Synthesis and Characterisation of Polythiophene and (Manganese) Mn Doped Polythiophene Thin Films by Chemical Bath Deposition.

R.S.Futane

Department Of Chemistry, GVISH College , Amaravati 444 604, MS, India

Corresponding Author E-mail- reenashahakar@rediffmail.com

Abstract

Chemical bath deposition method is successfully used for the synthesis of PTh was successfully doped with Mn on glass slide surface using $FeCl_3$ as an oxidant at room temperature. Effect of Mn dopant properties of PTh thin film was then studied. Chemical composition of films was investigated by FTIR spectroscopy. SEM image of composites exhibit nano size grains, a tube like structure formed by the nanoparticles and seems like random network of interconnected bundles.XRD analysis showing little change in crystallinity of the polythiophene. TGA-DTA results indicates composites of polythiophene with Mn are found to be most thermally stable than undopedPTh.

KEYWORDS-Polythiphene, Manganese,Chemical bath Deposition, Morphology.

Introduction

In polymer science, due to interesting chemical and physical properties, conducting polymers have been studied extensively during the last two decades as an important semiconductor material [Karim et al.,2007;Ahn et al.,2007;Daik et al.,2007**]**.Dopant plays an important role in conjugated polymers because these polymers become conductive when charge carriers, generated by dopants are present in their structure [Groenewoud et al.,2002].There are lots of conjugated polymers and one of the most widely studied conjugated polymers is polythiophene, which becomes highly conductive upon doping [Paosawatyanyong et al.,2010].Intrinsic Conductive Polymers ICPs are particularly important because they exhibit good electric conductivity and chemical stability in the ambient atmosphere, and they have revealed numerous areas of application such as materials for battery electrodes [Amanokura et al.,2001], gas sensors [Sotzing et al.,2000], chemical sensors [Lin et al.,1999; Malinauskas et al.,2005; Guernion et al.,2004; Vidal et al.,2003; Dai et al.,2002; Trojanowicz et al.,1997; Trojanowicz et al.,2003],corrosion protection and microwave shielding [Buckley and Eashoo,1996].

Thereare several routes for synthesis of polythiophene thin films the chemical bath deposition method for polythiophene thin films is important, (CBD) method appears most suitable for integration in large scale fabrication process. In present research work weused Mn as a dopant and work covers synthesis of PTh thin films with different %w/v of Mn. Structural investigation and characterization with their properties were determined by using FTIR, SEM, XRD, TGA-DTA techniques.

Materials and Method: Thiophene (AR grade, Merck), iron chloride (Sd-Fine), methanol (CH_3OH), Mn, and chloroform are used for synthesis.

2.1 Preparation of polythiophene and PTh/Mncomposite:

PTh thin films were synthesized by CBD method initially,substrate were washed with deionized water, boiled in chromic acid and washed with detergent, rinsed in acetone before deposition of thin film.Monomer solution was prepared by dissolving 0.1 M of thiophene in chloroform, oxidant solution was prepared in a glass beaker with 0.5 M concentration of $FeCl_3$ in chloroform the ratio of monomer to oxidant was kept 1:5 0.5% and1% w/v Mn added in oxidant solution. Substrates were immersed in bath at constant stirring. Monomer solution was added drop wise in an oxidant solution reaction being carried out at room temperature. During precipitation, heterogeneous reaction occurred and deposition of polythiophene took place on substrate, films were removed after a time interval of 1 h from the bath, washed with methanol followed by chloroform and acetone repeatedly to remove residual oxidant and unreacted monomers. Dried in air and preserved in an airtight container.

Results and Discussion:

3.1 Fourier Transform Infrared (FTIR) investigation

IR studies of undopedPTh and PTh/Mn composites synthesized in present research work are given in Fig-1,2,3.

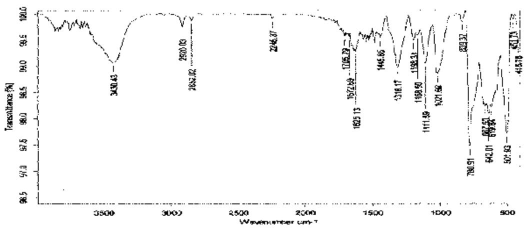

Fig. 1 : FTIR of PTh film.

