

Facile Rapid Synthesis of Polyaniline (PANI) Nanofibers

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A Polyaniline (PANI) nanofibers have been successfully synthesized by a facile rapid oxidative polymerization of aniline hydrochloride and ammonium persulfate at high temperature (60 °C). The structural and optical properties of PANI nanofibers are investigated by using X-ray diffraction (XRD), UV-VIS Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR). The XRD analysis ascertains formation of PANI with nanocrystalline nature with average crystallite size 30 nm. Further, FTIR pattern confirmed the formation of PANI. SEM analysis has revealed homogeneous fibrous morphology of PANI nanofibers, a well formed mesh of interconnected and entangled PANI nano-fibers over the scanned area. The UV-VIS spectroscopic analysis shows three major absorption peaks at 256.73, 361.17 and 480.95 nm confirmed the PANI formation with conducting state.

Keywords: Mesh, Nano-fibers, Polyaniline, Rapid mixing, Synthesis

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1. INTRODUCTION

Polyaniline (PANI) is the oldest and potentially one of the most useful conducting polymers because of its facile synthesis, environmental stability and simple acid/base doping/de-doping chemistry. Besides, low cost, high conductivity, and high pseudo-capacitance [1, 2] underlines its importance. It must be noted that nano-form of this polymer could offer new properties or enhanced performance hence nanostructured polyaniline (PANI) has attracted a great deal of interest during the past few years. The polyaniline nanostructures could be formed using simple method of chemical oxidative polymerization of aniline. Taking advantage of the unique reduction/oxidation chemistry of polyaniline and polyaniline/metal nanoparticle composites (nano-composites) could be of great use for various applications in ultrafast nonvolatile memory devices and for chemical catalysis. In addition, the use of polyaniline nanofibers or their composites can significantly enhance the sensitivity, selectivity, and response time of polyaniline-based chemical sensors. Recently conducting polymers found place as a gas sensor because of chief merits such as easy synthesis and room temperature operation. Furthermore, an extensive range of potential technological applications of PANI includes storage batteries, electrochemical devices, light emitting diode, corrosion inhibitor and various types of chemical sensor and bio-sensors [2,3]. The first step towards realizing the applications of nano PANI and its composites is to synthesize the nano PANI films. The focus of this work is to study the standard method reported in literature (Kener et. al. [1]) with little or more variation in synthesis parameters to synthesize the nano-sized PANI powders and thin films.

2. EXPERIMENTAL

2.1 Materials

AR grade chemicals were used for synthesis of Poly-

aniline (PANI) nano-fibers. Aniline Hydrochloride (C₆H₈ClN), Ammonium Persulfate (NH₄)₂S₂O₈ were purchased from Loba Chemie Pvt. Ltd. Mumbai, Maharashtra, India while Hydrochloric Acid (HCl, 35-38 %) was purchased from Thomas Baker Chemicals Pvt. Ltd. Mumbai, Maharashtra, India. All the reagents used in above mentioned methods used without any further purification for PANI synthesis.

2.2 Method

Typically, 1 g of aniline hydrochloride and 0.230 g of ammonium per-sulfate were dissolved in 20 ml of double distilled water in two separate beakers. Both the solutions were heated up to 60 °C then rapidly mixed together to undergo polymerization. The reaction temperature was maintained at 60 °C precisely for 5 minutes till the proper completion of polymerization process. This results into the formation of dark green colored emeraldin salt of polyaniline. Afterwards, heating was stopped and beaker containing PANI solution was allowed to cool naturally. No stirring and shaking was done throughout the synthesis. Later it was filtered and washed with distilled water and 0.2 M HCl to remove the impurities. Then a part of it was dried to get dark green emeraldin salt form of nanocrystalline PANI powder. The other part of PANI solution was then poured carefully drop wise (4-5 drops) on the cleaned and dried substrates and spread uniformly to form thin layer. All the substrates were first thoroughly washed with soap solution and rinsed with water. Then they were ultrasonicated in distilled water for 5 min and subsequently in 0.6 M HCl for 5 min; and later washed by ethanol followed by distilled water. Subsequently substrates with PANI layer were dried at 52 °C temperature under IR illumination to obtain a uniform PANI film. Fig. 1 depicts photographic illustration of different steps involved in the synthesis of PANI nano-fibers.

