Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 2(3), 2012, 413-418
ISSN 2277-2669

SYNTHESIS AND DC CONDUCTIVITY OF POLYPYRROLE/SnO_2 NANOCOMPOSITES

M. S. BHENDE[a], R. S. BOBADE[a], S. P. YAWALE[b] and S. S. YAWALE[*]

Govt. Pre-Indian Administrative Services Training Institute, NAGPUR – 440001 (M.S.) INDIA
[a]First Year Engineering Department, Prof. Ram Meghe Institute of Technology and Research, BADNERA (M.S.) INDIA
[b]Department of Physics, Govt.Vidarbha Institute of Science & Humanities, AMRAVATI – 444604 (M.S.) INDIA

(*Received : 17.02.2012; Revised : 14.03.2012; Accepted : 23.03.2012*)

ABSTRACT

Conducting polymer composites of polypyrrole/tin oxide (PPy/SnO_2) are synthesized by *in-situ* polymerization of pyrrole with SnO_2 using $FeCl_3$ as an oxidant. The SnO_2 was varied in five different wt. % of SnO_2 in PPy/ SnO_2 composites. The dc conductivity and impedance were studied. It was observed that the values of conductivities increase up to 20 wt. % of tin oxide in polypyrrole and decreases thereafter. It reveals that the SnO_2 concentration in PPy is responsible for the variation of conductivity of the composites. The grain size of SnO_2 is found to be of the order of 10 to 20 nm and of polypyrrole is 200 to 500 nm by TEM analysis techniques.

Key words: Tin oxide, Polypyrrole composite, Impedance, DC Conductivity, Surface morphology.

INTRODUCTION

The conducting polymers have emerged as a new class of materials because of their unique electrical, optical and chemical properties. By proper doping the conductivity of these materials can be varied from semiconducting to metallic regime, which has offered new concept of charge transport mechanism. Researches in the field of such polymers aim mainly at some suitable modifications of existing polymers, so that their applicability can be improved. Some of these modifications involve preparing hybrid materials in which organic materials and inorganic oxides or salts of different metals, viz. SnO_2 (Bhattacharya *et al.* 1996), CeO_2 (Galembeck and Oswaldo 1997), V_2O_5 (Harreld *et al* 1999), TiO_2 (Su and Kuramoto 2000), fly ash composites (Raghavendra *et al* 2003), Fe_3O_4 (Chen *et al* 2003, *Zhong et al 2008*), ZrO_2 (De *et al* 2004) Fe_2O_3 (Zhanhu et al 2009) etc. combine in some special fashion with the conducting polymers to give rise to the composites. In almost all the cases some specific nature of association between the two components has been observed. Polypyrrole is an important conducting polymer with high electrical conductivity, appreciable environmental stability (Chen *et al* 1997) and photoluminescence properties (Shuxiang et al 2011), PPy/ SnO_2 composition gives very good results in gas sensing (Waghuley 2011). The present study deals with the synthesis & characterization of PPy/SnO_2 composites and evaluation of dc and ac conductivity for different wt. % of SnO_2 in PPy composites with an intension to know the effect of SnO_2 doping. The characterization of the composites has been done by TEM analysis techniques.

---

[*]Author for correspondence; E-mail: ms.bhende@rediffmail.com

EXPERIMENTAL

Materials

Anhydrous iron (III) chloride (FeCl3) from Fischer (AR-grade), methanol, stannous chloride ($SnCl_4$) and pyrrole from SD-Fine chemicals (AR-grade) are obtained and used in the present study. Pyrrole monomer is purified by distillation under reduced pressure and stored at 4°C in the absence of light.

Synthesis of PPy

Polymerization of pyrrole monomer was carried out in chemical oxidative environment. 0.1 M of $FeCl_3$ is added in 100 mL of methanol. After complete dissolution, about 0.2 mole of pyrrole is inserted drop wise under constant magnetic bar stirring for 4h.The resulting black precipitates are filtered and washed with copious amount of distilled water until the washings are clear. PPy so obtained is dried by keeping in oven at 60^0 C for 3 h. The yield of PPy is 79%.

