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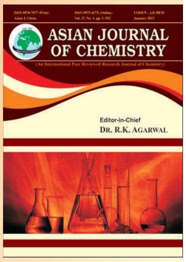

Electrical and Optical Properties of Synthesized Composite Material Polyaniline-Ti(IV) Arsenophosphate

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Nanocomposite material polyaniline-Ti(IV) arsenophosphate with varying concentration of inorganic precipitate [Ti(IV) arsenophosphate] have been synthesized by employing the sol gel method. Prepared samples were characterized by scanning electron microscopy and transmission electron microscopy. Optical absorption spectra was recorded by using UV-visible absorption spectral techniques. From the analysis of absorption spectra, observed band gap for the different samples was found to be in the range of 3.12 to 3.60 eV. Electrical conducting studies show that conductivity of nanocomposites increases with increase in temperature, which is the observed behaviour of semiconductor materials.

Keywords: Synthesis, Nanocomposite, Conductivity, Optics.

INTRODUCTION

Conducting polymers (CPs) have potential applications in many areas such as electrochemistry, electromagnetic systems, electronics, electromechanical systems, electroluminescence and sensors. Polyaniline and its derivatives have received much attention because of their various technological applications such as solar cells, electromagnetic shielding, electrodes for rechargeable batteries and sensors[1-7]. Reversible proton doping, high electrical conductivity and ease of bulk synthesis make polyaniline a suitable candidate for its environmental applications.

Recently heterogeneous conducting polymer composites, especially organic-inorganic composites, became the subject of extensive study. Organic/inorganic nanocomposites are extremely promising for applications in light-emitting diodes, photodiodes, photovoltaic cells, smart microelectronic device and gas sensors[8]. The properties of nanocomposites films can be adjusted by varying the composition. Their fabrication shares the same advantages of organic device technology, such as low cost production and the possibility of device fabrication on large area and flexible substrates. The most widely studied conducting polymers are polypyrrole, polyaniline, polythiophene *etc*. Among all these, polyaniline is one of the most extensively studied conducting polymer. Polyanilines exist in a variety of protonation and oxidation forms. The most important form of polyaniline is green protonated emeraldine which is produced by oxidation polymerization of aniline in aqueous acids. It is electrically conducting due to the presence of cation radicals in its structure. The positive charge on aniline units is balanced by negatively charged counter ions, mostly chloride ions[9,10]

The incorporation of inorganic matrix into conducting polymers leads to interesting physical properties and important applications in different fields and therefore can be successfully used as a sorbent[11] ion-exchanger[12,13], catalyst[14], ion selective electrode[15] and also in the host guest chemistry[16]. Reports have also been published regarding the incorporation of metal nanoparticles constituting gold[17-19], copper[20,21], platinum[22,23] and palladium[24,25] into conducting polymers such as polyaniline or substituted polyaniline. The present paper reports the conducting and optical properties of composite material polyaniline-Ti(IV) arsenophosphate.

EXPERIMENTAL

Reagents used for the synthesis were titanium tetrachloride, carbon tetrachloride, sodium arsenate, aniline, potassium persulfate and perchloric acid (E-Merck and Central Drug House, India). Other chemicals and reagents were of analytical grade and used as received without further purification. Titanium tetrachloride was prepared in CCl_4 while 10 % aniline and 0.10 M potassium persulphate solutions were prepared in 1 M HCl. Solutions of orthophosphoric acid (0.10 M), sodium arsenate (0.20 M) were prepared with demineralized water.

Synthesis of polyaniline: The polymerization of aniline was initiated by adding potassium persulphate into 10 % solution of aniline in 1:1 ratio while maintaining the temperature below 10 °C under constant stirring for 1 h[26] a dark green gel of polyaniline was obtained.

Synthesis of polyaniline-Ti(IV) arsenophosphate: Different samples of polyaniline-Ti(IV) arsenophosphate composite were synthesized by adding polyaniline gels (stock solution of 10 % polyaniline) to the solution of inorganic precipitate [Ti(IV) arsenophosphate] in different weight ratios (5, 10, 15, 20, 25 wt. %) and mixed thoroughly with constant stirring for 1 h. The green gel so obtained was kept overnight at room temperature for digestion. Afterward, it was filtered and excess acid was washed with demineralized water and then dried in an oven at 45 ± 2 °C. The dried material is converted into H^+ form by treating with 1 M nitric acid solution with occasional shaking and finally dried. The material was fruitfully applied for their conducting and optical properties.

