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Synthesis and characterization of crystalline polyaniline

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The present paper deals with the synthesis and characterization of crystalline polyaniline (PANI). In the present work the crystalline PANI was synthesized in two steps. Firstly, the amorphous polyaniline was prepared by co-precipitation method using aniline as precursor and ammonium peroxodisulfate as reagent. In second stage the crystalline PANI was prepared by the melting and slow cooling. Pellets of PANI were prepared at pressure of 3000-4000 kg/cm^2. The resulting crystalline PANI was characterized by powder X-ray diffraction (PXRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM). The PXRD pattern confirms the crystalline behaviour of PANI. The AFM results also support PXRD result due to presence of tiny crystals on the surface of PANI. TEM analysis reveals various nanorings connecting the characteristics diffraction spots of PANI nanoparticles.

Keywords: AFM, Crystalline PANI, crystals, TEM, XRD

1 Introduction

Polymers had been mainly used as an electrical insulator for long time, but their conventional role was gradually changed to an electrical conductor with a wide range of novel applications. Owing to many researcher's effort, a new class of polymers known as conducting polymers has emerged during the last twenty years. Conducting polymers are organic based polymers having alternative single and double bond conjugation which is mainly responsible for its conductivity. Among the various conducting polymers, PANI is the oldest one. PANI is extensively studied due to its better conductivity, cost effectiveness, environmental stability, redox reversibility and ease of synthesis[1-5]. PANI exist in three forms namely Emerlidine (EB), Luecoemerlidine, Perilinigreen, among these Emerlidine is the conducting form of PANI[6]. When aniline is oxidized with ammonium peroxidisulphate it becomes conductive which is PANI–EB. The application field of nanostructure PANI is very broad. PANI salts are currently used as electrode materials in the supercapacitor application, symmetric two-electrode cell configuration, nanostructured composite with graphene as anticorrosion materials, chemical sensor, conversion and storage, light emitting display device, microelectronics, optical storage, supercapacitors *etc*[7]. The power density of supercapacitor is much higher also since it has high energy density compared to conventional electro-chemical double layer capacitor. Therefore its application field is broad which includes digital communication devices, digital cameras, mobile phones, power supplies and hybrid electric vehicles.

Since the crystallization affects the optical, mechanical, thermal stability and chemical properties of the polymer, so the synthesis of crystalline polymers in which either the partial or full alignment of their molecular chains is feasible, is the current demands among the materials scientists. A number of different methods for the synthesizing crystalline, nanoststucture polyaniline have been reviewed by the Tran *et al.*[8], Kaykha & Rafizadeh[9] incorporated unsaturated polybutylenes fumarate (PBF) and reduced graphene oxide (RGO) as a polymeric dopant in the synthesis of PANI to prepare the conductive and anticorrosive compound. PBF:RGO exhibited higher thermal stability, higher crystallization rate, and lower crystallinity compared with pristine PBF. Xinxin *et al.*[10] reported the synthesis of flake-like PANI using cetyltrimethyl ammonium bromide (CTAB) by cationic emulsion polymerization. For the first time uniform two-dimensional PANI structure was made by them in presence of cationic surfactant for a wide concentration range. Highly crystalline PANI

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structure was also obtained. Bolagam, Boddula & Srinivasan[11] prepared PANI (PANI) salt with 3-(Cyclohexylamino)-1-propanesulfonic acid by aqueous polymerization pathway, also examined the effects of sodium lauryl sulfate surfactant, mineral acid (H_2SO4), and combination of surfactant with mineral acid during the polymerization. These PANI salts were used as electrode materials in the supercapacitor application, in a symmetric two-electrode cell configuration. They observed phase angle value close to 90^0 at lower frequencies hence indicated good capacitive behaviour. Kulkarni[12] in their study reported polyaniline (PANI) nanofibers growth on porous three dimensional graphene (PANI/3D graphene) as supercapacitor electrode material with enhanced electrochemical performance. They observed that the 3D grapheme based polymer (*i.e*. PANI) electrode amply allowed simultaneous increase in pseudo-capacitance, charge transport and storage processes. Kavitha *et al.*[13] synthesized PANI emraldine salt by chemical oxidation of aniline and observed semi-crystalline structure of the prepared polymer.

From above literatures it is observed that work on crystalline nature of pure PANI is scanty, hence in this study an attempt has been made to examine its crystalline nature, which is generally amorphous in its pure form. In this present investigation we have synthesized crystalline PANI and examined its various characteristics such as crystalline behaviour, strain-strain characteristics, crystallite size, crystal growth rate and particles size.

