



Investigation of Structural and Thermal Properties of Nanostructured PANI

B. Sathish Mohan¹, Y. Pavan Kumar¹, D. Ramadevi², K. Basavaiah³

^{1,2}Research Scholar, ³Professor

¹Dept. of Inorganic & Analytical Chemistry, ²AU College of Pharmaceutical Sciences,

³Dept. of Inorganic and Analytical Chemistry,

Andhra University, Visakhapatnam, Andhra Pradesh, India

ABSTRACT

In this paper, we report a preparation of poly aniline (PANI) nanostructure by oxidative polymerisation in presence of HCl as do pant. The structural, morphological and thermal properties of as-prepared PANI was investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR), UV-Visible diffuse reflectance spectrophotometer (DRS), Field emission scanning electron microscopy (FESEM) and Thermo gravimetric analysis (TGA). It is found that the morphology of PANI is fibril like shape with band gap of 2.74eV. Thermal conductivity of PANI nanostructure was calculated as a function of temperature.

Keywords: PANI, oxidative polymerisation and thermal conductivity.

1. INTRODUCTION

Intrinsic conducting polymers (ICPs) have been emerged as potential materials for many technological applications such as sensors, EMI shielding, electro chromic displays, batteries, energy storage, solar cells and catalysis [1-3]. Among all ICPs such as, polypyrrole, Poly (3,4-ethylenedioxythiophene), poly aniline (PANI) and its derivatives have received great attention due to their unique red ox chemistry and electrical properties, high chemical and environmental stability [4, 5].

The structure and properties of PANI are firmly connected to their synthetic methods, there are numerous methods like emulsion, micro-emulsion, diffusion polymerization and interfacial polymerization have been reported earlier [6-8].

Generally, each of these methods has its own advantages and limitations. To the best our knowledge, these synthetic methods can be broadly divided into two categories like chemical and electrochemical [9]. Chemical polymerization can result in various morphologies, like nanorods, nanospheres, nanofibers, nanotubes, nanoflakes, and nanoflowers [10,11]. This paper addresses the preparation of PANI nanofibrils by chemical oxidative polymerization of aniline in aqueous medium using APS as oxidant and studies its structural and thermal properties.

2. Experimental section

2.1 Materials and method

Aniline (C₆H₇N), hydrochloric acid (HCl) and ammonium persulfate, APS ((NH₄)₂S₂O₈) were procured from Sigma Aldrich. The Milli Q water used throughout the synthesis of PANI,

2.2 Synthesis of PANI

In typical synthesis, 0.1 M of aniline was dissolved in 1 M HCl solution in a round bottom flask with constant stirring at 0-5°C. Then an aqueous solution of APS (0.1 M) was added drop wise to the reaction mixture under constant stirring for 4 h. The reaction mixture is turned from pale blue colour to dark green colour, which indicates the formation of PANI. The reaction was further preceded for 12 h at 0-5 °C. Then, the reaction mixture was allowed to attain room temperature. As formed green precipitate was centrifuged and washed periodically with water and method to remove the oligomers, unreacted in material. Then, finally dried under vacuum for 12 h,

2.3 Characterisation

The crystalline and phase formation of PANI was studied by X-ray diffraction (XRD, Bruker D8 Focus) with a Cu k alpha radiation source with scan range of $2\theta = 10-70^\circ$ at a speed rate 0.02° per step. The morphology of the PANI was characterized by scanning electron microscope (FESEM, JEOL field emission scanning electron microscope, JSM-6700F). The band gap was calculated by UV-Visible diffuse reflectance spectrophotometer (DRS, Shimadzu, 2700R) in the range from 200 to 800 nm. The thermogravimetric analysis of PANI was carried out by TGA (TA instruments Q-500) in the temperature range of 30 to 700°C with an air flow rate of 60 mL/min and a heating rate of $10^\circ\text{C}/\text{min}$ under Ar atmosphere.

3. Results and Discussion

The XRD patterns of PANI were depicted in Figure 1(a). The characteristic diffraction peaks centred at

$2\theta = 14.5^\circ, 20^\circ, 25.9^\circ, 27.8^\circ$ which corresponds to parallel and perpendicular to phenyl rings of PANI. The XRD of PANI is in well agreement with the literature report [12].