A digital pH meter Elico (EL-10, India) was used for pH measurements, four-in-line-probe electrical conductivity-measuring instrument (Scientific Equipment India) was used for measuring the DC electrical conductivity. UV-visible spectrophotometric experiments were carried out using a Shimadzu UV-1601 spectrophotometer. The external morphology of composite material was characterized by scanning electron microscopy, SEM (SEM; LEO, 435 VF). Transmission electron microscopy (TEM) analysis was carried out by Jeol H-7500 Microscope.

Electrical conductivity measurements: A fixed amount of composite material (300 mg) was finely grounded and pellets were made at a pressure of 25 kN. The thickness of pellet was measured by a micrometer. Electrical conductivity measurements were performed at room temperature by using a four-in-line-probe DC electrical conductivity-measuring instrument.

RESULTS AND DISCUSSION

To study the conducting and optical properties of polyaniline-Ti(IV) arsenophosphate, diifferent samples were prepeared by varying the percentage of inorganic precipitate [Ti(IV) arsenophosphate]. As it is observed from Table-1 that mixing volume ratios of reactants affect ion exchange capacity and yield of composite material. On increasing the amount of inorganic precipitate, ion exchange capacity of composite material increases, due to increase in number of ionongenic group (ionogenic group is the inorganic part of the material to which counter ions are attached).

Morphological characterizations: SEM image depict irregular morphology (Fig. 1a) of the composite material. TEM studies revealed that the composite material shows particle size in the range of 20 nm. Thus, it can be considered as nanocomposite material (Fig. 1b).

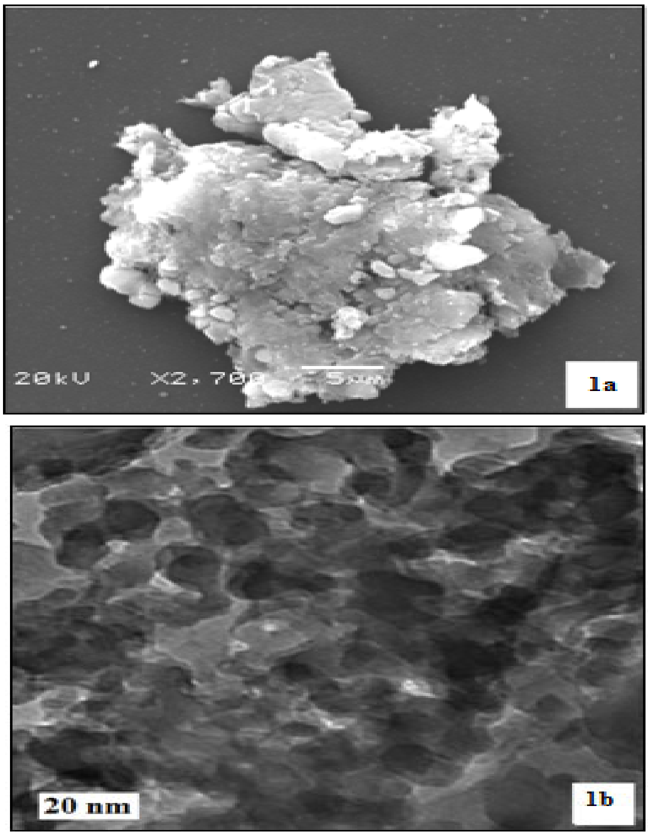

Fig. 1. (a, b) SEM and TEM images of composite material polyaniline-Ti(IV) arsenophosphate

DC Electrical characterization: The electrical conductivity of polyaniline and polyaniline-nanocomposite samples were measured at room temperature by using four-in-line-probe DC electrical conductivity-measuring instrument. Conductivity results reveal a variation in electrical conductivity of the prepared samples of nanocomposite [varying percentage of Ti(IV) arsenophosphate] with temperature (Fig. 2). It was found that conductivity increases with an increase in temperature, showing a semiconductor behaviour. DC conductivity

TABLE-1
SYNTHESIS OF POLYANILINE-Ti(IV) ARSENOPHOSPHATE COMPOSITE MATERIAL WITH VARYING PERCENTAGE OF INORGANIC PRECIPITATE

