National Conference on Recent Trends in Synthesis and Characterization of Futuristic Material in Science for the Development of Society (NCRDAMDS-2018)
In association with
International Journal of Scientific Research in Science and Technology

Synthesis and Characterization of TiO_2 and SnO_2 Doped Polypyrrole Nano Composites

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ABSTRACT

Polypyrrole and its nano-composites are synthesized using in-situ chemical oxidative polymerization technique using pyrrole monomer. Crystalline nano sized TiO_2 & SnO_2 are embedded in amorphous Polypyrrole in 10% by weight. Ammonium Per Sulphate is used as oxidizing agent for polymerization. The structure of composites was confirmed by the characterization techniques XRD, FTIR and UV Visible spectra.
Average particle size and chain separation is determined from XRD. UV-Visible studies show that the composites exhibit absorption peaks at 678 nm and 267 nm; for PPy/TiO_2 which corresponds to band gap energies 1.836 eV and 4.663 eV respectively. The PPy/SnO_2 doped Polypyrrole nano composite exhibits absorption peaks at 996 nm, 914 nm, 804 nm, 652 nm & 586 nm which corresponds to band gap energies 1.25 eV, 1.36 eV, 1.548 eV, 1.9 eV and 2.12 eV respectively.
Keywords: Polypyrrole, nano-composites, band gap energy, TiO_2, SnO_2.

I. INTRODUCTION

Conducting polymers have widely been studied in the last two decades due to their potential applications as chemical sensors, electrochemical super capacitors, electro-chromic devices, photovoltaics, light-emitting diodes, optical computers, microwave absorbers, batteries etc. In recent years, extensive research has been performed on creating conducting polymer matrix composites with the aim of improving physical and structural properties of conducting polymers. One such class of these, attracting a special attention is to create composites which contain inorganic materials which are usually metals or metal oxides filled into the conducting polymers via various methods.

Experimental parameters such as polymerization method, type of the oxidant and temperature used during preparation of polymeric composites seemed to be of crucial importance in terms of their physical and structural properties. Physical and chemical properties of these inorganic materials should also be well known as these would also play an important role in choosing the most appropriate preparation method for composites. PPy is one of the most extensively studied conducting polymers due to its high electrical conductivity and chemical stability and as well as its easy preparation through chemical and electrochemical oxidation of pyrrole in the organic solvents and in aqueous medium. [1].

In the present study, polypyrrole/titanium di-oxide 10% by weight (PPy/TiO_2) and Polypyrrole/tin oxide 10% by weight (PPy/SnO_2) composites were prepared by chemical polymerization. TiO_2 and SnO_2 which are used as a filler, also have important applications as gas sensors. Samples were characterized by using X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and ultraviolet-visible spectroscopy (UV-vis).

II. EXPERIMENTAL

Pyrrole was supplied by Shah Scientific Mumbai; ammonium peroxydisulphate ($(NH_4)_2S_2O_8$) by Fisher scientific, nitric acid (HNO_3) by Loba; TiO_2 and SnO_2

nano powders by Nanolab, Jamshedpur, Jharkhand. These materials were used without any preprocessing.

In a 40 ml of deionized water 1.2 ml concentrated nitric acid, 2 ml pyrrole and 0.2 gm titanium dioxide (10 % by wt.) were added. The mixture was kept for continuous stirring.

Aqueous solution of oxidant was made by adding 4.5 gm of ammonium per sulphate into 8 ml of deionized water. This solution was added drop wise into a mixture of pyrrole-acid-TiO_2 in half an hour. Gradual change in color from light black to dark black indicated formation of PPy/TiO_2 nano-composite. After addition of APS solution, the stirring was continued at room temperature for four hours and then kept overnight to ensure complete polymerization. The precipitate obtained after polymerization was filtered and washed with deionized water several times. The black colored PPy/TiO_2 powder so obtained was dried at 60°C for 24 hours. [2]

The process was repeated by adding tin oxide (10% by weight) instead of TiO_2.

III. RESULTS AND DISCUSSION

Characterization:

a) XRD

Samples obtained were powdery with black in colour. These were characterized by XRD. The 2θ scans were recorded using Cu Kα radiation of wavelength 1.5418 A in a range of (5-70) degree as shown in Figure1(a) and (b).

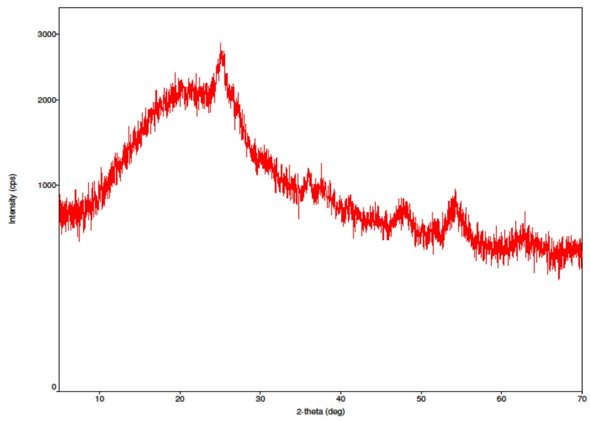

Figure 1(a). X-ray diffraction of PPy/TiO_2(10%)

In the composite PPy/TiO_2 diffraction peaks are found at 2θ values: 24.75. 35.25, 46.5, 53.25 and 62.5 degrees confirming presence of TiO_2. Whereas in case of PPy/SnO_2 diffraction peaks are found at 2θ values: 20.38, 26.47, 33.84, 51.76, 54.73 and 65.60 which confirms presence of SnO_2.