The band gap energy of as-prepared PANI was calculated using UV-Visible DRS and the UV DRS spectrum was depicted in Figure 1(b). The band gap of PANI was calculated from diffuse reflectance spectra by using equation 1.

$$E_g = h\nu = hc/\lambda = 1240/\lambda \quad \text{Eq. (1)}$$

Where E_g is band gap energy, h is planks constant, ν is wave frequency, c is light of speed and λ is the wavelength. It can be found that the PANI has an absorption edge around 457 nm corresponds to the band gap of 2.74eV.

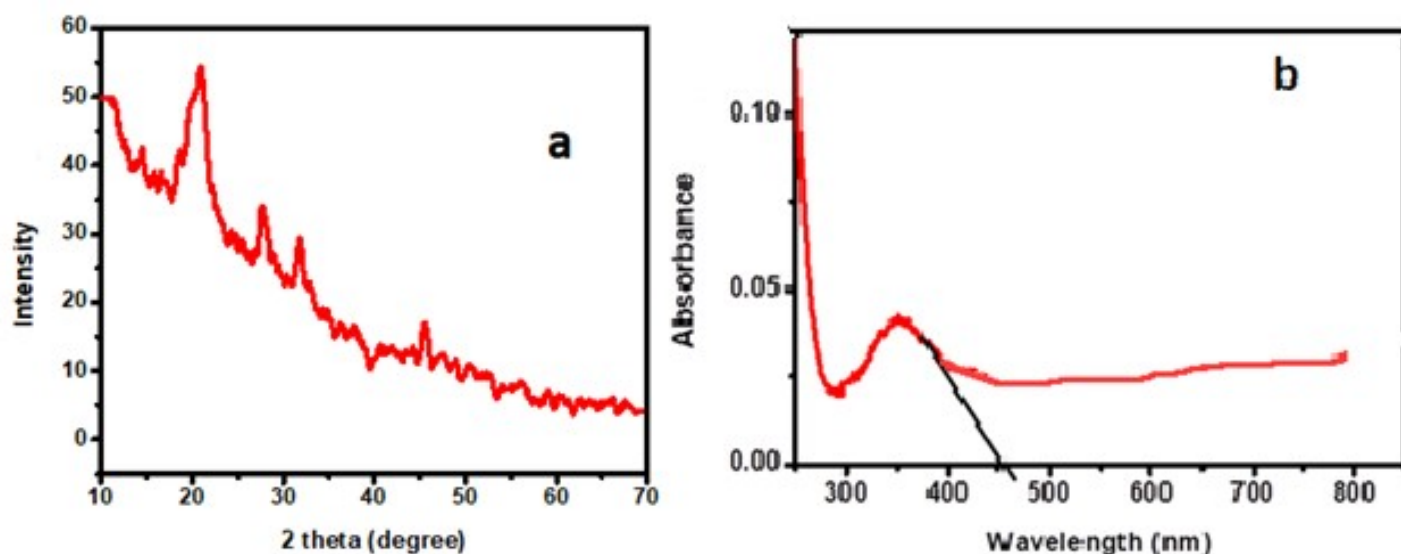


Figure 1: a) XRD patterns and b) UV DRS spectrum of PANI

FTIR spectrum of PANI is shown in Figure 2. The characteristic peaks at 515 and 808 cm^{-1} were due to the presence of C-H out-of planes bending vibrations and para-disubstituted benzene rings respectively [12]. The peak at 1307 cm^{-1} is ascribed to C-N stretching vibrations. The three characteristic peaks at 1154 , 1491 and 1589 cm^{-1} are corresponds to in-plane bending vibrations in C-H, C-N and C-C respectively. A broad peak at 3403 cm^{-1} is associated to the presence of N-H stretching of aromatic amines in PANI.