Samples	Stock solution (10 % polyaniline) (mL)	Ti(IV) arsenophosphate (wt. %)	Yield (g)	IEC (meq g^{-1})
E-0	100	0	0.40	0.82
E-1	100	5	1.17	0.91
E-2	100	10	1.37	1.0
E-3	100	15	2.77	1.7
E-4	100	20	1.55	1.10
E-5	100	25	2.30	1.13

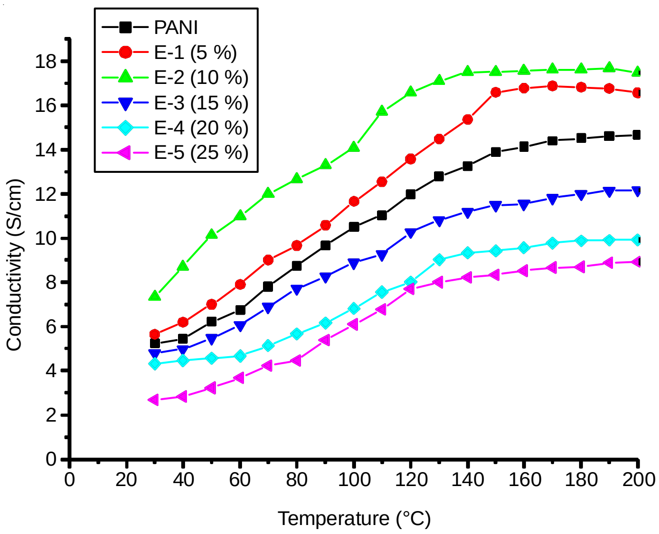

Fig. 2. Temperature dependence of the electrical conductivity of polyaniline and polyaniline Ti(IV) arsenophosphate

of a conjugated polymer depends on the doping level and for a given dopant in a particular polymer, the conductivity increases up to a certain level and then saturates. It is evident from Fig. 3, that the electrical conductivity of doped polyaniline is much higher in magnitude than pure polyaniline, which is due to the fact that increased percentage of inorganic acid (up to 10 %) lead to the reduction of the conjugated lengths in the polyaniline chains and one more reason behind is that it acts as a more efficient network for the charge transport. Further increase in percentage of inorganic acid (content 15-25 %) leads to decrease in conductivity, because a higher percentage of inorganic precipitate hinders the carrier transport between conjugated chains of polyaniline[27,28].

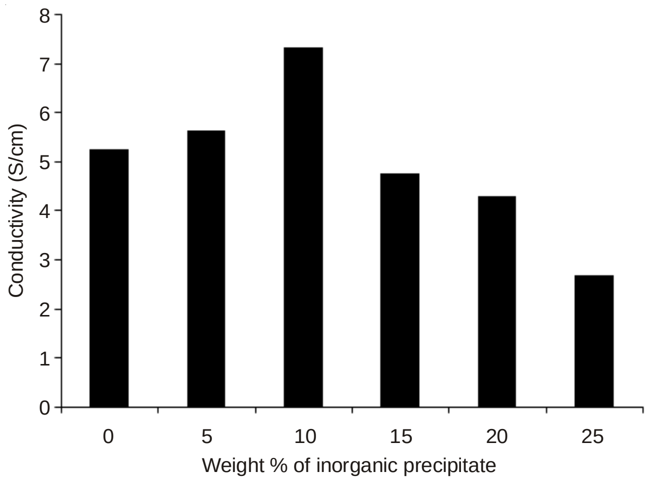

Fig. 3. Electrical conductivity *versus* the varying percentage of inorganic precipitate in nanocomposite

Optical properties: UV-visible spectroscopy was employed to characterize the optical properties of the various synthesized nano-composite materials. The optical absorption spectra of poly-aniline and doped polyaniline-nano-composite was recorded at room temperature using UV-visible spectrophotometer (Shimadzu UV-1601). From these spectra optical constants such as optical band energy gap have been determined.

The absorbance in aromatic compounds is due to the $\pi \rightarrow \pi^*$ transitions and it tend to be sensitive to the change in the environment around the phenyl ring[29]. The occurrence of peaks in the visible region is due to the presence of defect levels below the conduction band[30,31]. In Fig. 4 hyperchromic shift is observed for doped sample(10 %). This red shift of the absorption transition to higher wavelength is due to the successful interaction of Ti(IV) arsenophosphate with the polyaniline chains. This characteristic features of absorption spectrum indicate that polyaniline- Ti(IV) arsenophosphate is in the conducting state. Optical absorption spectrum is an important tool to obtain optical energy band gap of crystalline and amorphous materials. The fundamental absorption, which corresponds to the electron excitation from the valence band to the conduction band, is used to determine the nature and value of the optical band gap. Tauc[32] and others[33] put the empirical relation between the optical energy gap and energy of incident photon which is:

