

Polyaniline-Tin Oxide Nanocomposites : Synthesis and Characterization

L.I.Nadaf¹, K.S.Venkatesh¹, M.A.Gadyal¹, Mohammed Afzal²

¹Department of Material Science, Gulbarga University, Kalburgi, Karnataka, India.

²SECAB A.R.S.Inamdar College for women, Vijayapur- 586101, Karnataka, India.

Abstract: Tin Oxide (SnO₂) nanoparticles have been synthesized by co-precipitation method. Aniline polymerized in the suspension of SnO₂. Ammonium per sulphate was used as oxidizing reagent to form organic – Inorganic nanocomposite materials. By this way SnO₂ nanoparticles were embedded in PANI matrix. XRD analysis was used to study the structure and estimate the size of the particles in the as synthesized powders. Scanning electron microscopy was used to study the morphology of composite materials. SEM images reveal that the as synthesized powders contain spherical particles and SnO₂ was uniformly mixed within PANI matrix. As synthesized PANI – SnO₂ nanocomposites have been tested for Gas sensing applications

Keywords: Co-precipitation, Tin Oxide nanoparticles, SnO₂ – PANI nanocomposites.

I. Introduction

Recently conducting polymers have attracted much attention due to high electrical conductivity, ease of preparation, good environmental stability, and wide variety of applications. Most widely studied conducting polymers are polyaniline, polypyrrole, polythiophene etc. Polyaniline composites with inorganic fillers have found a wide applications in electronics and electrical engineering due to their properties. Organic and inorganic hybrid material nanocomposites are particularly in demand in micro electronics[1-3]. They possess sensitivity to light and various gases and exhibit catalytic activity[4-5]. Polyaniline nanocomposite materials containing tin oxide are catalysts for oxidation of methanol[6] and have been used as gas sensors[7]. They have also been used in nonlinear optics and electro chemistry[8,9]. No sufficient work has been done in the synthesis of nanocomposites material of PANI- SnO₂. There is a need for the development of methods to synthesize PANI-SnO₂ nanocomposites, particularly polymerization of aniline in the suspension of target size filler powders[10].

The fundamental process of doping depends upon geometric parameters such as bond length and bond angle. The charge is localized over the several repeating units. Conducting polymers have been found suitable for micro electronic device fabrication due to their excellent electric characteristics and ease of processibility. Among these polymers polyaniline has emerged as promising candidate with great potential for practical uses such as light emitting diode, transparent electrodes, corrosion protection of metals, gas sensors and humidity sensors etc., Polyaniline exists in a variety of protonation and oxidation forms. The most important form of polyaniline is green protonated emeraldine, produced by oxidation polymerization of aniline in aqueous acids. It is electrically conducting due the presence of cation radicals in its structure. The positive charge on aniline units is balanced by negatively charged chloride anions[11].

Tin oxide is widely used and studied n-type semiconductor with wide band gap and crystalline structure. Studies have been carried out on tin oxide based gas sensors, dye sensitized solar cells optical devices, optoelectronic devices and hybrid microelectronic devices. The compound has lately also been identified as possible electrode material for lithium cells and photo catalysis. With properties such as transparency in semi conductivity it is an oxide of great interest from the technological point of view for white pigment for conducting coatings. Tin oxide nanoparticles are synthesized through different chemical routes such as co-precipitation, hydrothermal, sol gel, sonochemical polymer, precursor method among others.

However PANI is not as sensitive as metal oxides towards gas species and poor solvability in organic solvents limits its applications, but it is suitable as a matrix for preparation of conducting polymers nanocomposites[12,13]. Therefore there has been increase in the interest of researchers for the preparation of nanocomposites based on PANI. The literature review on conducting polymer nanocomposites shows that PANI has been successfully utilized for the preparation of nanocomposites [14,15].

II. Experimental Techniques

Materials and Methods

2.1 Materials

All the chemicals used were of analytical grade. Aniline purchased from Central drug house (P) Ltd., New Delhi India, Ammonium persulphate from Qualigens fine Chemicals Mumbai, India and hydrated stannic

chloride($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) used was obtained from Thomas Baker Mumbai, India, sodium carbonate anhydrous was obtained from Qualigens Fine Chemicals Mumbai, India and demineralised water from Nice Chemicals (p) Ltd. Kochi, Kerala, India are used directly without any further purification for the synthesis of SnO_2 nano particles. The as prepared PANI- SnO_2 nanoparticles were used for further characterization. X-ray diffractometer (Ultima IV Japan) with $\text{CuK}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) at 40 mA and 40 kV at a scanning rate of 0.02° per second was used to study the crystals and SEM images of all composites are obtained from IISC, Bengaluru, Karnataka, India.

