

Fabrication and Characterization of Polyaniline Nanofiber Films by Various Techniques

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In this paper, the polyaniline nanofibers (PAni NFs) were successfully synthesized by chemical oxidation and hydrothermal methods. The structural, surface morphological, optical, and electrical properties were investigated for PAni NFs films deposited by spin coating technique. The XRD results showed that PAni films have crystalline nature. The average crystallite sizes were 7.5 and 9.9 nm for PAni prepared by hydrothermal and chemical methods, respectively. The FESEM images of PAni clearly indicated that it has nanofiber like structure. The presence of characteristic functional groups in FTIR spectrum confirmed the formation of PAni. Optical characterization showed that the direct electronic transition is allowed in the energy gap. The values of energy gap for PAni NFs are 2.46 eV and 2.63 eV at hydrothermal and chemical oxidation methods, respectively. The absorbance decreases rapidly at short wavelengths corresponding to the energy gap of the film. AC electrical properties showed that the PAni NFs prepared by chemical method have higher AC conductivity than those prepared by hydrothermal method, whereas the capacitance decreases when frequency increases. The values of frequency exponent (s) of the investigated thin films lie between 1.15 and 0.16 at hydrothermal and chemical oxidation methods, respectively. The dielectric constant (ϵ_1) and dielectric loss (ϵ_2) were found to be influenced by preparation method.

Keywords: Hydrothermal method, Chemical oxidation, Polyaniline, Structural properties, Nanofibers, AC conductivity.

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1. INTRODUCTION

Polyaniline (PAni) is one of the most promising organic polymers due to its potential technological applications such as gas sensors, storage batteries, light emitting diodes (LEDs), corrosion control, electrodes for redox super capacitors, protection coatings, electrochromic display biosensors, and photovoltaic devices [1, 2]. PAni is considered environmentally stable, has well-behaved electrochemistry and high electrical conductivity “upon doping” [2, 3]. Conducting polymer CP nanostructures (i.e., nanotubes, -rods, -fibers, and -wires) combine the advantages of organic conductors with low-dimensional systems and therefore create interesting physicochemical properties and potentially useful applications [4-6]. Traditionally, the advantage of polymeric materials is that they can be synthesized and processed on a large scale at relatively low cost [1, 7, 8]. In this paper, we have reported the synthesis of a conducting polymer (PAni) by two methods (hydrothermal and chemical). PAni thin films were made by the spin coating technique. These films were further investigated for their structural, morphological, optical and AC electrical properties.

2. EXPERIMENTAL

2.1 Materials and Method

PAni NFs were synthesized by different methods such as chemical oxidation and hydrothermal methods using aniline (ANI), monomer (99.5 %), ammonium peroxydisulfate (APS) and HCL [New Delhi Co., India]. In a typical procedure, 0.083 g of ANI was added to 74 ml of water with vigorous stirring for 10 min to form

the homogeneous solution. In addition, 6 ml of 0.274 g ammonium APS aqueous solution was slowly added into the monomer solution under drastic stirring. After that, 1.5 ml of HCL was added to the above solution and stirred for 10 min. Then the mixture was transferred according to different methods:

– For chemical oxidation method, the above mixture was left for 24 h at room temperature.

– For hydrothermal method, the mixture was transferred into 100 ml of a Teflon-lined stainless steel hydrothermal reactor and sealed. The reactor was maintained at 120 °C for 6 h in an electric oven, and then allowed to cool at room temperature quickly by putting into an icy water bath.

The resulting precipitate from those two different methods was centrifuged and washed using deionized water and ethanol repetitively. The final products were dried in vacuum at 70 °C for 3 h to obtain the powder. For chemical oxidation method, 0.01 g of PAni powder was dissolved in 50 ml of water, and then this solution was placed in an ultrasonic for 2 h to be well dispersed. Finally, the solutions were deposited on clean glass and silicon substrates by spin-coating technique to prepare thin films as following. An excess amount of the PAni solution is firstly dropped onto the surface of silicon (111) wafer substrate. The spin coating rotates the substrate at a speed of around 1200-1800 rpm for 1 min in order to spread the solution by centrifugal force. To get homogeneous films, several factors are important and have to be considered, which are angular velocity (rotating speed), viscosity of the fluid, evaporation rate of the solvent spinning time, and concentration of the solution. A similar experiment was carried out in hydrothermal method instead of chemical oxidation one to

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see the influence of different methods on the structural, surface morphological, optical, and electrical properties of the PANi nanostructure.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Fig. 1 shows the XRD pattern of PANi thin films by hydrothermal and chemical techniques. The XRD pattern of PANi exhibits a broad peak at $2\theta = 24^\circ$ and 24.66° for PANi prepared by hydrothermal and chemical methods, respectively, which corresponds to (200) plane that is in agreement with other reports [9, 10]. The crystalline nature of PANi is due to its nanofiber form and planer nature of benzenoid and quinoid functional groups [10, 11].