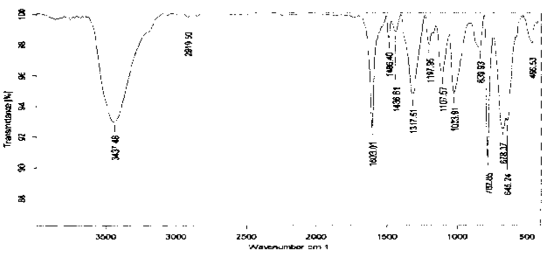

Fig. 2: FTIR of PTh /0.5w% Mn film.

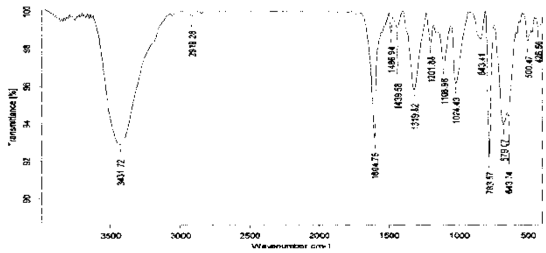

Fig. 3: FTIR of PTh /1 w% Mn film.

Absorption band in region 2920.03 cm^{-1} is due to aromatic C=C-H strech frequency of PTh which is shifted to ranges 2919.50 cm^{-1} and 2919.28 cm^{-1} in PTh/Mncomposite. Band in region 1625.13 cm^{-1} is due to aromatic C=C stretching frequency of undopedPTh which is shifted to the ranges 1603.01 cm^{-1}, 1604.75 cm^{-1}. Peak at 1318.17 cm^{-1} for PTh is assign for C-C stretching frequency are shifted to 1317.51 cm^{-1}, 1319.82 cm^{-1}. Absorption band in region 780.91 cm^{-1} is due to C-S stretching frequency of pure PTh which is shifted to ranges 782.85 cm^{-1}, 783.57 cm^{-1}. In PTh/Mncomposite absorption peak at lower frequency 466.53.

3.2 SEM Analysis:

SEM images of thin film are shown in Fig 4,5 and 6. (SEM) of undoped and Mn doped PTh thin films shows nanoparticles agglomerated with micropores in between the size of the agglomeration is found to be increased.A tube like structure formed by the nanoparticles and seems like random network of interconnected bundles. If the dopant concentration increases it gives fiber's like structure.

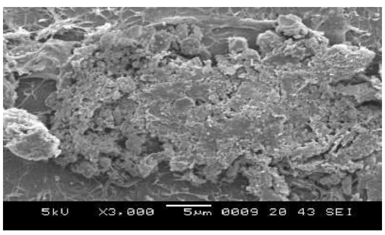

Fig 4: SEM of PTh film.

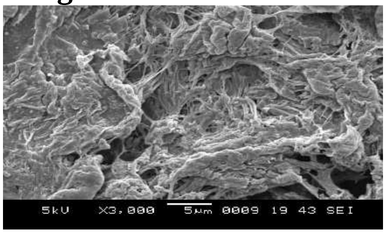

Fig. 5: SEM of 0.5% Mn film.

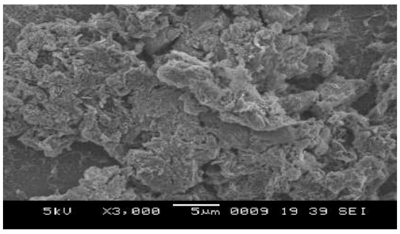

Fig.6:SEM of 1%w/vMn.

3.3 XRD Studies:

A typical XRD pattern obtained for composites are shown in Fig-7,8,9. In undopedPTh only one broad peak observed suggesting amorphous nature of PTh in PTh with different w/v% of Mn composite only one intense peak observed at 2 theta =35.07 showing little change in crystallinity of the PTh after addition of different w/v% of Mn.

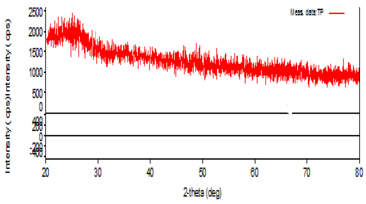

Fig.7: XRD of Pure PTh.

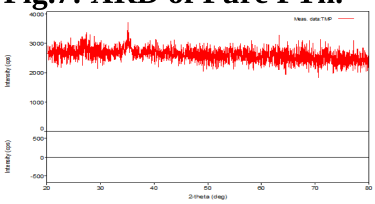

Fig.8:XRD of 0.5%Mn PTh.