2.2 Synthesis of Polyaniline

Polyaniline was synthesized by the oxidation of Aniline with ammonium per sulphate. A solution of 0.5 M Aniline is prepared in 0.5M HCl (already prepared). A solution of 0.5M ammonium persulphate is also prepared in distilled water. A known volume of Aniline hydrochloride solution is taken in a 1000 ml beaker and is stirred for about five minutes. Now an equivalent quantity of 0.5M ammonium per sulphate is added drop by drop by using a barrette and continuously stirred using a magnetic stirrer.

The colour less solution of Aniline hydrochloride solution slowly turns to green. After addition of entire quantity of ammonium per sulphate stirring is continued for 15minutes. Now stirring is stopped and allow the precipitate to settle down and then it is filtered. The dark green coloured precipitate of polyaniline is obtained. The precipitate is washed with distilled water several times to remove the impurities. Finally the precipitate was washed with acetone to remove the foreign bodies. Now the precipitate was allowed to dry completely on its own at room temperature. The dried material was grinded to fine powder using mortar and pestle for about 20 minutes.

2.3 Synthesis of tin oxide nanoparticles

A solution of hydrated stannic chloride and anhydrous sodium carbonate were separately prepared in demineralised water. The concentration of hydrated stannic chloride solution and Sodium carbonate solution are prepared in the ratio 1:2 molar. First a known quantity of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution was taken in a 1000 ml clean and dry beaker and subjected constant stirring using a magnetic stirrer at room temperature. After 5 minutes of stirring of this solution, the already prepared Sodium carbonate solution was added to this SnCl_4 solution under constant stirring drop by drop by taking Sodium carbonate solution in a 50ml burette and setting the rate of addition to 55-60 drops per minute till an equal quantity of sodium carbonate solution to that of SnCl_4 solution is added. This process is continued for about 1 hour 30minutes. During the process the solution of SnCl_4 turns into a white gelatinous precipitate. Stirring is continued further for about 30 minutes even after the entire Sodium carbonate solution is added. The stirring is stopped and the white gelatinous precipitate is allowed for about 4 hours to settle down. The particles settled at the bottom of the beaker were separated from solution by decantation. In the present work we tried to filter the precipitate using Whatmann filter paper number 41 and 42 but the complete precipitate passed through the filter paper, indicating that the particle size is much smaller than the pore size of the Whatman filter paper. Repeated washing and decantation process is used to separate the precipitate. In order to remove the impurities from the precipitate demineralised water is added to the precipitate, stirred for 5 minutes, allowed the precipitate for about 4 hours to settle down and decanted. This process is repeated for several times. Finally the same process of removal of impurities repeated using ethyl alcohol in place of demineralised water. This ensures complete removal of impurities from the precipitate. The beaker containing the precipitate is heated at low temperature for four hours and made it perfectly dry. The crystalline powder grinded for 10 minutes with mortar pestle. The powder was taken in silica crucible and calcinated at 325°C for 1 hour in muffle furnace. The muffle furnace was switch off and allowed it to reach the room temperature on its own. The final product was the SnO_2 nanoparticles.

2.4 Synthesis of PANI- SnO_2 Nanocomposites.

A known quantity of Aniline solution dissolved in HCl is taken in 1000 ml beaker and stirred for 5 minutes and 0.5 g (10wt %) of SnO_2 nanoparticles were added and stirred with magnetic stirrer for about 15 minutes then ammonium per sulphate was added drop by drop. Even after complete addition of ammonium per sulphate stirring was continued for another 10 minutes and allowed the precipitate for about 30-40 minutes to settle down. Now precipitate was filtered and washed with distilled water several times to remove the impurities. Finally washed with acetone and precipitate was dried on its own at room temperature and was grinded for 15 minutes with mortar and pestle. Now the resultant sample is the PANI- SnO_2 nanocomposite with 10 wt% of SnO_2 .

In the same manner, PANI- SnO_2 nanocomposites with 15wt%, 20 wt%, 25 wt% and 30wt% of SnO_2 are synthesized. The prepared PANI- SnO_2 nanocomposites were characterised by XRD and SEM.

III. Results and Discussion

The XRD patterns of pure PANI and SnO₂ nanoparticles are shown Figure-1 and 2 respectively. The XRD pattern of pure PANI shows three broad peaks at 2θ values 15°, 20° and 25° and indicates its amorphous nature. The Figure-2, reveals the crystalline structure of the sample, the peaks are observed at 2θ values 32.76° and 46°, and hence the SnO₂ nanoparticles possess the monoclinic structure. The average crystallite size of the SnO₂ nano crystals is estimated to about 23.782 nm by Scherrer's formula.

