SYNTHESIS AND CHARACTERIZATION OF ZnO and SnO_2 DOPED POLYANILINE NANO COMPOSITES

Hamjade PT[1], Khaire ND[2], Motke SG[3]
[1,2]Associate Professor, Department of Physics, Phulsing Naik Mahavidyalaya, Pusad.
[3]Principal, Phulsing Naik Mahavidyalaya, Pusad, Maharashtra, India..

ABSTRACT

Polyaniline and its nano-composites are synthesized using in-situ chemical oxidative polymerization technique using aniline monomer. Nano sized ZnO & SnO_2 are used as received from the manufacturers. Ammonium Per Sulphate is used as oxidizing agent for polymerization. Crystalline ZnO & SnO_2 are embedded in amorphous Polyaniline. The structure of composites was confirmed by the characterization techniques FTIR, UV Visible and XRD.

Average particle size and chain separation is determined from XRD. The little shifting of the wavelengths towards higher values in FTIR confirms the formation of Polyaniline. UV Visible studies show that the composites exhibit absorption peaks at 371 nm, 368 nm, 355 nm, 266 nm and 248 nm for ZnO which corresponds to band gap energies 3.34 eV, 3.37 eV, 3.496 eV, 4.5 eV and 5 eV respectively. The SnO_2 doped Polyaniline nano-composite exhibits absorption peaks at 368 nm, 313 nm and 266 nm which corresponds to band gap energies 3.3eV, 3.9 eV and 4.5 eV respectively.

Keywords: Polyaniline, nano-composites, band gap energy, ZnO, SnO_2.

INTRODUCTION

The conducting polymers made significant impact in the field of materials science due to their potential applications in many electronic devices [1]. Technological uses depend crucially on the reproducible control of the molecular and supramolecular architecture of the macromolecules via a simple methodology of organic synthesis [2]. Polyaniline is one of the important conducting polymers among all other conducting polymers because of its stability in air, easy polymerization, low cost, good conductivity, and solubility in some organic solvents. It is the type of conducting polymer whose properties can be changed by protonation state, oxidation state, and also by nature of dopant [3-6]. In general the change in properties make polyaniline a versatile material. The preparation of polyaniline composites with various materials has received great attention because of their unique properties and allocations in various electrical and electronic devices. Several reports dealing with the preparation of conducting composites such as Fe_3O_4:PANI, MnO_2:PANI, TiO_2:PANI, ZrO_2:PANI [7,8], as well as preparation and characterization of ZnO:PANI composites have been published [9-11] . Due to the reasons it has been studied extensively for making optical and electronic devices like LEDs, solar cells, transducers, photodetectors, etc. [12-14]. In particular ZnO nanostructures are of intense interest since it can be grown by a variety of methods with different morphologies.

On the other hand, functional metal oxides have received increasing attention due to their unique physical properties. Functional oxide have two structural characteristics- cations with mixed valance states and anions with deficiencies (vacancies). By varying either or both of these characteristics , the electrical, optical, magnetic, and chemical properties can be tuned, giving the possibility of fabricating smart devices that utilizes the semiconducting , superconducting, ferroelectricity and/or magnetism offered by the oxides. Among the technologically promising

functional metal oxides, tin oxide (SnO_2) is used in various opto-electronic devices like flat panel display, photoconductor and solar cells. SnO_2 is n-type semiconductor with a band gap of 3.6eV at 300 k where as PANI is a typical conductive polymer which is usually considered as a p-type material. In view of forgoing, by synthesizing nano-composite of SnO_2/PANI, electrical and optical properties can be enhanced.

In the present work the composites of polyaniline with ZnO and SnO_2 were synthesized at a ten (10) weight percentage by chemical oxidation polymerization method using ammonium persulphate as an oxidizing agent. ZnO is n-type semiconductor and has wide band gap of energy (3.4eV), large excitation binding energy, effective ultraviolet absorbance and good chemical stability. It shows great potential application in solar cells, gas sensors, varistors, etc. With this background of multifunctionality ZnO and SnO_2 are used in preparation of composites [9-11]. The formation of composites were characterized by using XRD, FTIR and UV/Visible.

II. EXPERIMENTAL

The chemicals aniline monomer, ammonium per sulphate (APS) $(NH_4)_2S_2O_8$, hydrochloric acid (HCl) Zinc Oxide (ZnO) and Tin Oxide (SnO_2) were procured from LOBA chemicals, Mumbai.

Aniline of 0.0548Mol was dissolved in 1ml HCl to form aniline hydrochloride. ZnO was added 10 wt % to the above solution with vigorous stirring to keep ZnO particles suspended in the solution. The oxidant solution was prepared by dissolving 0.022mol APS in 50ml of distilled water. It is added drop wise to the reaction mixture with continuous stirring for about 4hrs. And the resulting mixture is kept overnight to polymerize completely .The resulting precipitate was filtered and Washed separately with deionized water. The product was dried in a furnace for 8 hrs at 60 C. The powder was used for characterization.