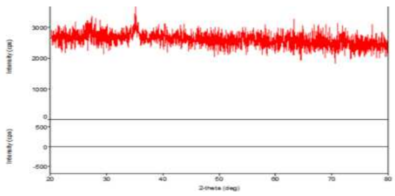

Fig.9:XRD of 1%Mn PTh

DTA analysis

TGA was performed on RigakuTG-8121 thermalanalyser with Pt pan in temperature range from room temperature to 550^{o}C.Thermogram of composite as shown in Fig.10,11,12.Three major weight losses are observed one around 50-80°C weight loss about 1-3% due to elimination of moisture, evaporation of solvent as well as unreacted monomer second weight loss around 280-300°C is due to loss of dopant component of polythiophene. Third major drop in weight observed at 350-400°C and beyond the range is due to degradation of polythiophene itself. DTA shows two exothermic maxima at near about 400° and 450°C.

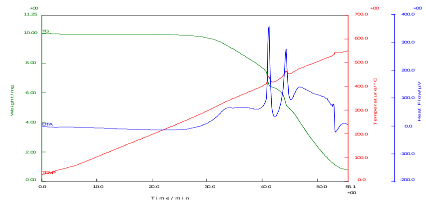

Fig.10:TGA of PTh.

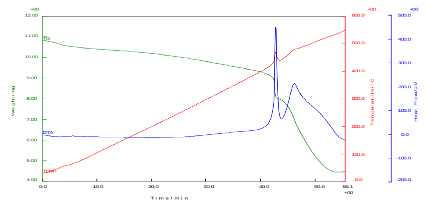

Fig.11:TGA curve of 0.5%Mn.

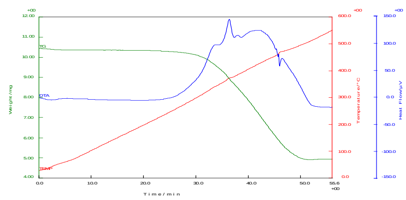

Fig.12 :TGA curve of 1%Mn

Conclusion

We have demonstrate successful synthesis of nanostructure PThandPTh/Mn composite thin film by CBD technique.The result of FTIR proved the formation of polythiophene. Morphology of thin film were analysed by SEM it shows change in morphology after doping.XRD shows showing little change in crystallinity of the polythiophene after addition of different w/v% of Mn.Thermal properties of nanocomposites were investigated by TG-DTA analysis shows composites of polythiophene are found to be more thermally stable than pure PTh.

Acknowledgement: Authors are thankful to the Director of G V I S H Amravati for providing facilities during the research work.

References

1- Karim M.R, Lim K. T.,Lee C. J., and Lee M.S.,Synthetic metal.,Vol.157, **2007**,1008-1011.

2- AhnS.H, CzaeM. Z, KimE. R., and Lee H., Macromolecules.,Vol.34, **2007**, 2522-2527.

3- Daik R. and Maniam S., Malaysian Journal of Chemistry,Vol.9, **2007,** 16-19.

4- Groenewoud L. M. H., Weinbeck A. E., Engbers G. H. M., J. Fejjen Synthetic metal,Vol.126**, 2002,** 143-145.

5- Paosawatyanyong B., Kamphiranon P., Bannarakkul W., Srithana-anant Y., Bhanthu Mnavin W. Surf. Coat. Technol,Vol.204, **2010,** 3053-3055.

6- Amanokura J., SuzukiY., ImabayashiS., and WatanabeM. J. Electrochem. Soc.,Vol. 43, **2001,** 148-151**.**

7- SotzingG. A., BriglinS. M., rubbsR. H**., and LewisN. S.,Anal. Chem.,Vol.72, 2000, 3181**.

8- LinC. W., HwangB. J., and LeeC. R.,J. Appl. Polym. Sci.,Vol.73, **1999,** 2079-2081.

9- Malinauskas A.,MalinauskieneJ.,andRamanaviciusA.,Nanotechnol.,Vol.16, **2005,** 51-54**.**

10- Guernion N. J. L. and Hayes W., Curr. Org. Chem.,Vol. 8,**2004,** 637-639.

11- VidalJ. C., Garciaruiz E., and Castillo J. R., Microchim. Acta.,Vol.143, **2003,** 93-97.

12- DaiL. M., Soundarrajan P., and Kim T., Pure Appl. Chem.Vol.74**, 2002,** 1753-1756.

13-Trojanowicz M., VelkrawczykT.K., and Alexander P. W., Chem. Anal.,Vol. 42,**1997,** 199-203.

14- Trojanowicz M., Microchim. Acta.,Vol.143,**2003,** 75-77.

15- Buckley L. J. and Eashoo M., Synth. Met.,Vol.78, **1996,** 1-4**.**