Synthesis of nano SnO_2

0.1 M of stannous chloride dehydrate is dissolved in 100 mL water. After complete dissolution, about 4 ml ammonia solution is added. White gel precipitate is immediately formed. It is allowed to settle for 24 h. Then it is filtered and washed with water 2-3 times so that clear solution is obtained. The obtained mixture is dried for 24 h at 70^0C. Dried powder is crushed and heated at 600^0C for 4 h.

Synthesis of PPy/ SnO_2 composites

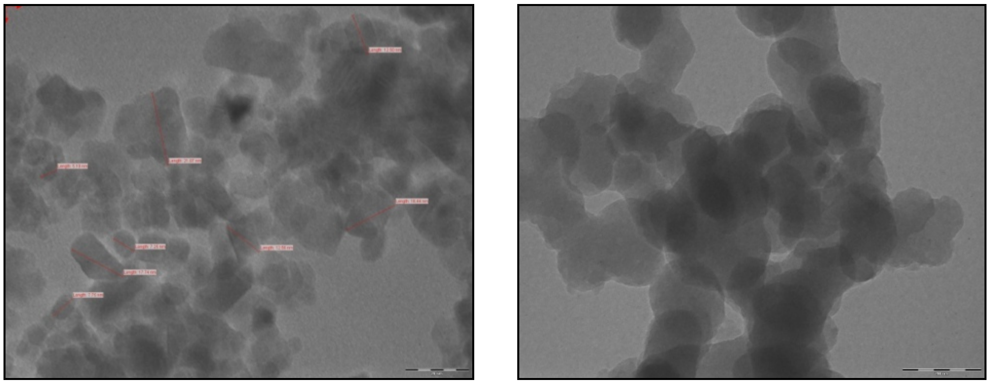
Chemically polymerized polypyrrole and its tin oxide (SnO_2) composites are obtained by oxidative polymerization by using $FeCl_3$ as oxidant in aqueous medium. 0.1 M of $FeCl_3$ is added in 100 mL of methanol. 0.02 mole pyrrole monomer is added drop wise in solution under constant magnetic bar stirring. During stirring, 10% of SnO_2 is added. Then it is stirring continuously for a 4 h. Greenish black precipitate is formed. It is allowed to settle for 5-6 h. Then it is filtered and washed with water 3-4 times to remove last traces of unreacted pyrrole so that clear solution is obtained. The obtained precipitate is dried for 2-3 h at 50^0C. This approach promotes molecular level mixing of precursor and the polymerization of initiators of both networks. The tin oxide is varied in wt% as 10, 20, 30, 40 and 50% and added to the PPy solution.

The composites obtained are characterized by transmission electron microscopic (TEM) techniques. The powders of PPy and PPy/SnO_2 so obtained are crushed and finely ground in agate mortar. The composite powders are pressed to form pellets of 10 mm diameter and 1–2 mm thickness by applying pressure in hydraulic press. Copper electrodes are placed on opposite sides of the sample to obtain good contacts. The electrical conductivity of PPy and PPy/ SnO_2 composites are measured using Wayne Kerr 4230 LCR meter in the frequency range 0.1 to 200 KHz at different temperatures. DC electrical conductivity of samples was measured by standard fro-probe technique at temperature ranging from 313ºK to 383ºK.

RESULTS AND DISCUSSION

Transmission electron microscopy

Fig. (1a and b) shows the TEM picture of pure PPy and pure SnO_2. Very high magnification of TEM images shows the presence of spherical ball like morphology. These balls are connected each other in chain like form. Tin oxide particles are of spherical nature to form multiparticle aggregates, presumably because of weak antiparticle interactions. The grain size of SnO_2 is also found to be from 10 to 20 nm and of polypyrrole are 200 to 500 nm.