The average crystallite size (D) is calculated according to the Debye-Scherrer equation [1, 12, 13]:

$$D = \frac{K\lambda}{\beta \cos \theta}, \tag{1}$$

where K is the shape factor (0.9), λ is the wavelength of X-ray radiation used (1.5406 Å), β is the full width at half maximum, θ is the diffraction angle. The determined average crystallite sizes were 7.5 and 9.9 nm for PANi prepared by hydrothermal and chemical methods, respectively, as shown in Table 1. The difference between the two XRD patterns and crystallite sizes is indicative of the influence of the method on the final morphology of the films [14].

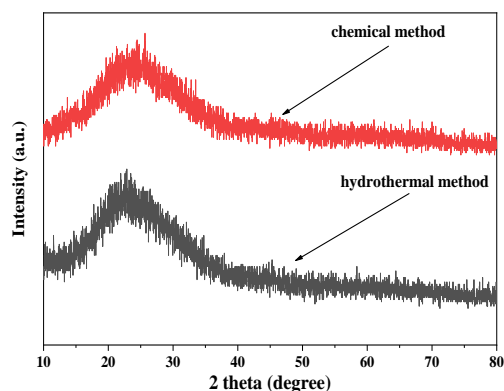


Fig. 1 – XRD pattern of PANi thin films at different methods

Table 1 – X-ray diffraction results of PANi thin films at different methods

Type of preparation	2θ , deg.	β , deg.	d_{hkl} , Å	D , nm	hkl
Hydrothermal method	24	1.08	3.7049	7.52	200
Chemical method	24.66	0.82	3.6070	9.92	200

3.2 FE-SEM Analysis

FE-SEM images of PANi NFs prepared by hydrothermal and chemical techniques are shown in Fig. 2. The porosity nature of the material and the fibers mor-

phology were confirmed by a FE-SEM study. SEM images showed smooth PANi NFs with several millimeters in length prepared by hydrothermal method. While comparing images with PANi NFs prepared by chemical method, they are well aligned with slight porosity. The orientation of structures and morphology of samples at the macroscopic level affect the mobility of charge carriers and, thus, influence conductivity of polymer [15].

3.3 FTIR Spectrum Analysis

FTIR is one of the most common methods of spectroscopy, IR spectroscopy analyzed polyaniline with different technique. Fig. 3 shows the FTIR spectra of PANi prepared by hydrothermal and chemical techniques. The main peaks appear at 623, 810, 1127, 1388, 1590, 2939 and 3449 cm^{-1} for PANi prepared by hydrothermal and chemical techniques. The bands at 623 and 810 cm^{-1} represent the C–C and C–H bands of benzenoid group. C=C stretch and C–H stretch modes for benzenoid group were at 2939 cm^{-1} and 1388 cm^{-1} respectively; the band at 3429 cm^{-1} referred to the stretching mode of the N–H band, while the band at 1127 cm^{-1} was attributed for quinoid unit of polyaniline which is in agreement with other reports [1, 16]. At chemical method, a shift of few peaks towards higher wavenumbers is possible with an increase in the intensity of peaks. This may be due to the increase in the degree of polymerization of PANi NFs [16].