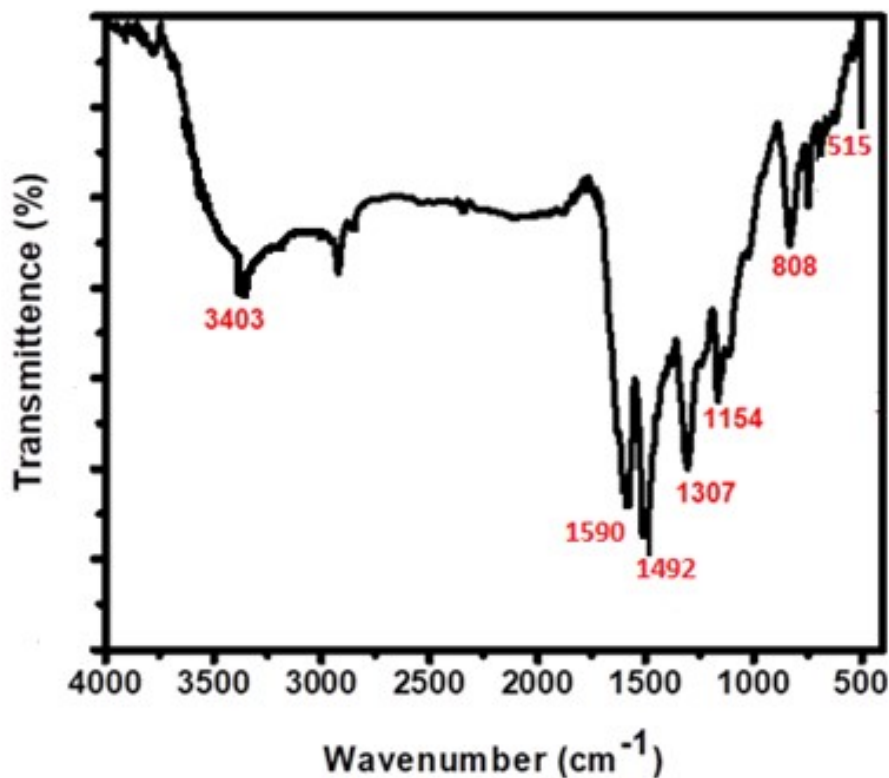


Figure 2: FTIR spectrum of PAN

The representative FESEM images of as-prepared PANI by chemical oxidative polymerization method were displayed in Fig. 3. The FESEM images clearly reveal the fibril like morphology.

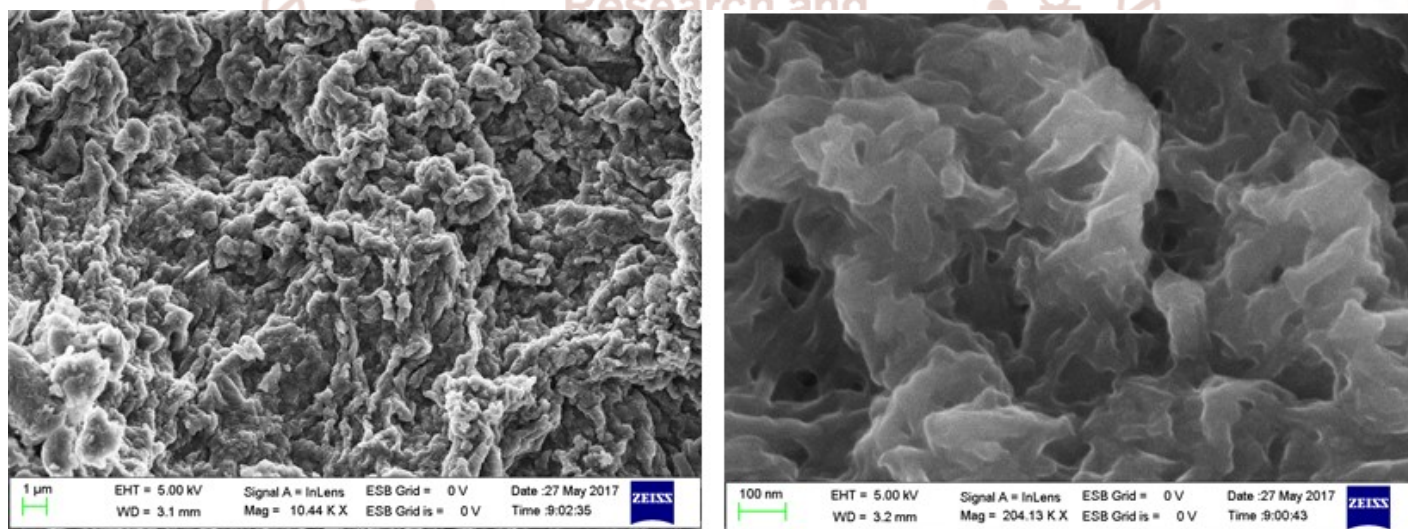


Figure 3: FESEM images of PANI

The TGA curve for PANI is presented in Fig. 4 (a). The TGA curve shows three characteristic weight losses at three different temperatures are 93, 455 and 550 °C. Figure 4a shows the thermal decomposition of PANI by weight loss percentage increases with the temperature. It shows a weight loss of 11.2 % up to 93 °C, 19 % from 94-455 °C and 49.4 % from 455-550°C respectively due to loss of water molecules and reduces the benzeneoid rings [13-15].