DC conductivity

The temperature dependence of conductivity of PPy and PPy/ SnO_2 composites is presented in the form of Arrhenius plots which shows a straight line in Fig. 2. The conductivity of composites increases with increase in temperature. The room temperature conductivity varies with SnO_2 composition. It shows maximum conductivity to 20% wt. % of SnO_2 (Fig. 3). The DC conductivity of PPy is 5.44 x 10^{-3} S cm^{-1} while in PPy/SnO_2 composites it decreases dramatically from 4.89 x 10^{-4} to 8.25 x 10^{-7} S cm^{-1} at 343ºK. The appreciable linear decrease in DC conductivity may be due to the loss of moisture by the samples, since conductivity depends on the moisture content and environmental humidity (Trravers and Nechtschein 1987; Javedi et al 1988).

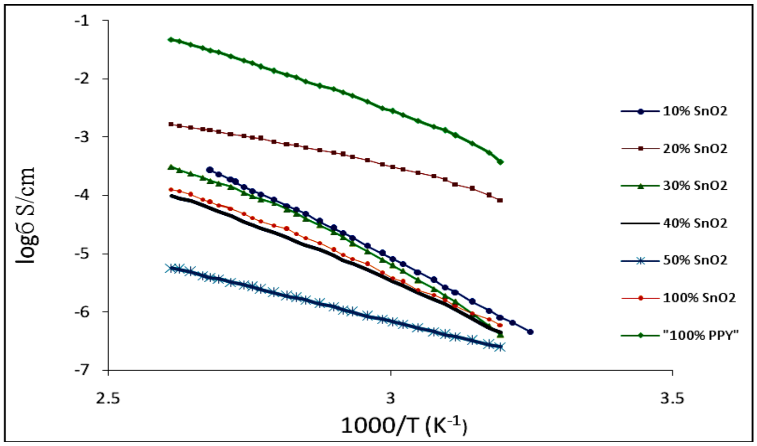


Fig: 2: Variation of log 6 with inverse temperature for different wt. of SnO_2 and pure SnO_2 and Pure PPy

Low DC conductivity of pure PPy is due to the random orientation of its particles, poor link among the polymer chains through the grain boundaries and compactness. In this respect increasing semiconducting SnO_2 content means better conjugation, an improvement in compactness and coupling through the grain boundaries to facilitate the charge motion (Vishuvardhan et at 2005). The PPy/ SnO_2 composites are inhomogeneous because of dispersion of SnO_2 particles in the polymer composites. In the present study, composites are synthesized in identical conditions by *in situ* polymerization of pyrrole in the presence of SnO_2. So the microscopic conductivities remain almost the same but the physical (macroscopic) properties viz. compactness and molecular orientations, may significantly vary due to the variation in the wt. % of SnO_2 in the composites. The activation energy is evaluated from the log 6 vs 1/T plot. The variation of activation energy with SnO_2 composition shown in Fig. 4. It is observed that the activation energy is found to be less i.e. 0.184 eV for 20 wt. % of SnO_2 nanocomposites. The trend of the conductivities of conducting polymer/ oxide composites is also same in case of polyaniline/fly ash (Raghavendra *et al* 2003). They explained conductivity on the basis of the electron hopping mechanism. In all their studies, there is not much variation in the conductivity.