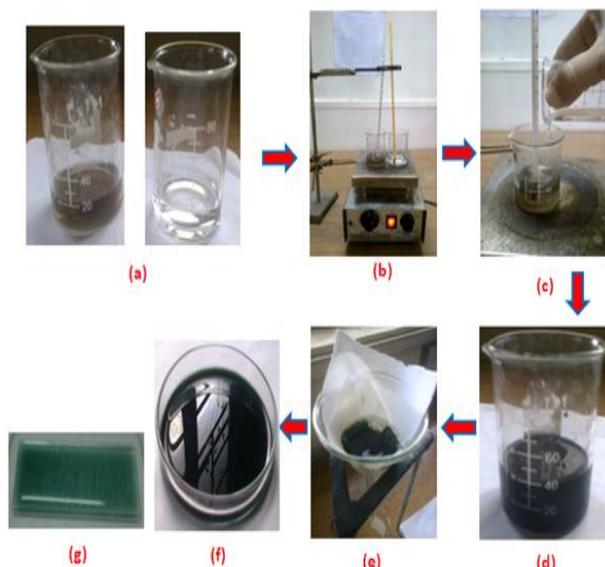


Fig. 1 – Photographic illustration of steps involved in PANI nanofibers synthesis (a) Solutions in beakers contain from left to right aniline hydrochloride and ammonium persulfate, (b) heating up to 60 °C, (c) rapid mixing, (d) PANI undergoing polymerization, (e) filtration and washing, (f) PANI and (g) PANI film on a glass slide

2.3 Characterization

Powder X-ray diffraction pattern (XRD) of PANI nanofibers in powdered form was recorded using a (Bruker D-8, Billerica, MA) advance diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) as a radiation source, operated at 40 kV and 30 mA with a scan rate of 0.02°/s over the range of 10°-80°. XRD analysis was done to identify the crystalline phase, structure and to estimate average crystallite size. The morphological features of PANI nanofibers were studied by using Scanning Electron Microscope (JOEL, FE-SEM 7000). FTIR analysis was performed in the range 4000-400 cm^{-1} with FTIR spectrophotometer (Perkin Elmer Spectrum BX, Waltham, MA) using PANI nanofibers seeded Potassium Bromide (KBr) powder. UV-VIS spectroscopic measurement of absorbance spectra for PANI nanofibers dispersed in double distilled water was performed using a (Shimadzu 1650PC) UV-VIS spectrophotometer.

3. RESULTS AND DISCUSSIONS

Fig. 2 shows the XRD pattern of PANI nanofibers. The XRD pattern reveals crystalline nature of PANI nanofibers. Fig. 2 shows three sharp peaks at $2\theta = 15.14^\circ$, 19.36° , 24.48° , which corresponds to (011), (020) and (200) crystal planes of PANI [4] whereas the peaks corresponding to $2\theta = 44^\circ$, 48° and 51.5° are attributed to the nanocrystalline nature of PANI [5]. The crystalline nature of PANI is due to its nano fibrous form and planer nature of Benzenoid and Quinoid functional groups [6]. The lattice constant (a) was calculated using the formula $a = d\sqrt{h^2 + k^2 + l^2}$ where d is inter-planer distance and (hkl) are Miller indices. The calculated average value of lattice constant (a) from XRD graph is $a = 8.2327 \text{ \AA}$. The reported values of inter planer distances are 42.14 nm at $2\theta = 21.10^\circ$ and 37.74 nm

at $2\theta = 23.59^\circ$ respectively [6]. However the as measured values of inter planer distances from XRD pattern in our experimentation were found to be 45.8 nm at $2\theta = 19.36^\circ$ and 36.3 nm at $2\theta = 24.48^\circ$ respectively. The deviation of the lattice parameters is mainly due to internal stresses which contribute to little shifting of XRD peaks from the expected 2θ values.

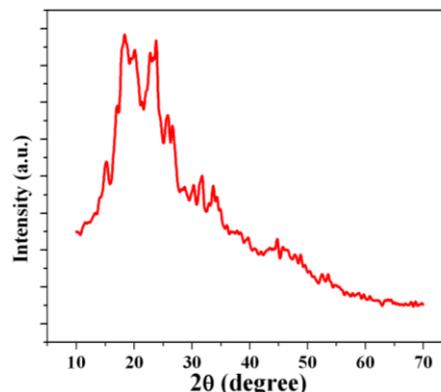


Fig. 2 – XRD pattern of PANI nanofibers

The 2θ values for prominent peaks, corresponding (hkl) planes and inter-planar distance (d) are represented in Table 1.

Table 1 – XRD analysis of PANI, nanofibers

2θ	(hkl) plane	Inter-planar distance (d) in \AA
15.14°	011	5.85
19.36°	020	4.58
24.48°	200	3.63

The average crystallite size (D) in \AA , was calculated by using Scherer's formula [7] given by (1).

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where K is the shape factor usually has a value 0.9, λ is the X-ray wavelength and θ the Bragg angle and β gives the full width of the half maxima (FWHM). The determined average crystallite size was 30 nm.