2 Experimental

2.1 Synthesis of PANI

The following chemicals have been used in this present investigation namely Aniline ($C_6H_5NH_2$), Ammonium peroxidisulphate ($H_8N_2O_8S_2$) or $(NH_4)_2S_2O_8$, Methanol solution, HCl, Acetone, NH_4OH solution which were obtained from MERC, India ltd. 1M concentration 20 ml solution of Ammonium peroxidisulphate and 8 ml of aniline were taken, these solutions were prepared by dissolving them in double distilled water in a volumetric flask separately. Both the solutions were kept for 1 hour at room temperature and they were then mixed with a continuous stirring with the addition of HCl and left for 7 hours for polymerization. After the polymerization process a dark green precipitate was obtained which was treated with the NH_3 solution to get undoped PANI in emeraldine base form PANI. The undoped PANI was dried in oven at 60 °C for 1 hour to get PANI. But we found that the precipitate was not completely dried. For complete drying it was kept into oven at a temperature 80 °C for 2 hours. The precipitate was converted into powder form by grinding it for 5 to 6 hours and then heated this powder in the furnace up to temperature 90 °C. After this pellets of 10 mm diameter of varying thickness (1-3 mm) were prepared by applying pressure 3000-4000 kg/cm^2 for 5 minutes using a hydraulic pressure machine. The above formed pellets were sintered in furnace at a temperature of 110 °C, 120 °C and 130 °C respectively for 2 hours. During the process it was found that the pellets which were annealed at temperature of 120 °C and 130 °C, started melting at a temperature around 120 °C. The molten mass of above two pellets were then cooled separately in the oven and after cooling the solidified mass of each pellets were ground in fine powder form separately and reconverted finally into pellets form.

2.2 Characterization

All the prepared PANI samples were characterized by XRD, AFM and TEM.

2.2 Characterization of PANI

2.2.1 Microstructural characterization

The gross (average) structural, microstructural and surface morphological characteristics were studied by powder XRD, AFM & TEM respectively.

2.2.1.1 Powder x-ray diffraction studies

Powder XRD of the prepared samples were recorded on Rigaku X-ray diffractometer (Ultima IV, Japan) using Cu Kα radiation (λ=0.15406 nm) at an accelerating voltage of 40 kV and filament current of 40 mA.

2.2.1.2 Atomic force microscopy

Multi mode SPM with nanoscope III a controller acquired from Digital/Veeco Instruments Inc. (under IRHPA programme of DST) at Inter-University accelerator centre (IUAC), New Delhi is extensively used in all the modes: AFM, MFM, C-AFM, STM, STS and F-d mode *etc*.

2.2.1.3 Transmission Electron Microscopy (TEM) analysis

TEM of the prepared samples were performed on TEM-FEI, Techni 20 G^2 (resolution of 2.04 A at 200 KV) using LaB_6 filament at UGC-DAE consortium for scientific research, Indore.

3 Results and Discussion

3.1 Structural and morphological studies

3.1.1 PXRD analysis

The representative X-ray diffraction pattern of pure PANI annealed at different temperatures 110, 120 and 130 ºC are shown in Fig. 1.

From the XRD characterization of the above three pellets it was found that the unmelted sample which was annealed at temperature 110 °C (Fig. 1a) shows amorphous nature whereas the pellets annealed at temperature of 120 °C (Fig. 1b) shows two peaks at 2θ of 10^0 and 30^0 respectively while the pellets which was annealed at temperature of 130 °C (Fig. 1c) shows maximum number of peaks, indicating higher crystallinity as compared to other two samples. The analysis of the powder x-ray diffractograms (XRD) reveals that prepared pure PANI is well crystalline and all observed peaks (reflections) matches well with JCPDS (053-1890)[14]. The XRD results thus obtained indicates that the product is highly pure since the peaks obtained matches with the JCPDS data and presence of any other peak other than JCPDS is not noticed. A noncrystalline peak below 20° also appears for the pellet which was annealed at temperature 110° C. According to Williamson and Hall (W-H) the broadening and disappearance of some peak is mainly due to both crystallite size and strain. Relationship between crystallite size (D) and microstrain (ε) was established by them which is given by Eq. 1.

