

Synthesis of Manganese chloride doped in Polyaniline and its characterization

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Abstract

The present work reports the chemical synthesis of polyaniline and its doping by manganese chloride. Polyaniline doped with Mn^{2+} was prepared by ammonium persulfate oxidative polymerization aniline monomer in the presence of manganese chloride in solution. And polyaniline doped with Mn^{2+} was prepared by chemical method. The composite was characterized by elemental analysis X-ray, FTIR, SEM, EDS, Raman spectroscopy, and electrical resistivity. All of these elemental analytical techniques were used for the identification and characterization of Mn metal ion incorporated into polyaniline. Electrical conductivity was measured by the four-probe method. The electrical conductivity of Polyaniline was increased by increasing metal ion doping in Polyaniline. The electrical conductivity value was observed for Mn-doped in Polyaniline.

Keywords: Polyaniline, conducting polymer, chemical synthesis, doping.

Introduction

During the last thirty years, the conducting polymer like polyaniline, polythiophene, polypyrrole polyacetylene, etc. was extensively studied by polymer researchers. Due to its electrical conducting capacity, it is used in the laboratory instead of the metal conductor all over the world.¹ polyaniline has received much attraction in the last ten years due to its properties like intrinsic electrical conductivity, simple and easy synthesis method, excellent environmental stability, cheap and easy availability of monomer, and behavior redox properties.²⁻⁴ Besides these properties, polyaniline(PANI) has much practical application such as chemical sensor device,⁵ light-emitting devices,⁶⁻⁷ electromagnetic interference shielding materials,⁸⁻⁹ electrode,¹⁰⁻¹² molecular sensors, lightweight batteries and surgical instrument,¹³ for making important constituent of solar cells,¹⁴ and as corrosion protecting agent in the paint industry¹⁵ polyaniline exists in various oxidation states fully oxidized pernigraniline and half oxidized emeraldine base EB and fully reduced leucoemeraldine.

The main aim of this research work is to develop high-performance and high conductive doped polyaniline for the present need by comparing their properties. The main aim of this research work is to develop high-performance and high conductive doped polyaniline for the present need by comparing their properties. In this research paper, we report the synthesis, the characterization of doped polyaniline prepared by chemical method.

2. Experimental Details

2.1 Materials

All chemical were supplied by Merck (Extra Pure) and were used without further purification.

2.2. Chemical Polymerization

The monomer Aniline, oxidizing agent Ammonium persulphate (APS) and Hydrochloric acid used as received without further treatment. Polyaniline was synthesized by the chemical oxidation method at lower temperatures (0-2°) C. APS (Merck, Germany) was used as an oxidant. Five ml aniline was first dissolved in 1.5 M, 70ml HCl (Merck, Germany). After this process, this solution was kept in an ice bath maintaining temperature below 5° C. Ten gram ammonium persulphate dissolved double-distilled deionized water. The solution of APS was added drop by drop into monomer solution and stirred at a constant speed. The polymerization process was performed for four to five hours. At the end of polymerization reaction , final green color polyaniline was formed , washed with dilute hydrochloric acid solution and dried at 70°C in hot air oven, for 10-12 hours. After forming polyaniline, an appropriate amount of Manganese chloride solution 0.2 M was dissolved in the Polyaniline solution. Doping of Mn in polyaniline was done by chemical doping method. In order to obtain the uniform distribution of Mn ion in the polyaniline solution, the mixture was stirred for 1 hour. The surface morphology of the doped polyaniline film was examined by analyzing FTIR, SEM, methods.

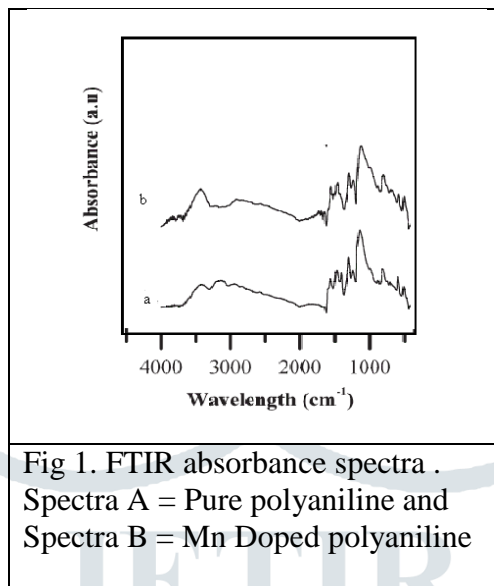
3. Results And Discussion

The sample of the deposition was characterized by the structural, morphological, optical characterization.