The SEM micrograph of as synthesized PANI nanofibers is represented by Fig. 3. The SEM micrograph demonstrates a homogeneous fibrous morphology of PANI nanofibers. It also shows a well formed mesh of interconnected and entangled PANI nano-fibers. The entanglement is mainly attributed to high temperature during actual polymerization process during the synthesis. The interconnected and entangled structure is also due to steady synthesis which allows the easy branching with other fibers growing during polymerization process. This facilitates homogeneous nucleation thereby giving fine uniform and interconnected nanofibers of PANI. On the other hand the low temperature process with stirring and shaking during PANI synthesis encourages heterogeneous nucleation which typically leads to cluster and granule (crystal) formation. The estimated average crystallite size of PANI nanofibers from SEM was 30 ± 5 nm which also corroborates the average crystalline size of 30 nm obtained from XRD.

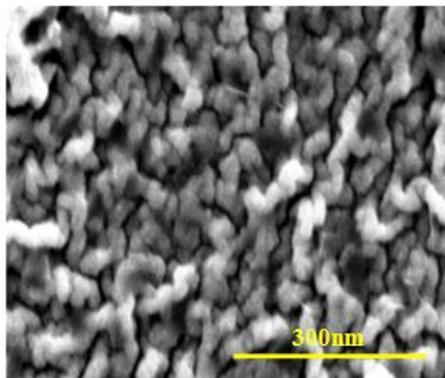


Fig. 3 – SEM micrograph of PANI nanofibers

The FTIR spectrum of PANI is represented in Fig. 4. The Fig. 4 shows vibration band around 3229.24 cm^{-1} is attributed to the N-H stretching vibrations [8]. The main characteristic peaks at 1568.95 , 1475.6 , 1297.6 , 1139.49 , and 812.94 cm^{-1} . The bands at 1568.95 , 1475.6 and 1297.6 are assigned to the stretching mode of N=Q=N ring, N–B–N ring, and C–N (C_{aromatic}–N) deformation, respectively [9] (where B refers to benzenoid ring and Q refers to quinonoid ring). Further, the observed band at 812.94 cm^{-1} attributes to the out-of-plane vibration of C–H on 1,4-disubstituted aromatic rings. The presence of characteristic absorption peaks in the FTIR spectrum in Fig. 4 substantiates the formation of PANI nanofibers.

Fig. 5 exhibits UV–VIS absorption spectrum PANI nanofibers. The Fig. 5 shows three major absorption peaks at 256.73 , 361.17 , 480.95 nm . The peak observed at $\lambda = 256.73\text{ nm}$ is due to the π - π^* transition of benzenoid ring which is related to the extent of conjugation between the adjacent phenylene rings in the polymeric chain [10]. The less intense band peak at $\lambda = 361.17\text{ nm}$ is due to π - π^* transition while the peak at 480.05 nm is on account of to polaron- π^* transition and shift of electron from benzenoid ring to quinonoid ring [11] which represents the protonation of PANI that suggests a conducting state [12]. Further, the peak at $\lambda = 820\text{ nm}$ is due to π -polaron transition.

4. CONCLUSIONS

PANI nano-fibers have been successfully synthesized by a facile rapid oxidative polymerization of aniline hydro-

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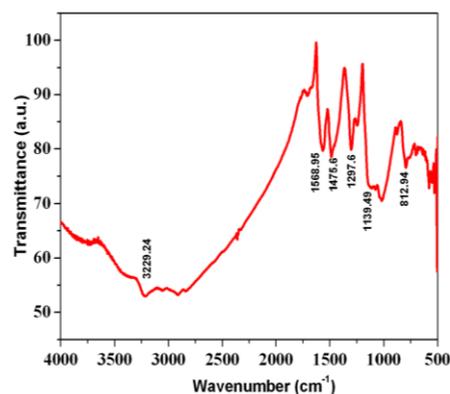


Fig. 4 – FTIR spectrum of PANI nanofibers

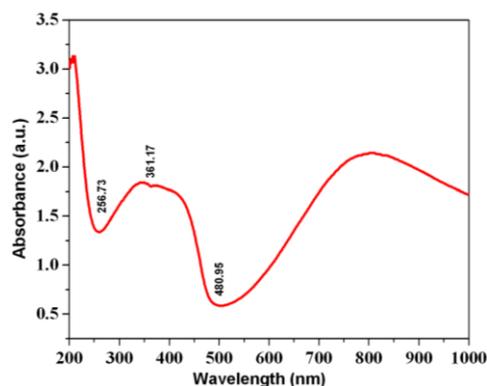


Fig. 5 – UV-VIS spectrum on PANI nanofibers.spectrum of PANI nanofibers

chloride and ammonium persulfate at high temperature ($60\text{ }^{\circ}\text{C}$). The XRD study reveals nanocrystalline nature of PANI with average crystallite grain size of 30 nm . SEM studies reveals homogeneous fibrous morphology of PANI nanofibers with a well formed mesh of interconnected and entangled PANI nano-fibers with average diameter of $30 \pm 5\text{ nm}$ over the scanned area. The presence of characteristic functional groups in FTIR spectrum confirmed formation of PANI.

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