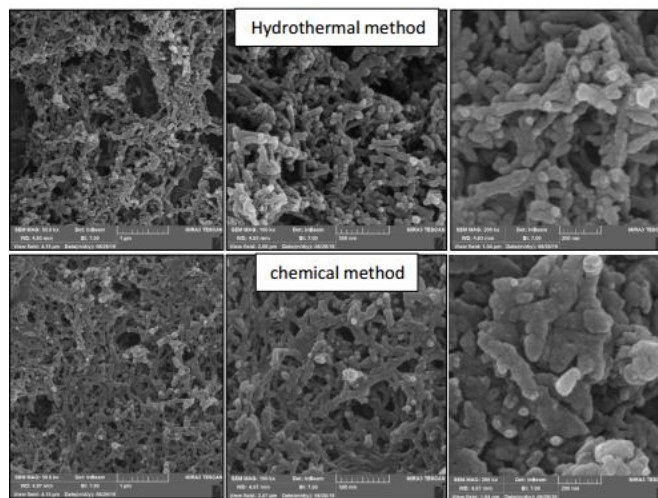


Fig. 2 – FE-SEM images of PANi NFs films at different methods

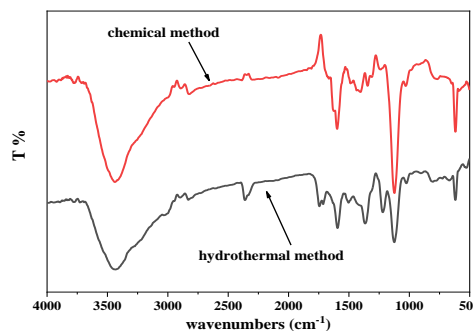


Fig. 3 – FTIR spectrum of PANi NFs films at different methods

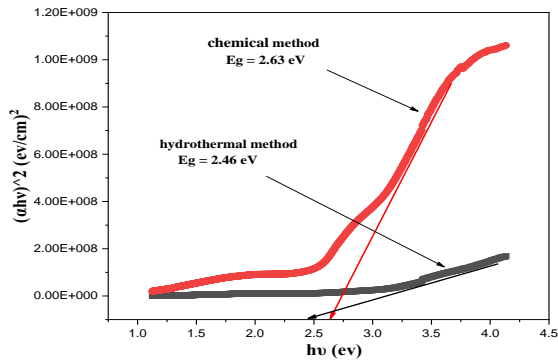


Fig. 4 – Tauc’s plot of PANi NFs films

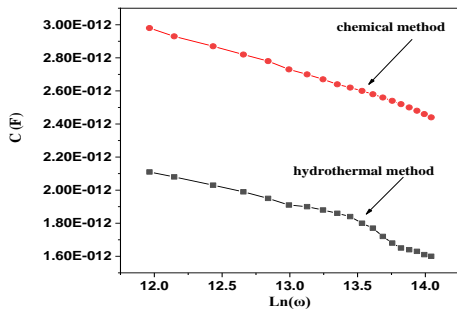


Fig. 5 – Capacitance against angular frequency for PANi NFs films

3.4 UV-Vis Spectroscopy Analysis

Optical absorption spectra of the films in spectral range of 180-1100 nm were recorded by using UV-Vis spectrophotometer. Fig. 4 shows the relation between absorbance (*A*) and wavelength for PANi NFs at different methods. The absorbance decreases rapidly at short wavelengths corresponding to the energy gap of the film. The peak observed at $\lambda = 301$ nm for PANi prepared by hydrothermal method 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 [11]. The high intense band peak at $\lambda = 355$ nm for PANi prepared by chemical technique is due to the π - π^* transition [9]. The energy gap (E_g) can be calculated from Tauc’s formula [1, 13]:

$$\alpha hv = C(hv - E_g)^n, \tag{2}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, C is a constant depending on the probability of the transfer of electrons and n has a value of 1/2 for allowed direct transitions. The relation is drawn between $(\alpha hv)^2$ and photon energy ($h\nu$), as shown in Fig. 4 which illustrates the allowed direct transition of electrons. The optical energy band gaps were found to be 2.46 eV and 2.63 eV for PANi NFs prepared by hydrothermal and chemical methods, respectively. This decrease in the band gap for PANi NFs prepared by hydrothermal method may be attributed to the changes in homogeneity and crystallinity of the PANi NFs caused by differences in experimental conditions, mainly the homogeneity of suspension and the rapid cooling to room temperature compared with PANi NFs prepared by chemical method.

3.5 Electrical Properties

The variation of capacitance as a function of angular frequency at different preparation methods for PANi thin films is shown in Fig. 5. Its absorbed capacitance decreases at the initial frequency. This decrease can be accounted by the increase in the space charge region at the electrodes [17]. Also, it was the maximum capacitance of PANi NFs prepared by hydrothermal method. The alternating current conductivity ($\sigma_{a.c.}$) is calculated from equation [18]:

$$\sigma_{a.c.}(\omega) = \sigma_t - \sigma_{d.c.} = A\omega_s, \tag{3}$$

where A is a constant, s is the frequency exponent, and $\omega = 2\pi f$. The angular frequency depends on the total conductivity (σ) of PANi NFs prepared by hydrothermal and chemical techniques at room temperature as shown in Fig. 6. It is noted that the total conductivity (σ) increases with the angular frequency. The PANi NFs prepared by chemical method have higher conductivity compared with those prepared by hydrothermal method because the rate of polymerization is higher in chemical method. This means that the molecular weight of the prepared polymer increases and effects the number of polarons in a polymer chain that leads to an increase in conductivity. From Fig. 6, it is seen that the $\sigma_{a.c.}$ increases as the frequency increases. The slope of the straight lines in Fig. 6 represents the frequency exponent. The values of s of the investigated thin films lie between 1.15 and 0.16 at hydrothermal and chemical oxidation methods, respectively.