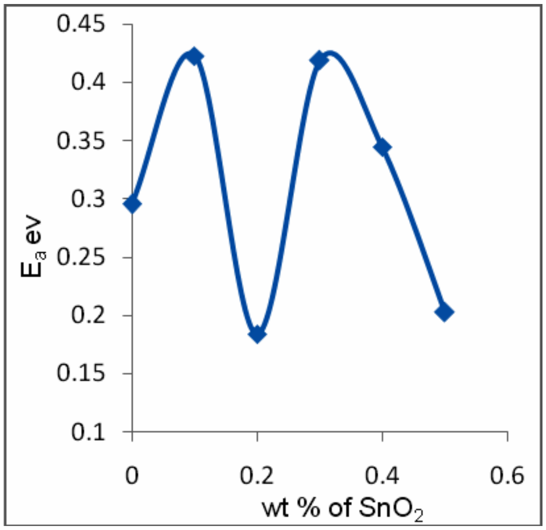


Fig. 3: Variation of log б for different wt. of SnO_2

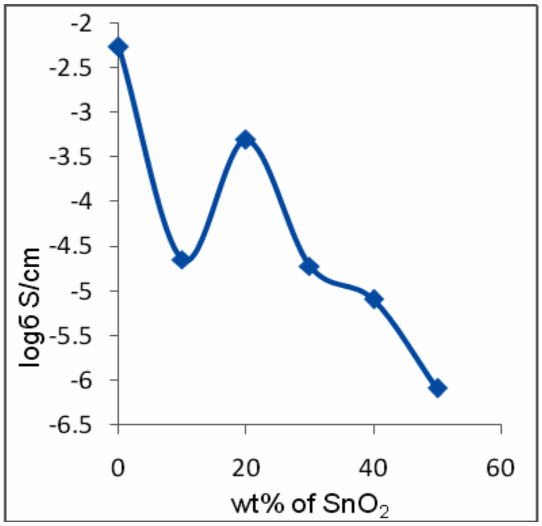


Fig 4: Variation of activation energy with wt. % of SnO_2

Impedance spectroscopy

The optimized sample 20% SnO_2 is selected for the study of impedance characterization. At different temperatures the real and imaginary components of impedance are measured. The complex impedance plots are shown in Fig. 5.

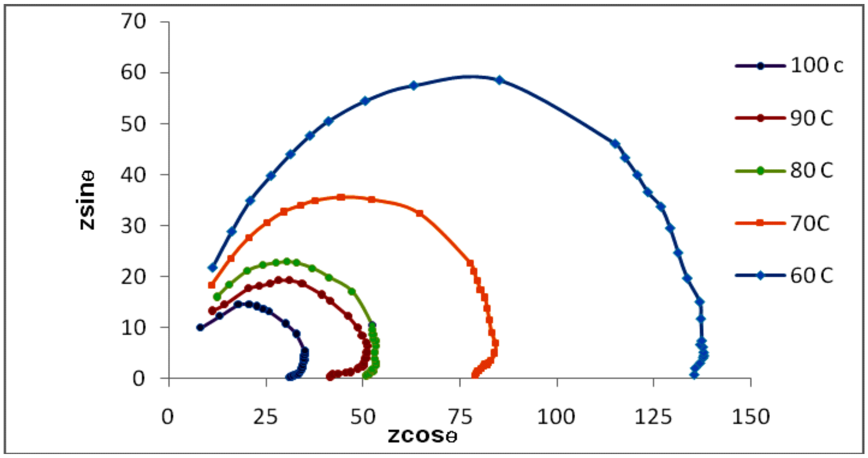


Fig. 5: Complex impedance plot for 20 wt% of SnO_2

The complex impedance plot shows semicircle, indicates single relaxation behavior. The Debye type molecular interaction is observed. The value of bulk resistance at 60ºC is found to be 160Ω. The relaxation time Ʈ is calculated at the apex of semicircle which is found to be 0.807sec (Fig. 6 & 7). A single semicircle suggests monodispersive relaxation. As seen from the Fig. 5 no grain boundaries and grain resistance were observed.