The above method was used to synthesis 10wt% SnO_2 /PANI nanocomposite. The nanosized SnO_2 powder was procured from nano labs, Jamshedpur, Zarkhand. The nanocomposite was characterized using XRD, FTIR and UV/Visible.

III. RESULT AND DISCUSSION

The PANI/ Metal oxide nanocomposite powder were used for XRD measurements using Cu(Kα) radiation of wavelength 1.5418A in a range 5˚-70˚.PANI metal oxide 10wt% nanocomposites were studied using FTIR Shimandzu, Japan in the range 500-4000cm¯1 and UV/Visible Shimadzu, Japan in the range 200nm to 1100 nm.

a) XRD

X-Ray diffraction pattern with two prominent peaks leads the amorphous nature. The XRD spectrum of PANI/ZnO 10wt% and PANI/SnO_2 10wt% are shown in fig. 1(a), 1(b).

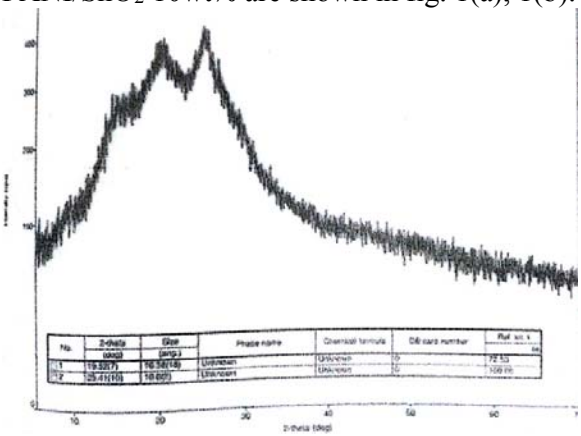

Fig. 1(a) XRD spectrum of PANI/ZnO 10wt%

It is notified that a broad and diffused peak is observed at around 2θ = 25˚.This shows polyaniline is amorphous in nature. The peaks are observed for the composite of polyaniline with ZnO at 2θ = 25˚, 38˚, 44˚, 65˚, 77˚ which depicted it has crystalline nature. The particle size could be estimated using Debye – Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where,

D is the particle size, β is full width at half maximum (FWHM) for stronger peaks and λ is the wave length of X-rays. From the high intensity peaks the particle size are calculated in the range 10-50 nm.

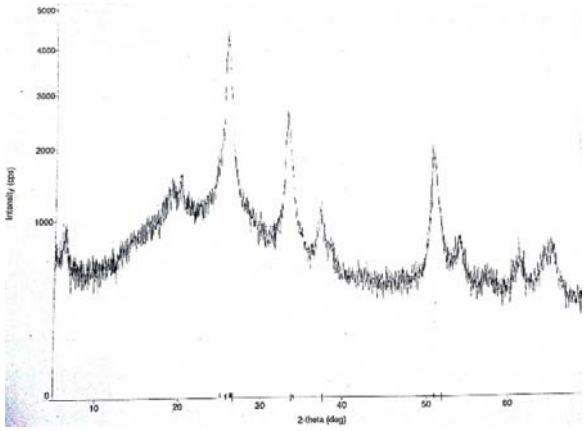

Fig. 1(b). XRD-pattern of PANI/SnO_2 10wt%

The XRD-pattern of PANI/SnO_2 10wt% shows sharp diffraction peaks at 26˚, 34˚, 51˚ which confirms the presence of SnO_2 nanoparticles are highly crystalline. The peaks at 26˚, 34˚, 51˚ can be indexed to (110), (101), and (211) planes of SnO_2 which matches with JCPDS card #41-1445.The average size of nanoparticles is calculated to be 7.57nm.

b) FTIR-

The FTIR spectra of PANI/ZnO 10wt% and PANI/SnO_2 10wt% are shown in fig 2(a), 2(b) respectively.

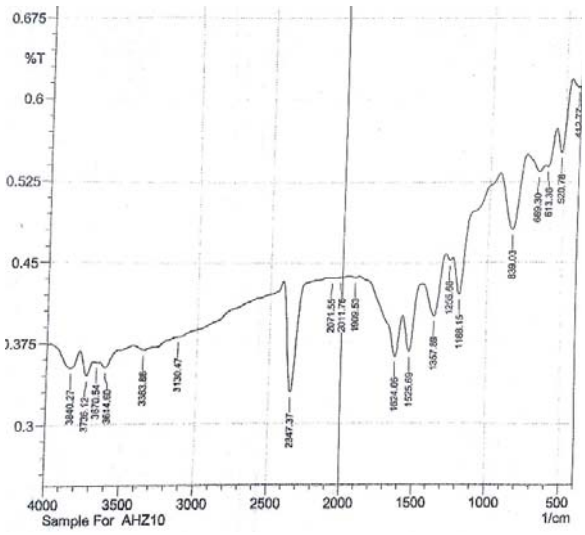

Fig 2(a). FTIR spectra of PANI/ZnO 10wt%

Fig. 2(a) shows characteristic peaks appear at 1624.06, 1525.69, 1357.89 and 1188.15 cm^{-1} which corresponds to PANI. The absorption bands at 500 cm^{-1} is the stretching mode of ZnO.