$$\alpha h\nu = A(h\nu - E_g)^n$$

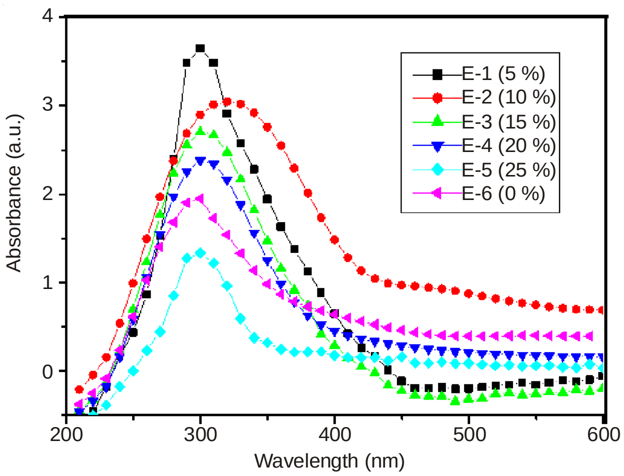

Fig. 4. UV spectra of polyaniline and different samples of polyaniline-Ti(IV) arsenophosphate nanocomposite

where α is the absorption coefficient, ν is the frequency, h is the Planck's constant, A is a constant and E_g is the optical energy band gap between the valence and the conduction bands and n is the power that characterizes the transition process, which assumes the values1/2, 3/2, 2 and 3 depending on the nature of electronic transition responsible for absorption. n is equal to 1/2 for direct allowed transitions. Therefore, by plotting a graph between $(\alpha h\nu)^2$ and $h\nu$, a straight line is obtained which gives the value of direct bandgap and their corresponding values are given in Table-2. As it is evident from Table-2 that

TABLE-2
BAND GAP ENERGY OF POLYANILINE-Ti(IV) ARSENOPHOSPHATE COMPOSITE MATERIAL

Composite material with varying amount of inorganic precipitate	Band gap (eV)
E-0 (PANI)	2.70
E-1 (5 %)	3.30
E-2 (10 %)	3.12
E-3 (15 %)	3.20
E-4 (20 %)	3.58
E-5 (25 %)	3.60

the value of optical band gap E_g decreases with increase in percentage of inorganic precipitate [Ti(IV) arsenophosphate] up to 10 %, after that further increase in dopant concentration leads to increase in the value of band gap[34]. The bandgap of pure polyaniline is 2.70 eV whereas the bandgap of the nanocomposite material with varying percentage of Ti(IV) arsenophosphate (5, 10, 15, 20 and 25 %) ranges from 3.12 to 3.60 eV. Increase in conductivity of the composite material leads to decrease in the band gap (up to 10 %) as a consequence of which red shift is observed in the absorption peak. Further increase in 10 % dopant concentration increase the value of band gap which is due to the aggregation of dopant in the host matrix which impede the motion of charge carrier in between the polyaniline chains.

Conclusion

Nanocomposite material polyaniline-Ti(IV) arsenophosphate was prepared by *in situ* chemical polymerization of aniline using potassium persulphate as an oxidizing agent. SEM image shows the amorphous morphology of composite material. The particle size of the nano-composite was 20 nm as obtained by TEM. Electrical conductivity of nanocomposite material increases with increase in temperature, which is the observed behaviour of semiconductor materials. The conductivity of samples shows strong dependence on the % age of inorganic precipitate within the composite. The synthesized samples exhibited direct band gap (E_g) in the range of 3.12-3.60 eV. Due to their good ion-exchange capacity along with optical and electrical properties, it is expect that this nanocomposite have applications in transparent electrodes in solar cells and in new electric and photoelectric devices.