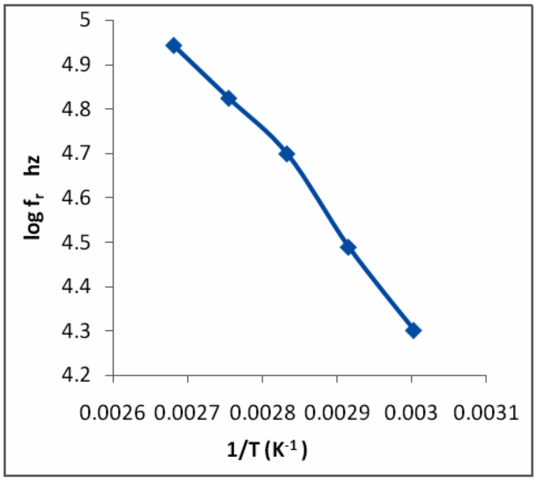


Fig. 6: Variation of zsinɵ with different log f

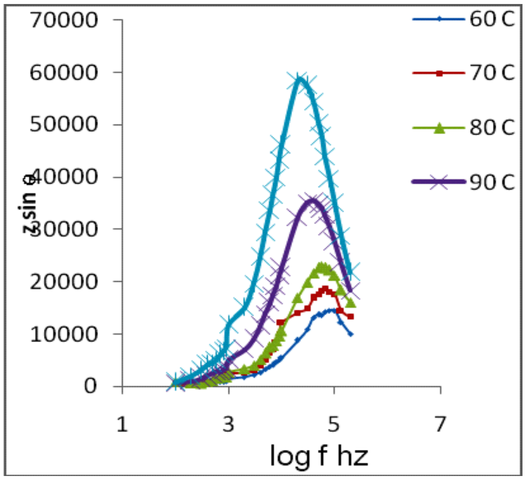


Fig. 7: Variation of peak frequencies with (1/T)

CONCLUSION

Highly conducting nano PPy/ SnO_2 composites are prepared by in-situ polymerization in the presence of SnO_2. These composites are characterized by TEM techniques. The TEM photographs of PPy and SnO_2 clearly show the presence of spherical molecules of the order of 200 to 500 nm and10 to 20 nm respectively. Our results on conductivity for various wt. % of SnO2 in PPy are interpreted in terms of the formation of polarons. PPy/ SnO_2 with 20 wt. % of SnO_2 shows higher value of conductivity among other composites.

ACKNOWLEDGEMENT

Authors are very much thankful to the Director, Govt. Vidarbha institute of science and Humanities, Amravati, for providing laboratory facilities.

REFERENCES

1. A. Bhattacharya, K. M. Ganguly, A. De and S. Sarkar, Mater. Res. Bull., **31**, 527 (1996).
2. X. B. Chen, J. P. Issi and J. Devaux, J. Polym. Sci., **32**, 1515 (1997).
3. W. Chen, L. Xingwei, X. Gi, W. Zhaoquang and Z. Wenquing, Appl. Surf. Sci., 218 216 (2003).
4. De Amitabha, D. Ajay and L. Susanta, Synth. Met., **144**, 303 (2004).
5. A. Galembeck and L. A. Oswaldo, Synth. Met. 84, 151 (1997).
6. J. H. Harreld, B. Dunn and L. F. Nazar, Int. J. Inorg. Mater., **1**, 135 (1999).
7. S. C. Raghavendra, S. Khasim, M. Revanasiddappa, M. V. N. Ambika Prasad and A. B. Kulkarni, Bull. Mater. Sci., **26**, 733 (2003).
8. H. H. S. Javedi, M. Angleopoulos, A. G. MacDiamid and A. J. Epstein, Synth. Mater. Sci., **26** (1988).
9. Mu Shuxiang, Dezhen Wu Shengli Qi and Zhanpeng Wu, J. Nano, Met., **10**, 1155 (2011).
10. Su Shi-Jain and N. Kuramoto, Synth. Met., **114**, 147 (2000).

11. J. P. Trravers and M. Nechtschein, Synth. Met., **21**, 135 (1987).
12. T. K. Vishuvardhan, V. R. Kulkarni, A. C. Basavaraj and S. C. Raghuvendra, Bull. Mat. Sci., **29**, 77 (2005).
13. S. A. Waghuley, J. Ele. Dev., **10**, 433 (2011).
14. Zhanhu Guo, Koo Shin, Amar B. Karki, David P. Young, Richard B. Kaner, David P. Young Richard B. Kaner and H. Thomas Hahn, J. Nanopart Res., **11**, 1441 (2009).
15. W. Zhong, P. Liu, H. G. Shi and D. S. Xue, Int. J. Electrochem. Sci., **3**, 1117 (2008).