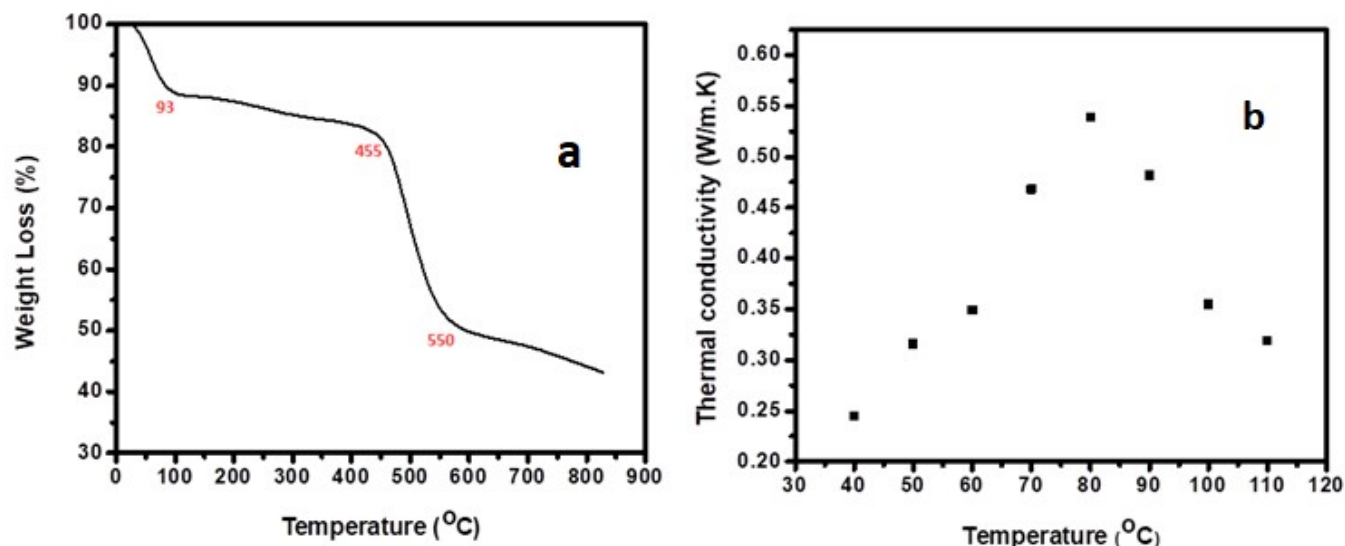


Figure 4: a) TGA curve and b) Thermal conductivity of PANI

The thermal conductivity of prepared PANI was measured using TA probe (Figure 4b). The temperature increases, thermal conductivity increases up to certain level and then decreases; this is due to the thermal conductivity is mostly depends on the motion of free electrons. As the temperature increases, the molecular vibrations increase (in turn decreasing the mean free path of molecules). Hence, they block the flow of free electrons, thus reducing the conductivity. The maximum thermal conductivity was shown at the temperature of 80 °C was shown in Table 1.

Table 1: Thermal conductivity of PANI at different temperatures

S. No	Temp (°C)	Thermal conductivity (W/m. K)
1	40	0.245
2	50	0.316
3	60	0.349
4	70	0.468
5	80	0.589
6	90	0.482
7	100	0.355
8	110	0.319

Conclusion

In summary, we have demonstrated a facile, reproducible method for the preparation of PANI nanofibrils via oxidative polymerization method using APS as an oxidant. The prepared PANI was characterized using XRD, FTIR, FESEM, UV-DRS and TGA to study its structural and thermal properties. The results clearly show that PANI has

high thermal conductivity and hence it has thermal stability.

Conflicts of Interest

The authors clearly declared that there is no any conflict of interest.

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