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REFERENCES

1. J. Aguilar-Hernández and K. Potje-Kamloth, *J. Phys. D Appl. Phys.*, **34**, 1700 (2001).
2. A. Dey, A. De and S.K. De, *J. Phys.-Condens. Mat.*, **17**, 5895 (2005).
3. T.K. Vishnuvardhan, V.R. Kulkarni, C. Basavaraja and S.C. Raghavendra, *Bull. Mater. Sci.*, **29**, 77 (2006).
4. S.D. Patil, S.C. Raghavendra, M. Revansiddappa, P. Narsimha and M.V.N. Ambika Prasad, *Bull. Mater. Sci.*, **30**, 89 (2007).
5. C. Li and G. Shi, *Electrochim. Acta*, **56**, 10737 (2011).
6. Y. Chen, C. Xu, L. Cao and Y. Wang, *Polym. Compos.*, **33**, 1206 (2012).
7. G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri and A.J. Heeger, *Nature*, **357**, 477 (1992).
8. D.Y. Godovsky, *Adv. Polym. Sci.*, **153**, 163 (2000).
9. X.G. Li, A. Li and M.R. Huang, *Chem. Eur. J.*, **14**, 10309 (2008).
10. A.V. Murugan, T. Muraliganth and A. Manthiram, *Chem. Mater.*, **21**, 5004 (2009).
11. O.M. Vatutsina, V.S. Soldatov, V.I. Sokolova, J. Johann, M. Bissen and A. Weissenbacher, *Funct. Polym.*, **67**, 184 (2007).
12. S.A. Nabi, M. Shahadat, R. Bushra, A.H. Shalla and F. Ahmed, *Chem. Eng. J.*, **165**, 405 (2010).
13. R. Bushra, M. Shahadat, A.S. Raeisssi and S.A. Nabi, *Desalination*, **289**, 1 (2012).
14. O. Arrad and Y. Sasson, *J. Org. Chem.*, **54**, 4993 (1989).
15. A.A. Khan and Inamuddin, *Sens. Actuators B*, **120**, 10 (2006).
16. N.K. Raman, M.T. Anderson and C.J. Brinker, *Chem. Mater.*, **8**, 1682 (1996).
17. J.M. Kinyanjui, D.W. Hatchett, J.A. Smith and M. Josowicz, *Chem. Mater.*, **16**, 3390 (2004).
18. T.K. Sarma and A. Chattopadhyay, *Langmuir*, **20**, 4733 (2004).
19. Y.-C. Liu and T.C. Chuang, *J. Phys. Chem. B*, **107**, 12383 (2003).
20. R.V. Kumar, Y. Mastai, Y. Diamant and A. Gedanken, *J. Mater. Chem.*, **11**, 1209 (2001).
21. S. Sharma, C. Nirkhe, S. Pethkar and A.A. Athawale, *Sens. Actuators B*, **85**, 131 (2002).
22. S. Yoda, A. Hasegawa, H. Suda, Y. Uchimaru, K. Haraya, T. Tsuji and K. Otake, *Chem. Mater.*, **16**, 2363 (2004).
23. S.W. Huang, K.G. Neoh, E.T. Kang, H.S. Han and K.L. Tan, *J. Mater. Chem.*, **8**, 1743 (1998).
24. M. Hasik, E. Wenda, C. Paluszkiewicz, A. Bernasik and J. Camra, *Synth. Met.*, **143**, 341 (2004).
25. M. Hasik, E. Wenda, A. Bernasik, K. Kowalski, J.W. Sobczak, E. Sobczak and E. Bielanska, *Polymer*, **44**, 7809 (2003).
26. S.A. Nabi, R. Bushra and M. Shahadat, *J. Appl. Polym. Sci.*, **125**, 3439 (2011).
27. S.-J. Su and N. Kuramoto, *Synth. Met.*, **114**, 147 (2000).
28. J.C. Xu, W.M. Liu and H.L. Li, *Mater. Sci. Eng. C*, **25**, 444 (2005).
29. S. Gupta, D. Choudhary and A. Sarma, *J. Polym. Sci., B, Polym. Phys.*, **38**, 1589 (2000).
30. P.D. Christy, N.S.N. Jothi, N. Melikechi and P. Sagayaraj, *Cryst. Res. Technol.*, **44**, 484 (2009).
31. Y. Zhao, C.Z. Li, X.H. Liu, F. Gu, H.B. Jiang, W. Shao, L. Zhang and Y. He, *Mater. Lett.*, **61**, 79 (2007).
32. J. Tauc, in ed: A. Ables, Optical Properties of Solids, North-Holland, Amsterdam (1970).
33. A.S. Ahmed, M. Shafeeq M., M.L. Singla, S. Tabassum, A.H. Naqvi and A. Azam, *J. Lumin.*, **131**, 1 (2011).
34. J.I. Pankov Optical Process in Semiconductors, Prentice Hall, Englewood Clips, New Jersey (1971).