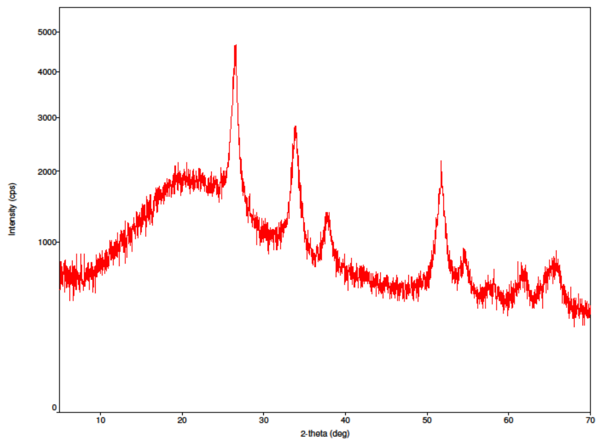

Figure1(b). X-ray diffraction of PPy/SnO_2(10%)

X-ray diffraction pattern shows that crystalline TiO_2 or SnO_2 is embedded in amorphous polypyrrole. Broad peak is found at $2\theta = (26.38)^{\circ}$. Average chain separation can be found from this maxima using the relation,

$$S = 5\lambda / 8 \sin\theta$$

Where S is polymer chain separation, λ is x ray wavelength and θ is the diffraction angle at maximum intensity of amorphous halo. The average chain separation was found to be 4.2196 A°.

The average crystallite size, can be estimated by using a Scherrer's formula.

$$D = K \lambda / \beta \cos\theta$$

Where D is the crystallite size, K is the shape factor, which can be assigned a value of 0.89 if the shape is unknown, θ is the diffraction angle at maximum peak intensity and β is the full width at half maximum of diffraction angle in radians. When applied to sharp peaks, the equation leads to the average crystallite size of about 19.68 nm. [3, 4].

b) FTIR spectra

Infra-red spectroscopy (FTIR) of the composites prepared were performed on Shimadzu FTIR 8201 spectrophotometer between 4000–400 cm $^{-1}$ as shown in Figure2 (a) and (b).

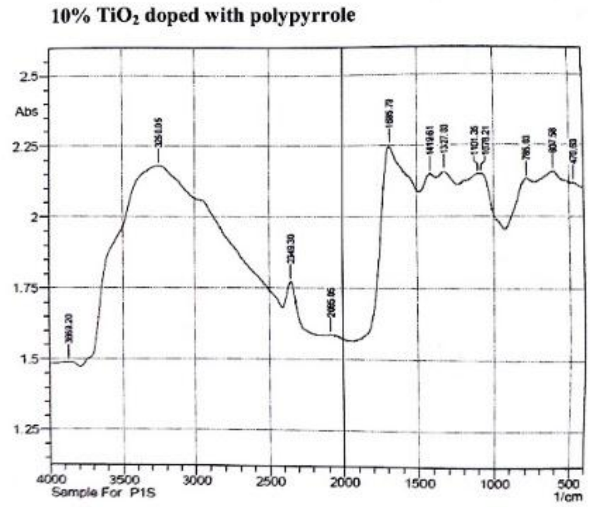

Figure 2(a). FTIR spectra of PPy/TiO_2(10%)

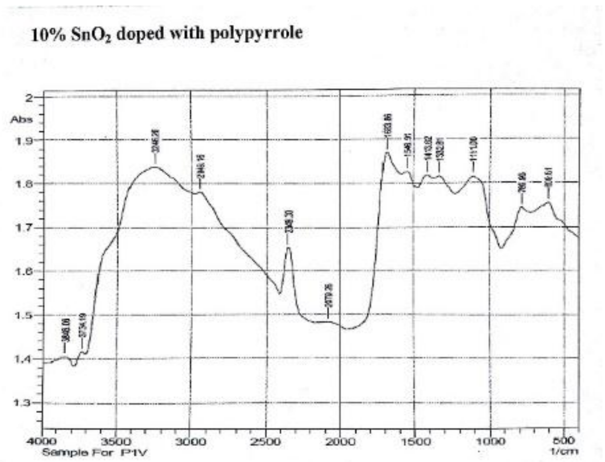

Figure 2(b). FTIR spectra of PPy/SnO_2(10%)

The peaks at around 3846 cm^{-1} indicates N-H stretch, 3248 cm $^{-1}$ indicates C-H stretch, 1684 cm $^{-1}$ indicates C= O stretch, 1419 cm^{-1} indicates pyrrole ring vibrations. 1330 cm^{-1} is related to C-N asymmetric vibration, 1106 cm^{-1} is indicative of =C- H bond vibration, 785 cm^{-1} indicates aromatic C-H bending of pyrrole. 470 cm^{-1} shows stretching vibrations of Ti– O–Ti. [5-9]

c) UV-Vis spectra

Ultra violet spectroscopy refers to absorption spectroscopy is made using Shimadzu UV-vis spectrometer between 200–1000 nm as shown in fig 3 (a) and (b).