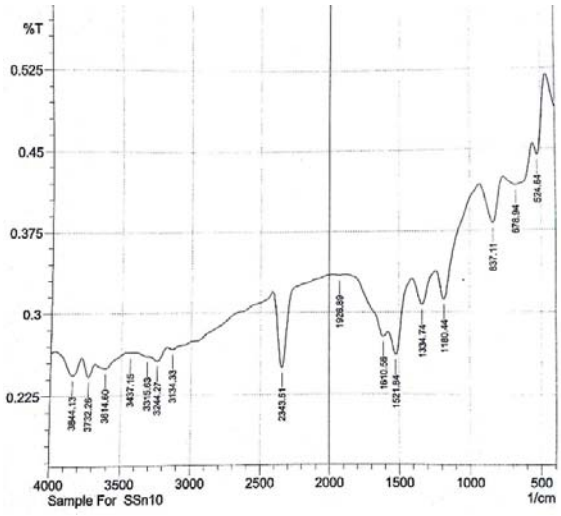

Fig 2(b). FTIR spectra of PANI/SnO_2 10wt%

Fig. 2(b) shows FTIR spectra of 10wt% SnO_2 doped polyaniline nanocomposite. The absorptions are 678cm^{-1} (C-H stretching), 1180.44cm^{-1} (C-H bending), 1344.74cm^{-1} (C=N stretching) and 1521cm^{-1} (C=C starching of the quinoid ring).

c) UV-Vis

The UV-Vis spectra of nanocomposites are shown in figs. 3(a), 3(b). Using these spectra the band gap energy can be found out. The formula is,

$$E_g = \frac{hc}{\lambda e}$$

Where h is Planck's constant (6.626 x 10^{-34} J-sec), c is the speed of light (3x 10^8 m/s), λ is the wave length and e is the charge of electron (1.602 x 10^{-19}C).

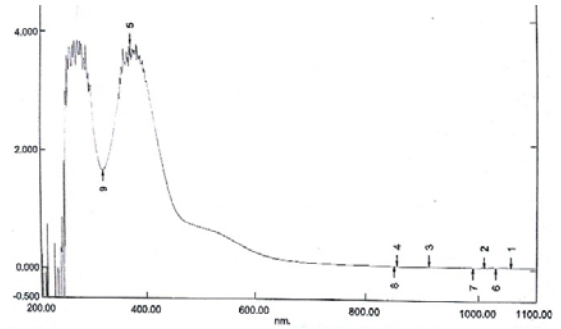

Fig. 3(a). UV-Vis spectra of PANI/ZnO 10wt%

The UV-Vis studies shows that the PANI/ZnO 10wt% composite exhibits absorption peaks at 371nm, 368nm, 355nm, 266nm and 248nm which corresponds to band

gap energies 3.34eV, 3.37eV, 3.496ev, 4.5eV and 5eV respectively.

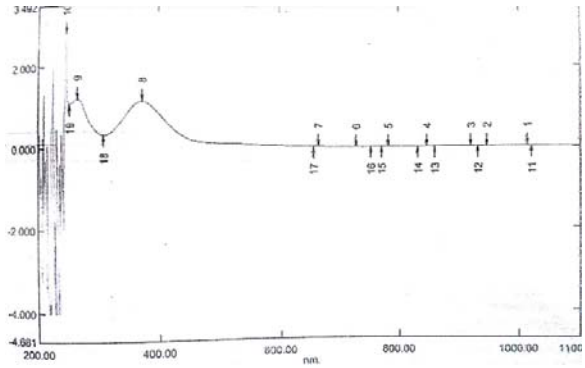

Fig. 3(b). UV-Vis spectra of PANI/SnO_2 10wt%

The SnO_2 doped polyaniline nanocomposite exhibits absorption peaks at 368nm, 313nm, and 266 nm which corresponds to band gap energies 3.3eV, 3.9eV and 4.5eV respectively.

IV. CONCLUSION

PANI/ZnO 10wt% and PANI/SnO_2 10wt% nano composites have been successfully synthesized by in – situ polymerization using chemical oxidation method. The XRD- spectra of composites reveals the crystalline nature. The peak positions differ from ZnO and SnO_2 compared to its composites and this indicates that the modification has occurred in the composite structure. The size of the grains is in the nano-meter range as found out from XRD. The PANI/metal oxide composites are promising materials which may be applicable in optoelectronic devices.

V. ACKNOWLEDGEMENT

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VI. REFERANCES

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