

Synthesis and characterization of various acid doped Polyaniline Nanofibers

M. Kuralselvi¹, M. Sivanantham²

^{1,2} Department of Physics, Centre for Research and Development,
PRIST University, Vallam, Thanjavur 613 403, Tamilnadu, India.

Abstract – We report the synthesis of PANI(PANI) nanofibers by carefully doping with different acids such as hydrochloric acid(HCL), acetic acid(AA) and perchloric acid (PCA). The role of doping on the structure and morphological changes in PANI nanofibers were characterized by Fourier transform infrared (FTIR) spectroscopy, ultra-violet-visible (UV-Vis) spectroscopy, dynamic light scattering (DLS) and scanning electron microscopy (SEM) analyses. FTIR results were utilized to reveal the functional groups present in the acid doped PANI nanofibers. DLS and SEM analyses have been employed to find out how the size and morphologies of PANI nanofibers vary with doping by various acid dopants.

Key words: Polyaniline, nanofiber, HCL, PCA, morphology

1. INTRODUCTION

Conducting polymers are fascinating category of materials since their electronic, optical and magnetic properties are analogous to those of metals, at the same time like other polymers, they can also able to maintain the flexibility and processibility [1]. Out of number of conducting polymers, polyaniline (PANI) is comprehensively studied polymers because it can be easily synthesized, environmentally stable and possessing interesting redox properties [2]. In addition, PANI based nanostructures have received great attention because of their wide range technological applications as field effect devices, chemical sensors, electromagnetic shielding and anti-corrosive coatings [3-9].

Recently PANI nanostructured materials have been prepared in the forms of nanofibers and nanotubes by interfacial polymerization and template synthesis. Su et. al [10] prepared the acid doped PANI nanofibers by interfacial polymerization. It was found that acid doped PANI nanofibers have different thermal stability than that of emeraldine base PANI nanofibers.

Tang and co-workers [11] examined the influence of different molar ratios of aniline (AN), ammonium peroxydisulfate (APS) and HCl on the polymerization of AN. Zhang et. al. [12] fabricated D-10-camphorsulfonic acid (D-CSA) doped PANI nanotubes. It was found that the diameter D-CSA) doped PANI nanotubes was 80–180 nm and conductivity of 3.4×10^{-3} to 3.5×10^{-1} S cm⁻¹. Li et. al. [13]

reported an easy route to the synthesis of PANI nanofibers by chemical oxidative polymerization of aniline in a surfactant gel. The prepared PANI nanofibers may be used in several applications such as chemical sensors or actuators, gas-separation membranes and neuron devices. Wang and colleagues [14] prepared the PANI nanofibers by polymerization of aniline using chloroaurate acid as the oxidant.

Herein, we report the fabrication of PANI nanofibers with same concentration of PANI and doping with different acids. In addition, we investigate the influence of these acids on the structure and morphological changes in PANI nanofibers by Fourier transform infrared (FTIR) spectroscopy, ultra-violet-visible (UV-Vis) spectroscopy, dynamic light scattering (DLS) and scanning electron microscopy (SEM) experiments.

2. EXPERIMENTAL

2.1 Materials

Different chemicals were used as follows: aniline as monomer, ammonium persulfate (APS) as initiator, perchloric acid (PCA), hydrochloric acid (HCL) and acetic acid (AA) as doping agents. Doubly distilled water was used for polymer preparation. All reagents were used without further purification.