The Figure-3-7, shows the XRD patterns of as prepared PANI- SnO₂ nanocomposites with different weight percentages (10 %, 15 %, 20 %, 25 % & 30 %) of SnO₂. The common peak at 2θ=26°, is present in all five prepared composites, indicates that the PANI retains its identity in composite phase. The peak height increases with increase in wt% of SnO₂ at 2θ=52.5°, and same peak was observed in XRD of pure SnO₂ nanomaterial. Thus the nanocomposite gradually takes the transition from the amorphous to crystalline phase with increase in the percentage of the SnO₂ nanoparticles. Average crystallite sizes of the nanocomposites were calculated using Scherrer formula and the values are 1.4nm, 1.303nm, 1.497 nm, 1.309 nm and 1.232nm for 10wt %, 15wt %, 20wt %, 25wt % & 30wt % of SnO₂ respectively.

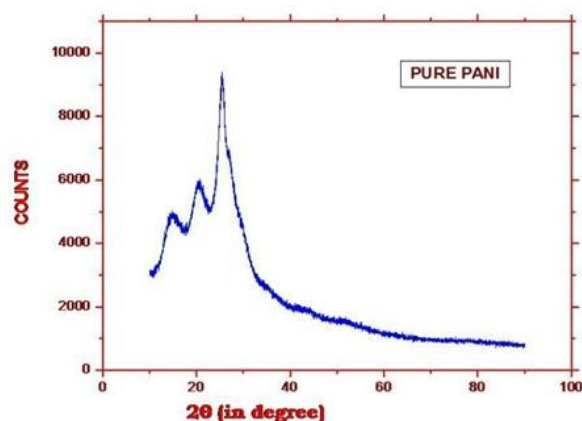


Figure 1: XRD of pure PANI.

