Synthesis And Characterization of Polyaniline Nano-Fibers

Raminder Kaur
[1, 2] Dept of Polymer Science and Chemical Technology
[1, 2] Delhi Technological University

Abstract- *The present study reports the synthesis and characterization of polyaniline nano-fibers. Interfacial polymerisation method was used to synthesize the polyaniline nanofibers using ammonium persulphate (APS) as oxidant and HCl as dopant. SEM investigation shows that the average diameter of the synthesised polyaniline nanofibers was 65 ± 5 nm, which is confirmed by HRTEM. In addition, PANI was also characterised by FTIR, BET and Four- probe conductivity techniques.*

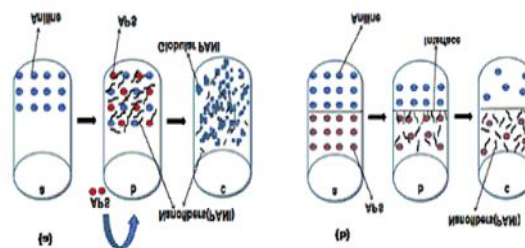*Keywords*- Polyaniline, Nano-fibers, Interfacial polymerization, Characterization

I. INTRODUCTION

Primitively (1835), polyaniline was known as "aniline- black", which is an oxidation product of aniline [1]. This earliest conducting polymer is potentially very useful by cause of its ease of synthesis, environmental stability, high surface area and exclusive oxidation/reduction and acid/base doping/de-doping chemistry [1,2]. Polyaniline (PANI) attains its reversible conductivity through doping (Figure 1) and act as a promising material for enormous applications such as super capacitors and energy storage devices [3, 4] actuators and sensors [5-7], flash welding [8], rechargeable batteries [9], electronic devices, corrosion protection, electromagnetic shielding, antistatic coating [10] and separation membranes [11].
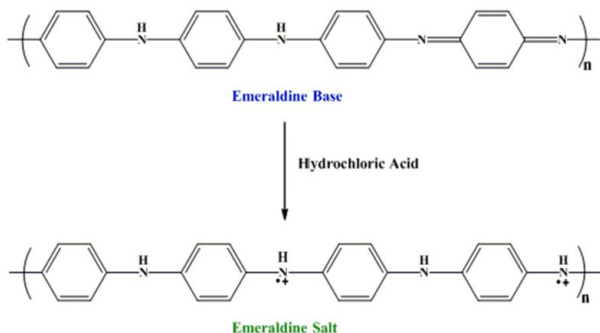
FIGURE 1: CHEMICAL STRUCTURE OF (A) POLYANILINE (EMERALDINE BASE) AND TRANSFORMATION TO A CONDUCTIVE SALT BY PROTOTONATION IN AN ACID MEDIUM [12]

In addition to the unanimously adopted recognition of polyaniline as a conducting polymer [13,14], it is now emerging as a novel material for enormous applications, with its improved properties, such as larger surface area, modified mechanical properties, low cost, high adsorption capacity and simplicity in preparation. Recently, Kaur and Duhan, 2017 has reviewed the utilization of polyaniline for the effective removal of dyes from the textile effluent [15]. In the present work, polyaniline nanofibers have been synthesized by interfacial polymerization method [16] using immiscible biphasic system i.e. aqueous/organic system (Figure 2).

FIGURE 2: CHEMATIC REPRESENTATION OF (A) SYNTHESIS OF POLYANILINE AGGLOMERATES BY CONVENTIONAL METHOD AND (B) SYNTHESIS OF NANOFIBERS BY INTERFACIAL POLYMERISATION METHOD [17].

The properties and the performance of the synthesised nanofibers is observed to be superior as compare to conventionally synthesised PANI due to the absence of large agglomerates and enhanced surface area, thus making them a suitable candidate for enormous applications.

II. MATERIALS AND METHOD

All the chemicals used in this study were of AR grade. Aniline (Sigma Aldrich) was distilled prior to the polymerisation. Ammonium persulfate $[(NH_4)_2S_2O_8]$: oxidizing agent (Sigma Aldrich); Hydrochloric acid: dopant (Rankem) and Toluene: Organic phase (CDH, India) were used as received. Double distilled water was used for washing purpose.

2.1 Synthesis of Polyaniline Nanofibers

Polyaniline nanofibers were synthesised by interfacial polymerisation method [16]. For the formation of a biphasic system, first, 0.73 gm of APS was added to 40 mL of 1 M HCl aqueous solution (for aqueous layer). Simultaneously, an organic solution was prepared by adding 1.16 mL of 0.3M Aniline (monomer) to the 40 mL of toluene. The APS solution prepared was then added to the organic solution dropwise in a span of nearly 1 h. After the complete addition of APS solution, the reaction mixture was left for 20 h undisturbed. In anticipated to literature studies, aniline polymerisation took place at the interface. Then the organic layer was isolated carefully and the lower aqueous mixture was filtered. The solid contents i.e. polyaniline was washed with distilled water several times and dried in vacuum oven at 60^0 C for 24 h to obtained a dark green coloured Emeraldine salt (a form of polyaniline). The molar ratio of the aniline to APS taken was 4:1 and maintained throughout the reaction. The Emeraldine salt as obtained above was characterised for its size, surface area, morphology and structure prior to be used as adsorbent.