Fig. 7 illustrates the frequency dependence of the dielectric constant (ϵ_1). It is seen from the figure that ϵ_1 decreases as frequency increases; this decrease may be

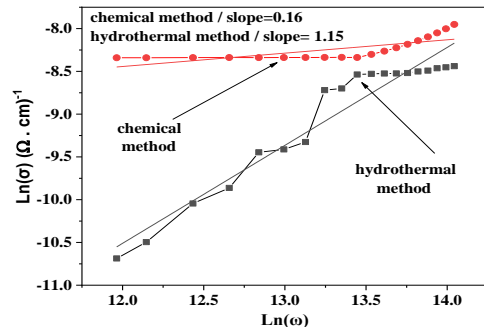


Fig. 6 – The variation of a.c. conductivity as a function of angular frequency

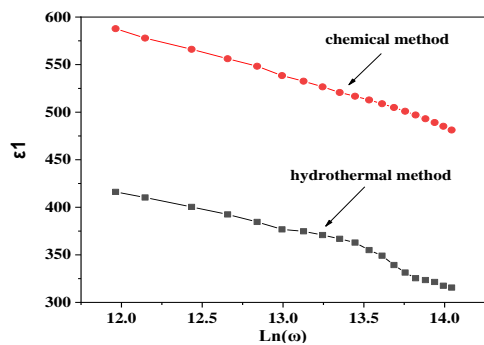


Fig. 7 – Dielectric constant ϵ_1 against angular frequency

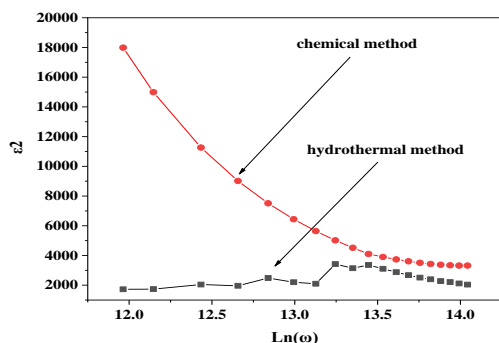


Fig. 8 – The dielectric loss ϵ_2 against the angular frequency

described as follows: at small frequencies, ϵ_1 of polar material causes the involvement of multicomponent of ability polarize deformational (ionic, interfacial, electronic and orientation). At large frequency, the dipole will no longer be able to rotate sufficiently rapidly. Therefore, their oscillations should lag behind those of the field. With increasing frequency the dipoles become completely incapable of following the fields, and the orientation may stop, so ϵ_1 decreases at greater fre-

quencies and imminent constant values cause the polarization of interface [18, 19]. The dielectric loss ϵ_2 is measured as a function of frequency as shown in Fig. 8. It is seen that ϵ_2 is found to be decreasing as the frequency increases for PANi prepared by chemical method, but increasing for PANi prepared by hydrothermal method. The backgrounds for the dielectric loss were considered conduction loss [20].

4. CONCLUSIONS

PAni NFs were successfully synthesized by chemical oxidation and hydrothermal methods. The XRD results showed that PANi films have crystalline nature. The FE-SEM images of PANi clearly indicated that it has nanofiber like structure. The presence of characteristic functional groups in FTIR spectra confirmed the formation of PANi. The band gap values of the polymer were calculated through the Tauc's relation and were found to be 2.46 eV and 2.63 eV at hydrothermal and chemical oxidation methods, respectively. The dielectric constant (ϵ) and loss factor ($\tan\delta$) were found to be influenced by the preparation method.