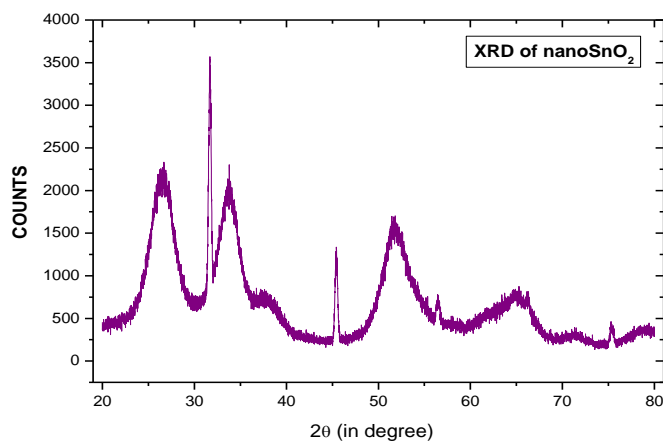


Figure 1: XRD of pure SnO₂

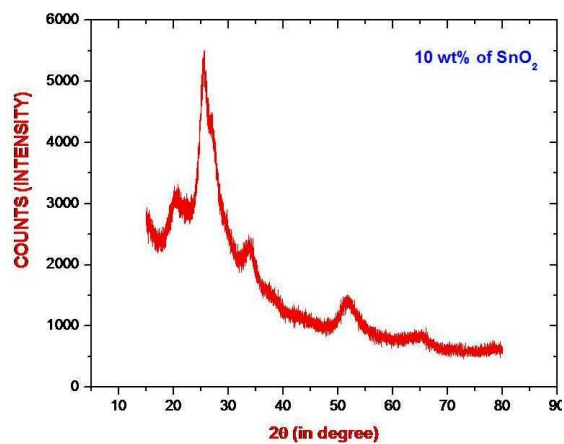


Figure 3: XRD of pure PANI with 10wt% SnO₂

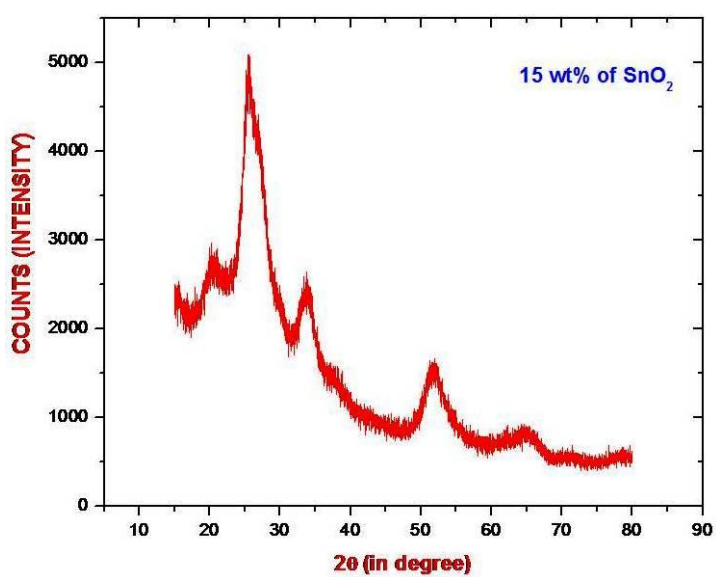


Figure 4: XRD of pure PANI with 15wt% SnO₂

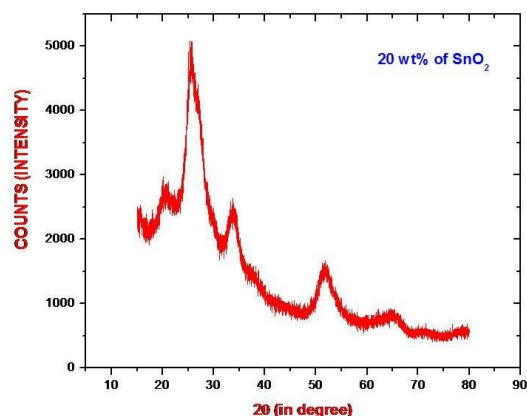


Figure 5: XRD of pure PANI with 20wt% SnO₂

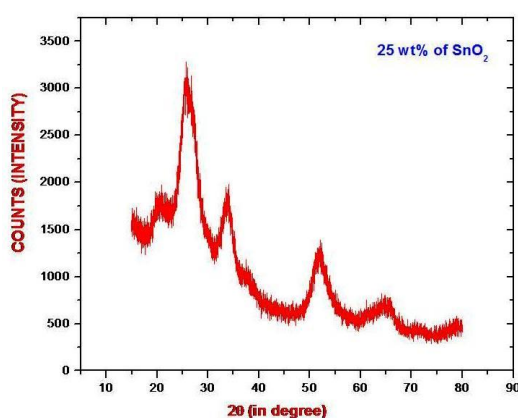


Figure 6: XRD of pure PANI with 25wt% SnO₂

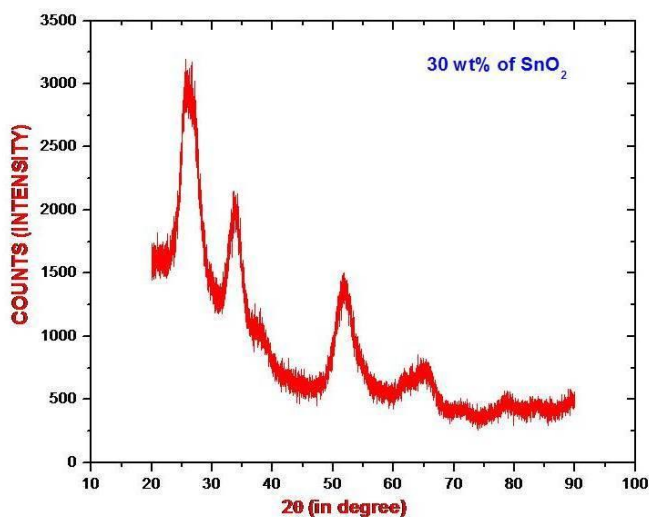


Figure 7: XRD of pure PANI with 30wt% SnO₂

The SEM images of pure PANI, SnO₂ nanoparticle and the five nanacomposites are given in Figures-8(a-g). Figure-8(a) shows SEM image of pure polyaniline, has amorphous nature and grains are well interconnected. The Figure-8(b) is the SEM image of SnO₂ nanoparticles which shows the homogeneous distribution of spherical particles. The Figure-4(c) is the SEM image of 10 wt % of PANI-SnO₂ composite, here the grains are irregular in shape, the SnO₂ oxide particles are not well dispersed. The Figures 8(d), (e), (f) and

(g) are the respective SEM images of 15 wt % , 20 wt % , 25 wt % and 30 wt % PANI- SnO₂ composites, with increase in wt% of SnO₂ results in increase of the crystallinity of composite materials.

