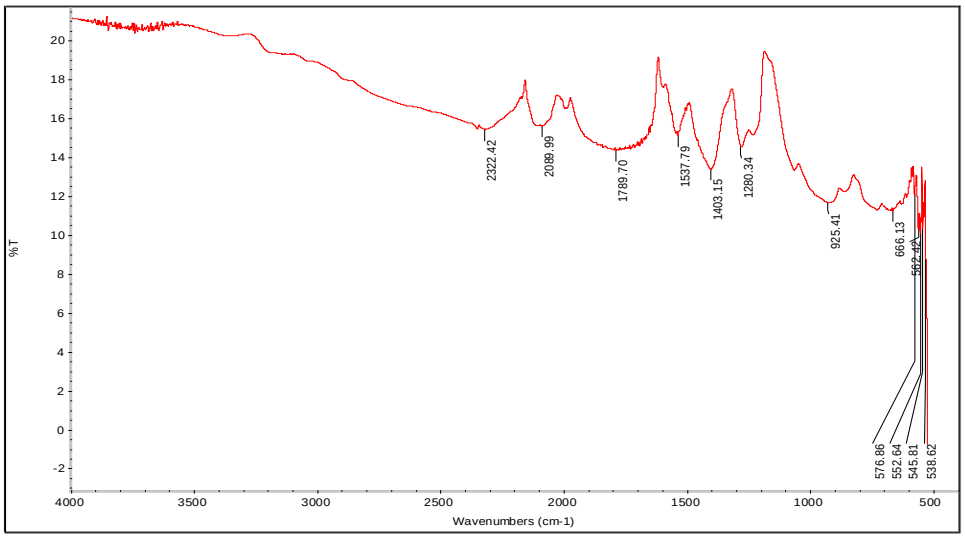

Figure 7: FTIR spectrum of pure PANI

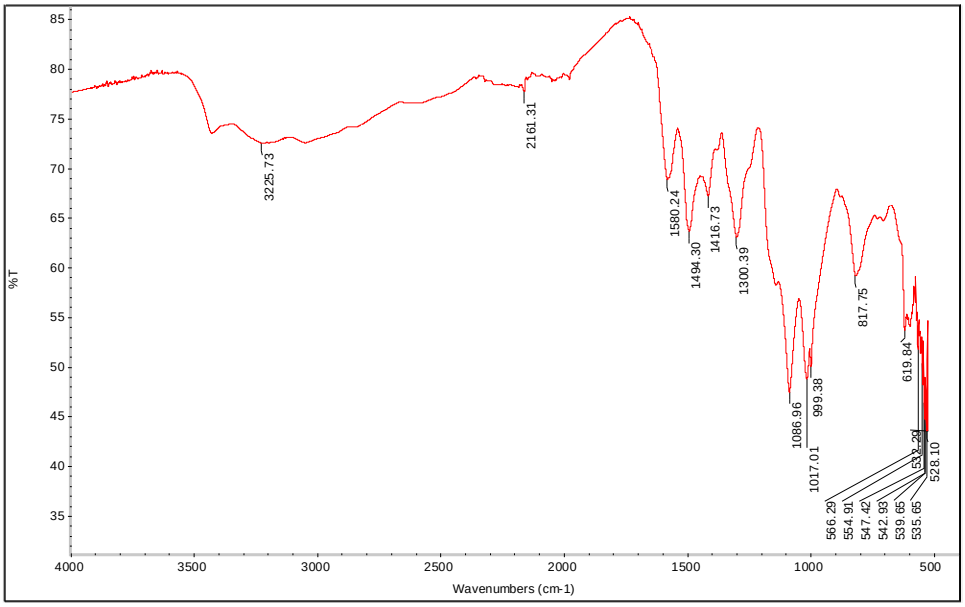

Figure 8: FTIR spectrum of PANI- In_2O_3 composite

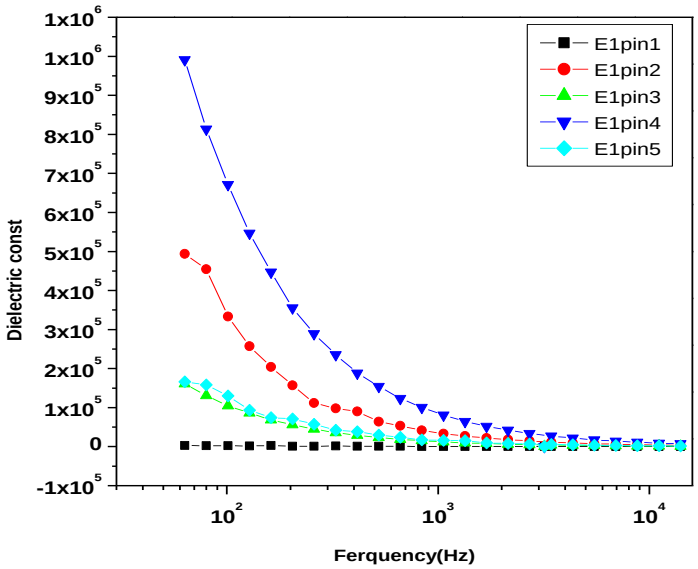

Figure 9: a c conductivity of PANI- In_2O_3 composite