REFERENCES

- I.M. Ali, A.M. Shano, N.A. Bakr, *J. Mater. Sci.: Mater. Electron. Mater.* **29** No 13, 11208 (2018).
- L. Hu, G. Gruner J. Jenkinsb, C.J. Kim, *J. Mater. Chem.* **19** No 32, 5845 (2009).
- Channu, Venkata Subba Reddy, *Iran. Poly. J.* **21** No 7, 457 (2012).
- Y. Huangfu, K. Ruan, H. Qiu, Y. Lu, C. Liang, J. Kong, J. Gu, *Composites Part A: App. Sci. Manufactur.* **121**, 265 (2019).
- X. Zhu, K. Hou, C. Chen, W. Zhang, H. Sun, G. Zhang, Z. Gao, *High Performance Polym.* **27** No 2, 207 (2015).
- R. Ashraf, A. Kausar, M. Siddiq, *Iran. Poly. J.* **23** No 7, 531 (2014).
- L.S. Carquigny, O. Segut, T. Patois, S. Lakard, *Metals* **9** No 5, 1371 (2015).
- Fortin, F.L. Weichman, Can, *J. Phys.* **40** No 12, 1703 (1962).
- A.D. Bhagwat, S.S. Sawant, C.M. Mahajan, *J. Nano- Electron. Phys.* **8** No 1, 01037 (2016).
- C.G. Wu, C.H. Chiang, U.S. Jeng, *J. Phys. Chem. B* **112** No 22, 6772 (2008).
- V.J. Babu, S. Vempati, T. Uyar, S. Ramakrishna, *Phys. Chem. Chem. Phys.* **17** No 5, 2960 (2015).
- N.A. Bakr, Z.T. Khodair, A.M. Shano, *Int. J. Thin. Fil. Sci. Tec.* **4** No 2, 111 (2015).
- A.M. Shano, I.M. Ali, N.A. Bakr, *J. Nano- Electron. Phys.* **11** No 6, 06016 (2019).
- N. Bohli, F. Gmati, A.B. Mohamed, V. Vigneras, J.L. Miane, *J. Phys. D: Appl. Phys.* **42**, 205404 (2009).
- A.N.J. AL-Daghman, K. Ibrahim, N.M. Ahmed, M.A. AL-Messiere, *J. Optoelectron. Biomed. Mater.* **8** No 4, 175 (2016).
- K.T. Vadiraj, S.L. Belagali, *J. Appl. Chem.* **8** No 1, 53 (2015).
- S.M. Hassan, H.I. Jafaar, *Int. J. Basic Appl. Sci.* **2** No 1, 352 (2012).
- Joshi, M. Jigar, V.K. Sinha, *Carbohydrate Polym.* **67** No 3, 427 (2007).
- M.A. Ali, E. Saion, N. Yahya, A. Kassim, K.M. Dahlan, S. Hashim, *J. Eng. Sci. Tech.* **2** No 1-2, 111 (2007).
- E.N. Zare, P.N. Moghadam, E. Azariyan, I. Sharifian, *Iran. Polym. J.* **20** No 4, 319 (2011).

Виготовлення та характеристика поліанілінових нановолоконних плівок різними методиками

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У роботі поліанілінові нановолокна (PANi NFs) були успішно синтезовані методом хімічного окислення та гідротермальним методом. Були досліджені структурні, поверхневі морфологічні, оптичні та електричні властивості плівок PANi NFs, нанесених методом центрифугування. Результати XRD показали, що плівки PANi мають кристалічну природу. Середні розміри кристалітів склали 7,5 та 9,9 нм для плівок PANi, отриманих відповідно гідротермальним та хімічним методами. FESEM зображення PANi чітко вказували на те, що він має структуру, подібну до нановолокон. Наявність характерних функціональних груп у спектрі FTIR підтвердила утворення PANi. Оптична характеристика показала, що в забороненій зоні допускається прямий електронний перехід. Значення ширини забороненої зони для PANi NFs становлять відповідно 2,46 еВ та 2,63 еВ при гідротермальном та хімічному методах окислення. Поглинання швидко зменшується при коротких довжинах хвиль, що відповідають ширині забороненої зони плівки. Електричні властивості змінного струму показали, що

PANI NFs, приготовлені хімічним методом, мають більш високу провідність змінного струму, ніж ті, що готуються гідротермальним методом, тоді як емність плівок зменшується при збільшенні частоти. Значення показника частоти (s) досліджуваних тонких плівок лежать відповідно між 1,15 та 0,16 при гідротермальному та хімічному методах окислення. Виявилося, що метод приготування плівок впливає на діелектричну константу (ϵ_1) та діелектричні втрати (ϵ_2).

Ключові слова: Гідротермальний метод, Хімічне окислення, Поліанілін, Структурні властивості, Нановолокна, Змінна провідність.