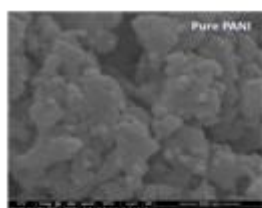


Figure 8c: SEM image of pure PANI

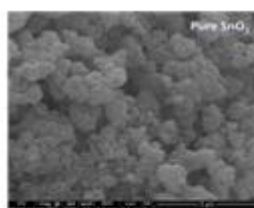


Figure 8b: SEM image of pure SnO₂

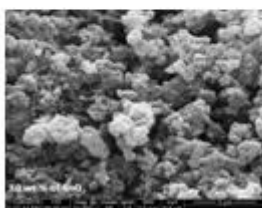


Figure 8c: SEM image of PANI with 10%wt SnO₂

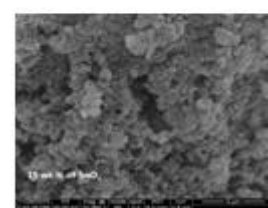


Figure 8d: SEM image of PANI with 15%wt SnO₂

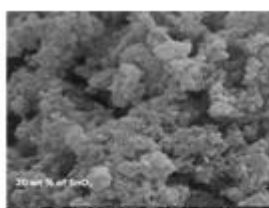


Figure 8e: SEM image of PANI with 20%wt SnO₂

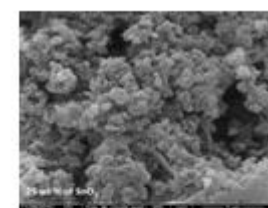


Figure 8f: SEM image of PANI with 25%wt SnO₂

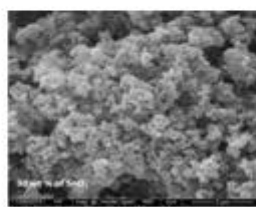
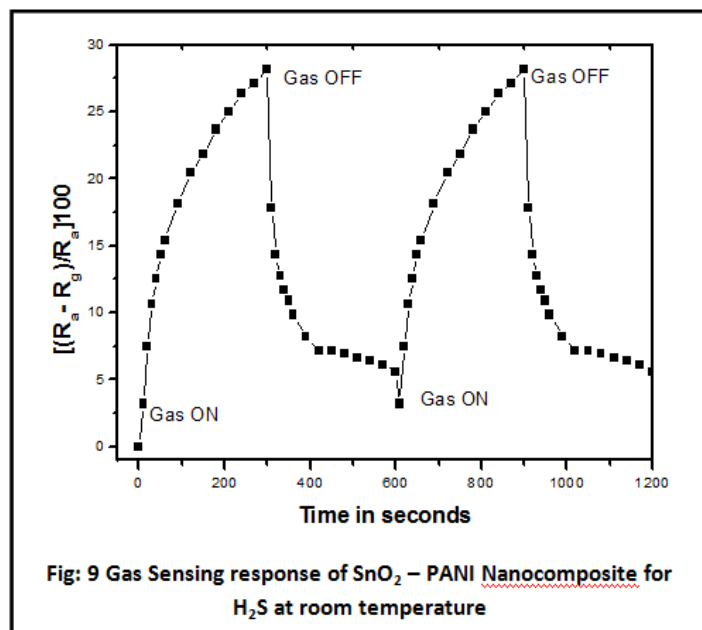


Figure 8g: SEM image of PANI with 30%wt SnO₂

Gas Sensor application

As synthesized PANI – SnO₂ nanocomposites have been tested for Gas sensing applications[16-18]. Gas sensing measurements have been carried out at room temperature. Hydrogen Sulphide is used as probing gas. The conductivity of PANI-SnO₂ nanocomposites was increased when exposed to H₂S gas. PANI with 30wt% SnO₂ sample has shown maximum sensitivity for H₂S. The nanocomposite material was taken in the form tablet and loaded in the gas sensing apparatus [19] and the variation in resistance with time when exposed to the gas is recorded. The sensitivity using the relation $[(R_a - R_g)/R_g]100$ verses time is plotted shown in figure 9. It is seen that though Pure PANI is conducting but not sensitive to gas.



IV. Conclusions

PANI -SnO₂ nanocomposites have been successfully synthesized by in situ chemical polymerization of Aniline using Ammonium persulphate as oxidizing agent by co-precipitation method. PANI-SnO₂ nanocomposites with different wt% of SnO₂ have been synthesized. As prepared material have been characterized by XRD and SEM, which reveals that SnO₂ nanoparticles were uniformly distributed through out the PANI matrix. The PANI -SnO₂ nanocomposite was used for sensing H₂S gas at room temperature.

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