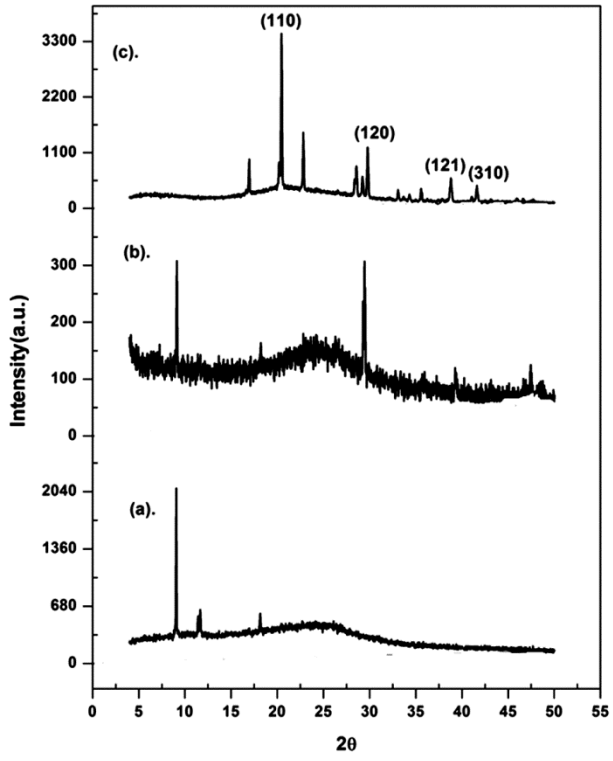

Fig. 1 The XRD pattern of pure PANI annealed at (a) 110 °C (b) 120 °C and (c) 130 °C

$$\beta \cos\theta = k\lambda/D + 4\varepsilon \sin\theta \quad \ldots (1)$$

Where β is full width half maxima, λ is the wavelength of the radiation (1.54060 *A* for *CuKα* radiation), k is a constant equal to 0.94, and θ is the peak position.

Crystallite size was also calculated by Scherrer's formula

$$D=k\lambda/\beta\cos\theta \quad \ldots (2)$$

Where λ is the wavelength of the radiation (1.54060 *A* for *CuKα* radiation), k is a constant equal to 0.94, and θ is the peak position.

Plot of β cosθ versus 4sinθ results is a straight line and the values for crystallite size (D) and lattice strain (***ε***) was obtained from the intercept and the slope of the straight line. W-H plots for the pellets sintered at different temperatures are shown in Fig. 2. Further, crystallite size were determined using both Scherer formula and Williamson-Hall plot using the above XRD data, the calculated values of crystallite size and strain are given in Table-1. The calculated value of strain (***ε***) from the above W-H plots, it was found that with the increase in sintering temperature there is decrease in the value of strain which might be due to crystallization and change in lattice strain of PANI.

The variation of crystallite size calculated by the Scherrer, W-H plots with varying annealing temperature are shown in Fig. 3.

3.1.2 AFM Analysis

The AFM was performed in dynamic mode. The surface morphological examinations with

Table 1 Crystallite size and strain of the PANI samples annealed at temperature of (a) 110 °C (b) 120 °C (c) 130 °C

Samples	Crystallite size (in nm)		Strain
	W-H Plot	Scherer formula	
PANI annealed at temperature 110 °C	125.62	67.4882	0.0078342523
PANI annealed at temperature 120 °C	102.35	52.27515	0.00906893
PANI annealed at temperature 130 °C	60.95	49.38566	0.001254988

AFM of the annealed sample are shown in Fig. 4.

The PANI particle sizes of nanometre order were obtained from the AFM images, which are in good agreement with XRD results. From the micrograph of PANI annealed at temperature of 110 ^{o}C (Fig. 4a), it can be observed that particles are not clearly seen but with the increasing annealing temperature particles have good visibility as indicated in Figs. 4 (b & c). AFM results also indicate that with the increasing annealing temperature crystallite size decreases while crystallinity increases. The surface roughness was calculated by WSxM 5.0 Devlop 8.5 software. The surface roughness of the above pellets is shown in Table 2.