3.1 Fourier Transform Infra-Red (FT-IR)

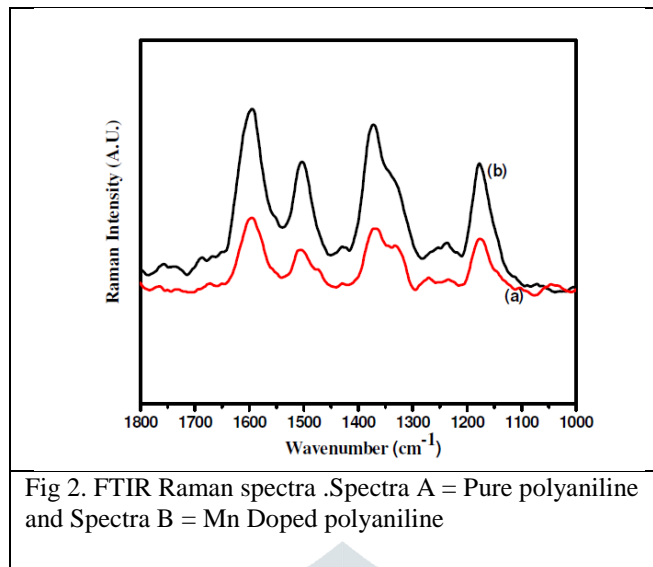
The samples were characterized by Fourier Transform Infra-Red (FT-IR) spectroscopy using Shimadzu FTIR 8201 spectrophotometer in the range of 4000-400 cm⁻¹. The absorption band at 820 cm⁻¹. It is associated with C-C and C-H for a benzenoid unit.^{19,21} The peak at 1146 is related to the in-plane bending of C-H.^{17,20} The peaks at 1305 cm⁻¹ and 1245 cm⁻¹ are related to C-N stretching mode for the benzenoid and quinoid units.^{16,20,14,22} The peaks at 1480 cm⁻¹ and 1560 cm⁻¹ are the related presence of benzenoid and quinoid rings respectively.²⁴⁻²⁸ C=N stretching and N-H deformation gives absorption between 1450 cm⁻¹ to 1600 cm⁻¹. The absorption band 2945 cm⁻¹ is related to C-H stretching vibration and N-H stretching vibration peak observed in the region 3500 cm⁻¹ to 3350 cm⁻¹.^{16,19,22,23,25,26,27} The clear shift was formed in the FT-IR spectra of Mn- polyaniline composite. For example absorption 820, 1146, and 2945 cm⁻¹ belong to undoped polyaniline shifted to 810,1135 and 2936

respectively. This shifting spectrum was formed by metal cation become absorbed by as a result of electrostatic attraction chloride ion on the surface of the polyaniline molecule.



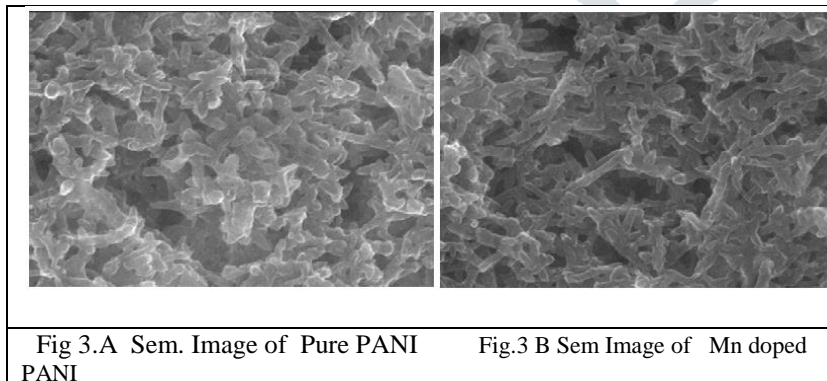
3.2 Fourier Transform Raman (FT-Raman)