2.2 Synthesis of acid doped PANI nanofibers

PANI nanofibers having same concentration (0.1 M) but doped by three different acids having same concentration of 0.1 M were synthesized. Aniline with concentration of 0.1 M was dissolved separately in the 0.1 M of HCl and 0.1 M of AA and 0.1 M of PCA. By mixing ammonium peroxydisulfate (APS) separately in the 0.1 M of HCl and 0.1 M of AA and 0.1 M of PCA to obtain the three different initiator solutions. Prior to polymerization, the monomer solution containing aniline and initiator solution having APS were subjected to degassing separately by nitrogen gas for 10 and 5 min respectively so as to remove the dissolved oxygen. After that the polymerization has been performed by adding the initiator solution drop wise into the solution having the monomer under continuous stirring for 1 day by magnetic stirrer. Light green colour was formed during the beginning

of polymerization. Later the colour was changed to dark green colour solution with increase in time. This colour change confirmed the formation of PANI nanofibers. Finally dark green precipitates were noticed for irrespective of acids. Polymerizations were carried out at room temperature. Final products were purified by centrifuge (REMI, India) at 3500 rpm. After purification the samples were utilized for characterization.

2.3 Characterization of acid doped PANI nanofibers

Perkin-Elmer Spectrum 2 model spectrometer was used to record the FTIR spectra by KBr pellet method. Systronics Double Beam UV-VIS Spectrophotometer, 2202 was employed to capture the UV-Visible spectra. Effect of acid doping on the hydrodynamic size of PANI nanofibers were determined by Particle analyser-Nano plus. Variation of surface morphologies of PANI nanofibers with respect to doping was monitored by Scanning electron microscope (Carl-Zeiss, EVO-18).

3. RESULTS AND DISCUSSION

3.1 UV-Vis spectroscopic results

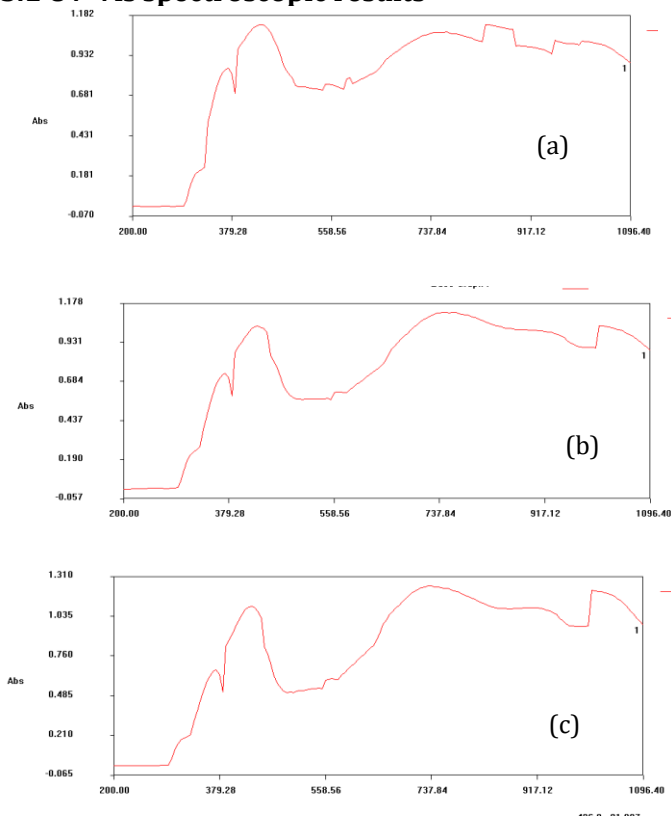


Fig-1: UV-Vis spectra of different acid doped PANI nanofibers. (a)- AA , (b) - HCL and (c) - PCA.