III. CHARACTERIZATION

The resulted Emeraldine salt (Polyaniline) was characterized by TEM (Transmission Electron Microscopy) for its size. PANI samples were first dispersed in ethanol and then transferred to copper grid for TEM. TEM images were observed on F 30 S twin 300 HRTEM at 300 kV. Morphology and texture of polyaniline was examined using a Scanning Electron Microscope (SEM) (S-3700N; Hitachi, Japan). FTIR spectra of polyaniline were obtained in the region 400-4000 cm^{-1} on a Nicolet 380 FT-IR spectrophotometer at 25^0 C by preparing KBr pellet. X-ray diffraction patterns of PANI powder were obtained by using BRUKER D8 ADVANCE diffractometer by employing CuKα (Kα –1.54056 Å) radiation. Diffractometer was conducted at 40mA and 40 kV. The scanning step was 0.02^0 in 2θ with a dwell period of 0.5s per step. Four point probe technique with digital micro voltmeter (DMV-00), low current source (LCS-02) and PID controlled oven (PID-200) was used to measure the electrical conductivity of the polyaniline sample (in pellet form) at room temperature. BET surface area of the prepared polyaniline was also determined by using surface area analyser (Micromeritics ASAP 2010).

IV. RESULTS AND DISCUSSION

4.1 Structural Characterization of PANI Nanofibers

4.1.1 FTIR

Figure 3 shows the main characteristic peaks of FTIR spectra of polyaniline (Emeraldine salt). N-H stretching of the

structure is represented by peak obtained at 3450 cm^{-1}. The absorption band at 2923cm^{-1} is due to asymmetric stretching mode of C-H aromatic bond. Peak at 1560cm^{-1} is attributed to the quinoid structure of the sample. C-N stretching of secondary amines is confirmed by peak at 1296 cm^{-1}. Absorption band observed at 1105 cm^{-1} is due to C-H bending vibration. Absorption peak at 1466cm^{-1} is attributed to C=N stretching in aromatic compounds. The absorption band lies at 799 cm^{-1} attributed to 1, 4 di-substituted benzene. The above given values of wave numbers are found to be comparable with the reported wave numbers i.e.3631 and 3288 cm^{-1} for N-H stretching [18], 2923 cm^{-1} for C-H asymmetric stretching [19],1588cm^{-1},1258cm^{-1} [20],1480 cm^{-1} for C=N stretching [21], 1296 cm^{-1} for C-N stretching,1010-1170 cm^{-1} for C-H bending, 800 and 860 cm^{-1} for 1,4 di-substituted benzene [22].
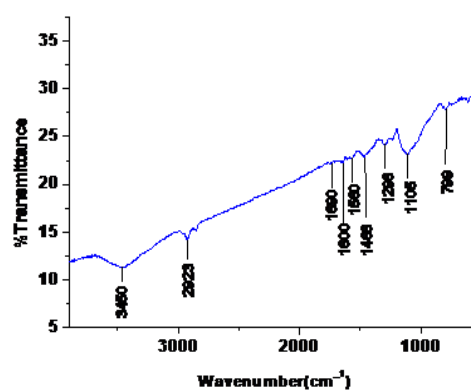

FIGURE 3: FTIR SPECTRUM OF POLYANILINE SALT SYNTHESIZED BY INTERFACIAL POLYMERIZATION METHOD.

4.1.2 *X-ray Diffraction*

Study of X- ray diffraction pattern of conducting polymers is quite important due to the more metallic properties of highly ordered system. As shown in Figure 4, two diffraction peaks were recorded by X- ray diffractometer at 20.56^0 and 23.58^0 respectively, at room temperature. Debye Scherer equation (as given below) was used to calculate the crystal size of the polyaniline.

$$D = \frac{K\lambda}{(\beta cos\theta)}$$

(1)

Where β is FWHM i.e. full width half maximum and k is Bragg's constant (0.9). According to the observed peaks (due to quinonoid and benzenoid groups) in X-ray diffraction pattern, polyaniline was found to be semi crystalline in nature and the size of the crystal was found to be 38.1nm. Similar results (2θ = 21.10^0 and 23.59^0) have been reported in the previous literature by some other research group [23].
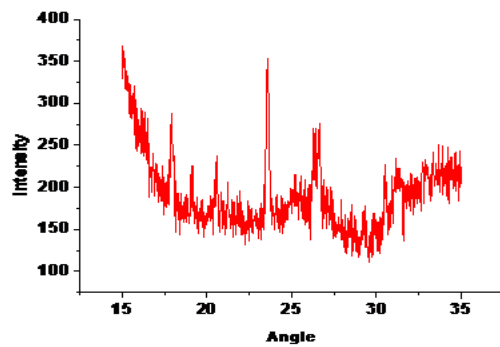
FIGURE 4: X-RAY DIFFRACTION PATTERN OF POLYANILINE NANOFIBERS AT ROOM TEMPERATURE.