The polyaniline film was characterized by their FT-Raman spectra. Figure 2 Spectra a shows the Raman spectra of Mn-Polyaniline at an excitation wavelength of 1064nm. Fig. 2 (a) shows 1185, 1360, 1505, and 1595 cm^{-1} corresponding C-N stretching, C-N⁺ stretching, C-C stretching of the benzene ring and C-C stretching of quinoid units respectively. The observed bands of Raman spectra agree well with the chemical structure of Polyaniline. Similar bands were also observed in the Polyaniline-Mn composite. figure 2 spectra b shows a small change in the intensity in Polyaniline-Mn composite spectra. C-N bands become broadens as the doping of Mn. And in the figure, a band and C-N⁺ and C-N bands moved toward the 3 to 5 cm^{-1} lower wavenumber. The broadening of bands, shifting, and decrease in intensity of bands indicating the presence of Mn content in polyaniline. J B M Krishna and A Saha chemically prepared pani-metal ion composite pani-Fe, pani-Ni, and pani-La. They observed that a broad hump in doped polyaniline than undoped polyaniline.²⁷ Hulbert et al. and Sloczynski et al. J. S. Shaikh et al, synthesized Ru doped CuO by a colloidal solution method. They were observed that ruthenium (Ru) doped copper oxide (CuO) film show a small shift in wavenumber as compared to undoped copper oxide film. Hence it was confirmed that ruthenium (Ru) present in copper oxide (CuO) film.²⁸⁻³⁰



3.3 SEM characterization

The SEM images of PANI and PANI-Mn are shown in fig. 3a and 3b respectively. The nanofiber's altogether structure is observed in the polyaniline (PANI) sample. Figure a shown an uneven irregular morphology. But in the figure of polyaniline -Mn composite the irregularity increase than the figure of pure polyaniline. And the pore size in polyaniline-Mn is larger and uneven than polyaniline. The surface morphology of the mixed Polyaniline -Mn does not differ from the pure Polyaniline. When $MnCl_2$ is added in polyaniline, the pore size of the mixture or composite becomes larger, which leads to the change in the morphological structure of polyaniline and manganese bind to various sites of polyaniline to form interchain linkage among several adjacent polyaniline chains by coordination bond. This porous structure and nanofiber are beneficial for supercapacitor because it decreases the diffusion resistance of the electrolyte into the electrode matrix.



3.4 Energy Dispersive X-Ray Spectroscopy

Fig.3 c shows EDS spectrum of Polyaniline-Mn composite which show presence of Mn in the sample.

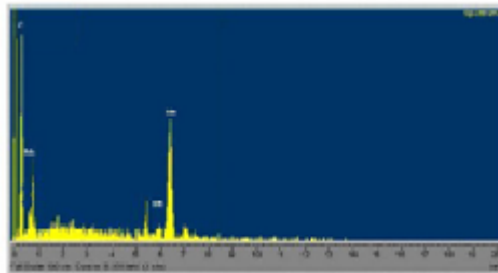


Fig. 3c EDS spectrum of Mn doped polyaniline

3.5 Electrical Resistivity

The DC electrical resistivity (ρ) of from pure polyaniline to Mn-doped polyaniline shown in figure 4. At room temperature electrical resistivity (ρ) pure polyaniline film is $1.14 \times 10^4 \Omega \text{ cm}$ and electrical resistivity (ρ) Mn polyaniline film $5.1 \times 10^3 \Omega$. Hence electrical resistivity (ρ) decreases and simultaneously electrical conductivity of the doped polyaniline increases.

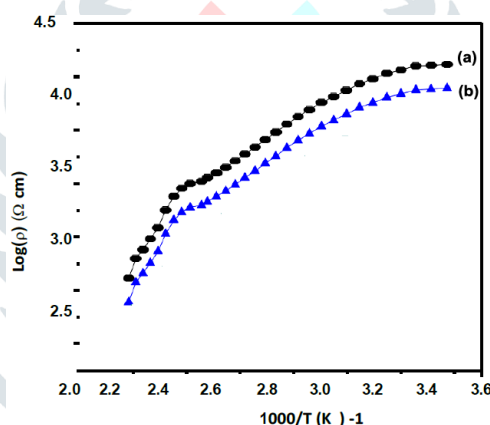


Fig 4 Electrical resistivity of the a) Pure polyaniline and) Mn doped polyaniline

Conclusion

Chemically synthesized polyaniline with Mn by chemical bath method. Synthesis of Mn-doped polyaniline films as an electrode for supercapacitor is important to increase the electrical conductivity and decrease the resistivity.

References

- [1] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, J. Chem. Soc. Chem. Commun. (1977) 578–580.
- [2] G. Ciric-Marjanovic, Synth. Met. 2013, 177, 1.