3.2 FTIR results

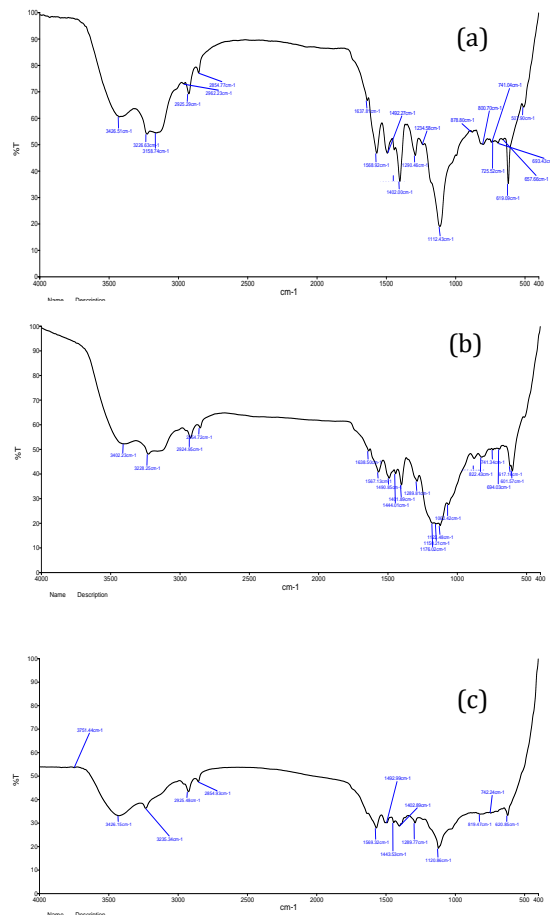


Fig-2. FTIR spectra of various acid doped PANI nanofibers. (a)- AA , (b) - HCL and (c) - PCA.

In order to verify the formation of PANI and examine the effect of acid doping on PANI nanofibers, FTIR measurements were carried out. Figure 2 represents the FTIR spectra for acid doped of PANI nanofibers. PCA treated PANI nanofibers showed poor transmission (55%) at wave number of 4000 cm^{-1} . All acid doped PANI nanofibers have the peak at 1569 cm^{-1} and this is attributed to quinoid deformations of the emeraldine form of PANI nanofiber. The creation of PANI nanofibers were validated by the FTIR spectra.

3.3 SEM observations

In this section, we discuss how the surface morphologies of the PANI nanofibers affected by doping of different acids. Figure 3 represents the SEM observations of three acid doped PANI nanofibers. In the case of AA doped PANI nanofibers, fiber-like structures were seen. In contrast, fiber-like and also bigger particles have been noticed for HCL and PCA doped nanofibers.