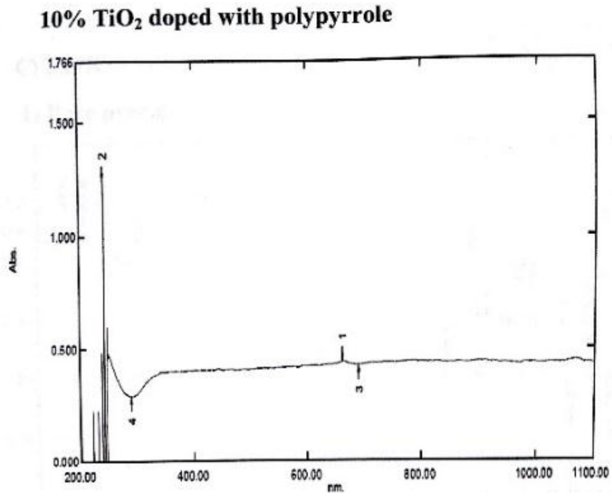

Figure 3(a). UV-Vis spectra of PPy/TiO_2(10%)

Using these spectra the band gap energy can be found out from the formula,

$$E_g = hc/e\,\lambda$$

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). For PPy / TiO_2 UV-Vis spectra exhibit absorption peaks are at 678 nm and 267 nm, which corresponds to band gap energies 1.836 eV and 4.663 eV respectively.

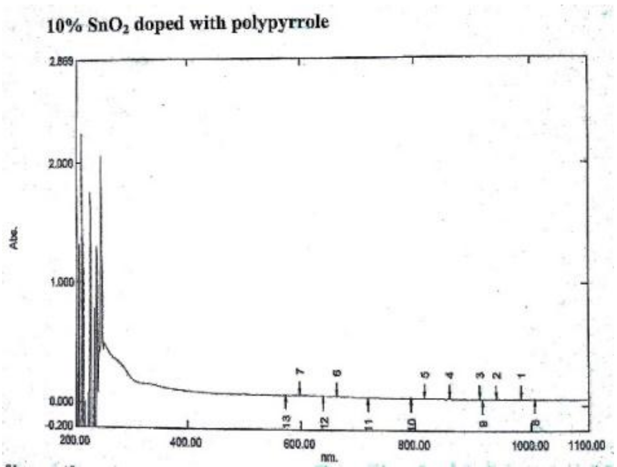

Figure 3(b). UV-Vis spectra of PPy/SnO_2(10%)

For PPy / SnO_2 composite the absorption peaks are at 996 nm, 914 nm, 804 nm, 652 nm and 586 nm which corresponds to band gap energies 1.25 eV, 1.362 eV, 1.548 eV, 1.9 eV and 2.1245 eV respectively.

IV. CONCLUSION

PPy/TiO_2(10%) and PPy/SnO_2(10%) nano-composites were successfully synthesized by in situ chemical oxidative method. The characteristic peaks of PPy /TiO_2 and PPy/SnO_2 nano-composites were observed in XRD, FTIR and UV-Vis spectra. X-ray diffraction pattern shows that crystalline TiO_2 or SnO_2 is embedded in amorphous polypyrrole. The average chain separation and grain size are in the nanometer range. Band gap energies are also evaluated. The PPy/ TiO_2, PPy/SnO_2 nano composites are promising materials which may have applications as gas sensors, optoelectronic devices, etc.

V. ACKNOWLEDGEMENT

The authors are grateful to UGC (WRO, Pune) for the financial support through minor research project.

VI. REFERENCES

[1]. S. Deivanayaki, et al, 2012, Elixir Polymer, 49B, PP 10182- 10185.

[2]. Ersel Ozkazanc, et al, 2013, Polymer Engineering and Science, PP 1131-1137.

[3]. Manik A Chaugule et al, 2011, Soft Nanoscience Letters, Scientific Research, published online, 1, (6-10)

[4]. T. K. Vishnuvardhsn et al, 2006, Bull. Mat. Sci., Vol. 29, No. 1, PP 77-83.

[5]. R Sharmila Devi et al, 2014, International Journal of Innovative Research In Science, Engineering And Technology, Vol. 3, Issue 8, 15206-15211.

[6]. Seyfullah Madakbas et al, 2013, Chemical Papers, 67(8) 1048-1053

[7]. V. Vetrivel et al, 2014-15, International Journal of Chemtech Research,Vol. 7, No. 3, PP 1090-1097.

[8]. Yiqing Lu et al, 1998, Journal of Applied Polymer Science, Vol.70, 2169-2172.

[9]. https://www.chem.wisc.edu/deptfiles/.../Simplified%20IR%20 Correlation %20 Chart.pd.