4.2 Morphology

4.2.1 SEM

Figure 5(a) and 5(b) show the scanning electron microscopy (SEM) images of conventionally and interfacial method synthesised polyaniline respectively. In convention method of synthesis of polyaniline, the lumps formation was observed, on the other hand, nanofibers were clearly visible in case of interfacial polymerisation method. The average diameter of the PANI nanofibers was found to be 65±5nm. The results are agreed with the recorded literature of PANI nanofibers synthesis by interfacial polymerization i.e. 30-60 nm [24]. Further, HRTEM investigation confirmed the fibrous nature of the polyaniline i.e. Figure 5(c).
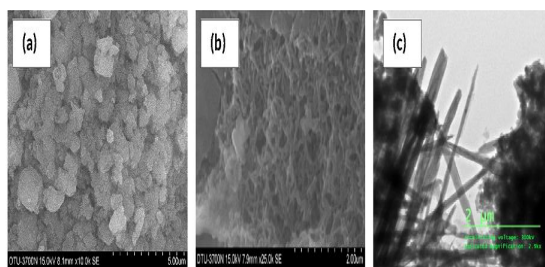
FIGURE 5: SEM IMAGES OF SYNTHESIZED POLYANILINE BY (a) CONVENTIONAL AND (b)INTERFACIAL POLYMERISATION METHOD (c) HRTEM IMAGE OF POLYANILINE SYNTHESIZED BY INTERFACIAL POLYMERISATION METHOD

4.2.2 BET Analysis

BET surface area of the synthesised polyaniline nanofibers was obtained by using surface area analyser. As expected, the BET surface area of the nanostructured polyaniline (48.83 m^2/g) is more i.e. nearly 4 times than that of conventionally synthesised polyaniline powder (13.65 m^2/g). This indicates the enhanced adsorption capacity of the PANI nanofibers due to the availability of more active sites.

4.3 Electrical Conductivity

A four point probe technique was used to measure the electrical resistance of the polyaniline nanofibers at room temperature. The equation used to measure the conductivity is

$$\sigma = \frac{1}{\pi/_{In2}} R \, d$$

(2)

Where $\left(\frac{\pi}{In2}R\right)$, is the sheet resistance and d, is the thickness of the polyaniline pellet. The conductivity of the pellet was measured at different voltage i.e. 0.006mA, 0.008mA, 0.01mA and 0.012mA respectively. The conductivity of the salt form of the polyaniline was found to be 0.98 S/cm which is in synchronization with the literature value for the conductivity of the chemical oxidative synthesised PANI that is apparently less than the electrochemically synthesised PANI [19].

V. CONCLUSION

The polyaniline fibers have been synthesized by interfacial polymerization process. The properties and the performance of the synthesized nanofibers is observed to be superior as compare to conventionally synthesized PANI due to the absence of large agglomerates. The synthesized polyaniline nanofibers were characterized by FTIR, XRD, UV-VIS spectroscopy, BET and Four-probe conductivity techniques. The BET surface area of polyaniline nanofibers was reported to be 48.83m^2/g which is more as compared to most of conventional adsorbents. The average diameter of the synthesized PANI nanofibers was found to be 60±5 nm, as detected by HRTEM and SEM techniques. This nano-sized polyaniline can be used in the manufacture of anti-rust and antistatic coatings, as adsorbent in effluent water treatment and in EMI shielding.

REFERENCES

[1] Genies, E.M., Boyle, A., Lapkowski, M. and Tsintavis, C., 1990, Polyaniline: A historical survey. *Synth Met.*, 36, 139-182.

[2] MacDiarmid, A.G., Chiang, J.C., Richter, A.F., Epstein, 1987, A.J, Polyaniline: a new concept in conducting polymers. Synth. Met., 18 (1987), pp. 285-290.

[3] Subramania, A, Devi, S.L.,2008, Polyaniline nanofibers by surfactantassisted dilute polymerization for

supercapacitor applications, Polym. Adv. Technol., 19, 725-727.

[4] Sun, L.J., Liu, X.X, Lau,K.K.T., Chen, L., Gu, W.M.,2008, Electrodeposited hybrid films of polyaniline and manganese oxide in nanofibrous structures for electrochemical supercapacitor,. Electrochim. Acta, 53, 3036–3042.