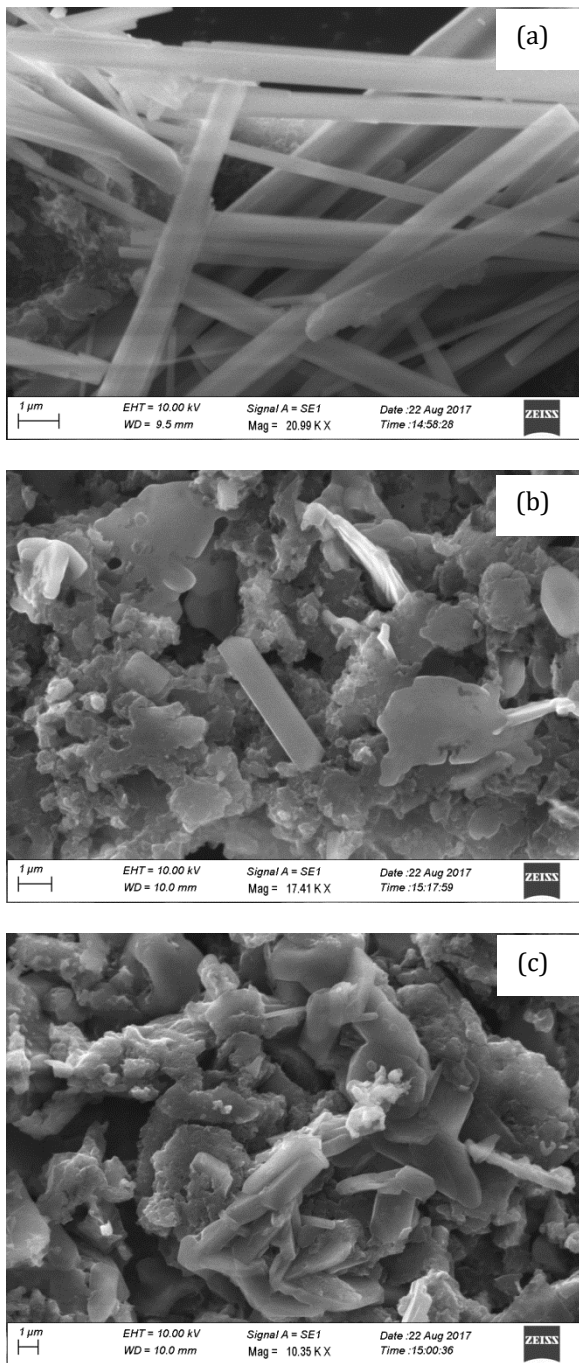


Fig-3. Variation of surface morphologies of PANI nanoparticles for different acid doping. (a)- AAC , (b) - HCL and (c) - PCA.

3.4 DLS results

To investigate the hydrodynamic behavior of different acid doped PANI nanofibers, DLS measurements have been conducted. Figure 4 shows the size distributions of PANI nanofibers upon doping with different acids. It was noticed from this figure that there are two distributions of particles for the cases AA and HCl. Mean particle size for the

first distribution was around 3 nm. For the second distribution, average size of about 400 nm was seen. In contrast, in the case of PCA doped PANI nanofibers, only one distribution was observed with average size of particles is 10 nm.

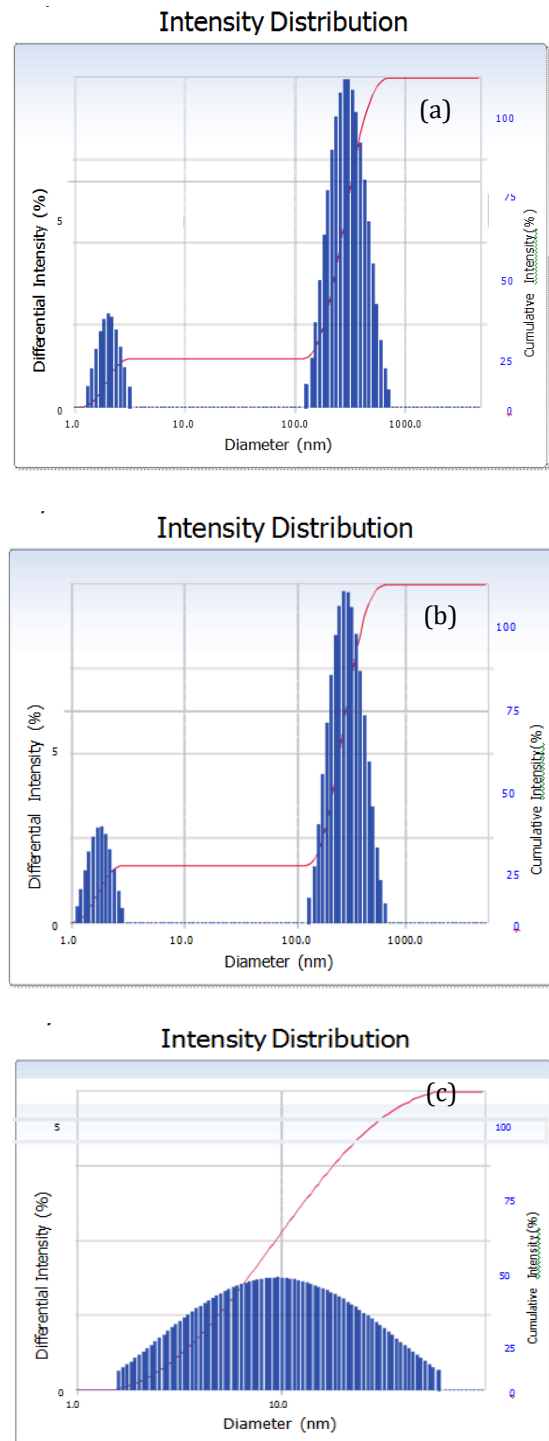


Figure 4. Effect different acid doping on the particle size of PANI nanofibers. (a)- AAC , (b) - HCL and (c) - PCA.