- [3] J. Wang, D. Zhang, *Adv. Polym. Tech.* 2013, 32, E323.
- [4] J. Huang, *Pure Appl. Chem.* 2006, 78, 15.
- [5] M. Joubert, M. Bouhadid, D. Begue, P. Iratcabal, N. Redon, J. Desbrieres, S. Reynaud, *Polymer* 2010, 51, 1716.
- [6] T. Griesser, S. V. Radl, T. Koeplmayr, A. Wolfberger, M. Edler, A. Pavitschitz, M. Kratzer, C. Teichert, T. Rath, G. Trimmel, G. Schwabegger, C. Simbrunner, H. Sitter, W. Kern, *J. Mater. Chem.* 2012, 22, 2922.
- [7] C. C. Chen, S. R. Hwang, W. H. Li, K. C. Lee, G. C. Chi, H. T. Hsiao, C. G. Wu, *Polym. J.* 2002, 34, 271.
- [8] P. Zhang, X. Han, L. Kang, R. Qiang, W. Liu, Y. Du, *RSC Adv.* 2013, 3, 12694.
- [9] P. Saini, V. Choudhary, S. K. Dhawan, *Polym. Adv. Tech.* 2009, 20, 355.
- [10] H. Mi, X. Zhang, S. Yang, X. Ye, J. Luo, *Mater. Chem. Phys.* 2008, 112, 127.
- [11] M. A. Bavio, G. G. Acosta, T. Kessler, *J. Power. Sources* 2014, 245, 475.
- [12] S. Chaudhari, Y. Sharma, P. S. Archana, R. Jose, S. Ramakrishna, S. Mhaisalkar, M. Srinivasan, *J. Appl. Polym. Sci.* 2013, 129, 1660
- [13] K. Naoi, H. Sakai, S. Ogano, T. Osaka, *J. Power Sources* 20 (1987) 237–242.
- [14] Y. Zhang, Q. Li, L. Sun, R. Tang, J. Zhai, *J. Hazard. Mater.* 175 (2010) 404–409.
- [15] S. Sathiyarayanan, V. Karpakam, K. Kamaraj, S. Muthukrishnan, G. Venkat-achari, *Surf. Coat. Technol.* 204 (2010) 1426–1431.
- [16] H.C. Pant, M.K. Patra, S.C. Negi, A. Bhatia, S.R. Vadera, and N. Kumar, *Bull. Mater. Sci.*, 29, 379 (2006).
- [17] S. Jing, S. Xing, F. Dong, and C. Zhao, *Polym. Compos.*, 29, 1165 (2008).
- [18] S.C. Raghavendra, S. Khasim, M. Revanasiddappa, M.V.N.A. Prasad, and A.B. Kulkarni, *Bull. Mater. Sci.*, 26, 733 (2003).
- [19] S. Ameen, V. Ali, M. Zulfequar, M.M. Haq, and M. Husain, *Curr. Appl. Phys.*, 9, 478 (2009).
- [20] X. Li, Y. Gao, X. Zhang, J. Gong, Y. Sun, X. Zheng, and L. Qu, *Mater. Lett.*, 62, 2237 (2008).
- [21] T.-C. Mo, H.-W. Wang, S.-Y. Chen, and Y.-C. Yeh, *Ceram. Int.*, 34, 1767 (2008).
- [22] B. Sreedhar, P. Radhika, B. Neelima, N. Hebalkar, and M.V.B. Rao, *Polym. Adv. Technol.*, 20, 950 (2009).
- [23] A. Tiwari, V. Sen, S.R. Dhakate, A.P. Mishra, and V. Singh, *Polym. Adv. Technol.*, 19, 909 (2008).
- [24] N. Arsalani and M. Hayatifar, *Polym. Int.*, 54, 933 (2005).
- [25] E. Ozkazanc, S. Zor, and H. Ozkazanc, *Polym. Compos.*, 31(11), 1862 (2010).
- [26] S. Zhou, T. Wu, and J. Kan, *J. Appl. Polym. Sci.*, 106, 652 (2007).

[27] J. Alam, U. Riaz, and S. Ahmad, *Polym. Compos.*, 31, 32 (2010).

[27] J. B. M. Krishna, A. Saha, G. S. Okram, A. Soni, S. Purakayastha and B Ghosh, *J. Phys. D: Appl. Phys.*, 42 (2009) 095404.

[28] S.L. Hulbert, B.A. Bunker, F.C. Brown, P. Pianetta, *Phys. Rev. B* 30 (1984) 2120.

[29] J. Sloczynski, R. Grabowski, A. Kozłowska, P.K. Olszewski, J. Stoch, *Phys. Chem. Chem. Phys.* 5 (2003) 4631.

[30] J. S. Shaikh, R.C. Pawar, R. S Devan, Y. R. Ma, P. P.Salvi, S. S. Kolekar and P. S. Patil, *Electrochim. Acta.*, 56 (2011) 2127.