[5] Baker, C. O.; Shedd, B.; Innis, P. C.; Whitten, P. G. Spinks,. G. M.; Wallace, G. G.; Kaner, R. B.,2008, Monolithic actuators from flash-welded polyaniline nanofibers. Adv. Mater. 2008, 20, 155 158.

[6] Virji S, Huang J, Kaner RB, Weiller B.H.,2004, Polyaniline nanofiber gas sensors: Examination of response mechanisms. Nano Lett 4:491–496.

[7] Sadek, A. Z.; Wlodarski, W.; Kalantar-Zadeh, K.; Baker, C.; Kaner, R. B.,2007, Doped and dedoped polyaniline nanofiber based conductometric hydrogen gas sensors. Sens. Actuators, B 2007, 139, 53-57.

[8] Huang J, Kaner R.B.,2004, Flash welding of conducting polymer nanofibres. Nat Mater 3:783–786

[9] Ghanbari, K, Mousavi, M.F.,Shamsipur, M., 2006, Preparation of polyaniline nanofibers and their use as a cathode of aqueous rechargeable batteries Electrochimica Acta 52 (4), 1514-1522.

[10] Hu, L., Gruner, G., Li, D., Kaner, R.B., and Cech, J., 2007, Patternable transparent carbon nanotubefilms for electrochromic devices, J. Appl. Phys. 101: 016102.

[11] Anderson, M.R., Mattes, B. R., Reiss, H., Kaner, R.B., 1991, Conjugated polymer films for gas separations, Sci. 252 :1412-1417.

[12] Llorens, E.; Armelin, E.; del Mar Pérez-Madrigal, M.; del Valle, L.J.; Alemán, C.; Puiggalí, J., 2013 Nanomembranes and Nanofibers from Biodegradable Conducting Polymers, Polym. 5 : 1115-1157.

[13] Ali, V., Kaur, R., Kamal, N., Singh, S., Jain, S.C., Kang, H.P.S., Zulfequer, M. and Husain, M. ,2006, Use of Cu^{+1} dopant and its doping effects on polyaniline conducting system in water and tetrahydrofuran. *J Phys Chem Solids.*, 67, 659-664.

[14] Ali, V., Kaur, R., Lakshami, G.B.V.S., Kumar, A., Kumari, K. and Kumar, S.,2012, Electrical conductivity and dielectric parameters of polyaniline doped with $CuClO_4.4BN$ in aqueous DMSO solvent. *Adv Polym Techanol.*, 31, 374-379.

[15] Kaur, R.; Duhan, M., 2017, In *Advanced Materials for Wastewater Treatment*; Chapter 3, pp. 51-100. Wiley: Martin Scrivener, Sweden.

[16] Huang, J., Virji, S., Weiller, B.H. and Kaner, R.B., 2003, Polyaniline Nanofibers: Facile Synthesis and Chemical Sensors. *J. Am. Chem. Soc.*, 25, 314-315.

[17] Wei, Y. Jang, G.W. and Hsueh, K.F.,1992, Thermal transitions and mechanical properties of films of chemically prepared polyaniline. *Polym.*, 33, 314-322.

[18] Abdelkader, R., Amine, H. and Mohamme, B.,2013, H-NMR Spectra of Conductive, Anticorrosive and Soluble Polyaniline Exchanged by an Eco-Catalyst Layered (Maghnite-H^+). *World J. Chem.*, 8, 20-26.

[19] Vivekanandan, J., Ponnusamy, V., Mahudeswaran, A. and Vijayanand, P.S., 2011, Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods. *Arch Appl Sci Res.*, 3, 147-153.

[20] Bhaumik, M., McCrindle, R.I., Maity, A., Agarwal, S. and Gupta, V.K. ,2016, Polyaniline nanofibers as highly effective re-usable adsorbent for removal of reactive black 5 from aqueous solution. *J. Colloid Interface Sci.*, 466, 442-451.

[21] Jin, Kim, B., Oh, S.G., Han, M. and Im, S.S.,2001, Synthesis and characterization of polyaniline nanoparticles in SDS micellar solutions. *Synth. Met.* 122, 294-304.

[22] Veerendra, B. and Sathyanarayana, D.N.,2005, Synthesis and characterisation of polyaniline salts with phenoxy acetic acids by emulsion polymerisation. *Indian J. Chem.* 44, 1133-1138.

[23] Kavitha, B., Siva Kumar, K. and Narsimlu, N.,2013, Synthesis and characterisation of polyaniline nano-fibers. Indian *J. Pure Appl. Chem.*, 51, 207-209.

[24] Zhang, X., Chan-Yu-King, R., Jose, A. and Manohar, S.K, 2004 Nanofibers of polyaniline synthesized by interfacial polymerization. *Synth. Met.* 145, 23-29.