4. CONCLUSIONS

PANI nanofibers were systematically doped by three different acids such as AA, HCl and PCA. We have also investigated the effect of doping of PANI nanofibers with different acids by UV-Visible spectroscopy, FTIR, SEM and DLS studies. It was found acid doping significantly affect the UV-Visible absorption peak of PANI nanofibers at wavelength of about 730 nm. Increase in order of affecting this peak is AA>HCL>PCA. With the aid of FTIR spectroscopy, the formation of PANI was verified. DLS results suggested the nano and sub-micrometer sized particles were formed. SEM observations revealed that fiber-like structures were formed after doping by AA whereas fiber-like and bigger particles have been seen for HCl and PCA doped nanofibers.

Acknowledgement

Authors gratefully acknowledge Mr. Mahesh for help during this work. Authors also thank Mr. Vincent for his assistance during characterization of the samples.

REFERENCES

- [1] Sawall, DD. Villahermosa, RM. Lipeles, RA and Hopkins, AR. Interfacial Polymerization of Polyaniline Nanofibers Grafted to Au Surfaces, *Chem. Mater.*, 2004, 16 (9), pp 1606–1608.
- [2] Tan, S. Zhai, J. Xue, B. Wan, M. Meng, Q. Li Y. Jiang, Y. and Zhu, D Property Influence of Polyanilines on Photovoltaic Behaviors of Dye-Sensitized Solar Cells, *Langmuir*, 2004, 20 (7), pp 2934–2937
- [3] Epstein AJ, Hsu FC, Chiou NR and Prigodin VN. Doped conducting polymer based field effect device. *Synthetic Metals* 137 (2003) 859–861.
- [4] Epstein AJ, Hsu FC, Chiou NR and Prigodin VN. Electric-field induced ion-leveraged metal insulator transition in conducting polymer-based field effect devices. *Current Applied Physics* 2 (2002) 339–343.
- [5] N.-R. Chiou, Ph. D thesis, ALIGNED AND ORIENTED POLYANILINE NANOFIBERS: FABRICATION AND APPLICATIONS, The Ohio State University (2006)
- [6] Huang J, Virji S, Weiller BH and Kaner RB. PANI Nanofibers: Facile Synthesis and Chemical Sensors. *J. AM. CHEM. SOC.* 2003, 125, 314–315.
- [7] Virji S, Huang J, Kaner R B and Weiller B H. PANI Nanofiber Gas Sensors: Examination of Response Mechanisms. *nano letters* 2004, Vol. 4, No. 3, 491–496.
- [8] Joseph N, Varghese J, Sebastian MT. Self assembled PANI nanofibers with enhanced electromagnetic shielding properties. *The Royal Society of Chemistry* 2015.
- [9] Radhakrishnan S, Sonawane N and Siju CR. Epoxy powder coatings containing PANI for enhanced corrosion protection. *Progress in Organic Coatings* 64 (2009) 383–386.
- [10] Su B, Tong Y, Bai J, Lei Z, Wang K, Mu H & Dong N. Acid doped PANI nanofiber synthesized by interfacial polymerization. *Indian Journal of Chemistry*, 46A, 2007, 595–599.
- [11] Tang, SJ. Wang, AT. Lin, SY. Huang, KY. Yang, CC. Yeh, JM and Chiu, KC. Polymerization of aniline under various concentrations of APS and HCl, *Polymer Journal* (2011) 43, 667–675
- [12] Zhang L and Wan M. Synthesis and characterization of self-assembled PANI nanotubes doped with D-10-camphorsulfonic acid. *Nanotechnology* 13(2002), 750–755.
- [13] Li G and Zhang Z. Synthesis of Dendritic PANI Nanofibers in a Surfactant Gel. *Macromolecules* 2004, 37, 2683–2685.
- [14] Wang Y, Liu Z, Han B, Sun Z, Huang Y, and Yan G. Facile Synthesis of PANI nanofibers Using Chloroaurate Acid as the Oxidant. *Langmuir* 2005, 21, 833–836.