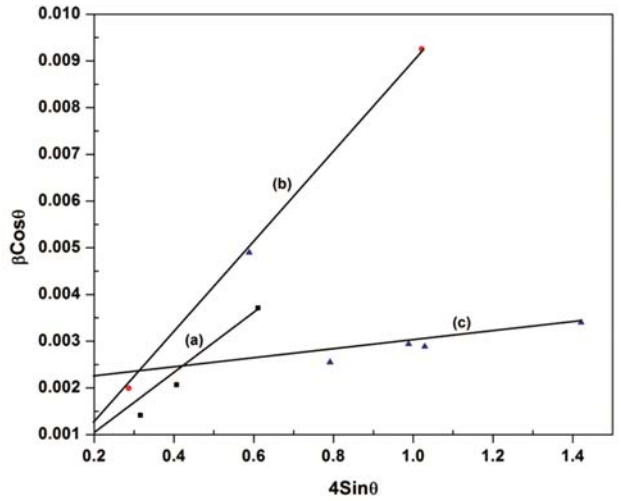

Fig. 2 W-H lot of PANI annealed at temperatures (a) 110 ^{o} C (b) 120 ^{o}C and (c) 130 ^{o}C.

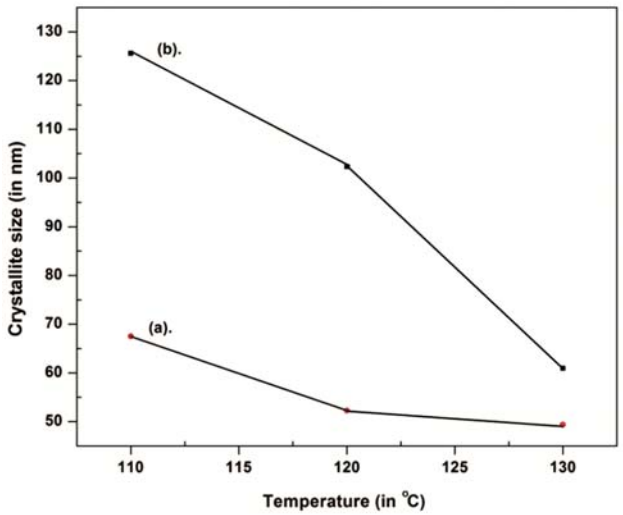

Fig. 3 Variation of crystallite size with annealing temperature

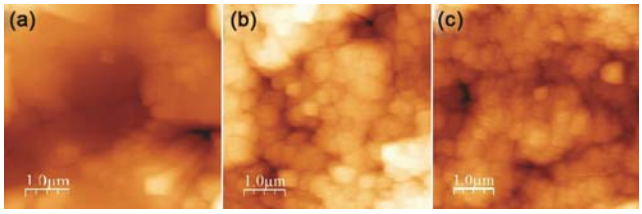

Fig. 4 AFM analysis of PANI annealed at (a) 110 °C (b) 120 °C and (c) 130 °C

3.1.3 TEM analysis

From TEM analysis of images shown in Fig. 5 [(i) (a & b, at the magnification of 17 KX and 63 KX)], reveals that PANI when annealed at 110 °C there is no crystal growth, indicating amorphous state which is in good agreement with the PXRD results. Crystal growth rate for PANI is highest when it is annealed at 130 ^{0}C as shown Fig. 5 [(iii) (a & b, at the

Table 2 — Particle size and surface roughness of the PANI at: a) 110 °C (b) 120°C (c) 130°C

	Surface roughness (nm)	Surface roughness (nm)
PANI annealed at temperature 110°C	76.684	0.1861
PANI annealed at temperature 120°C	66.8282	35.4685
PANI annealed at temperature 130°C	52.2693	111.677

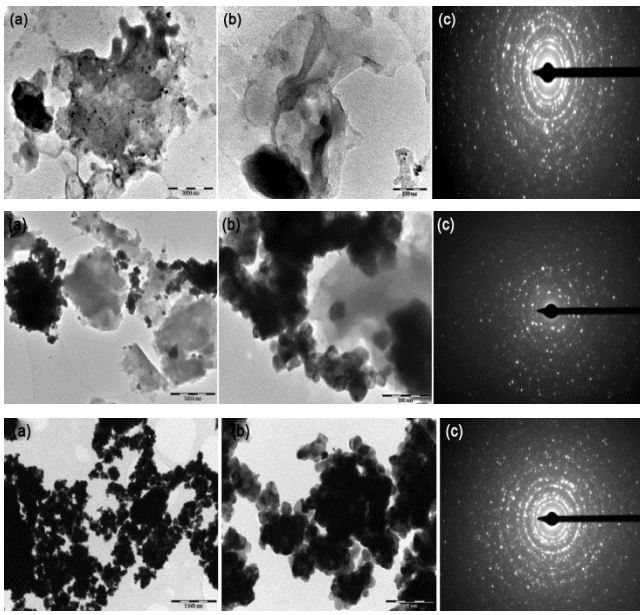

Fig. 5 (i) TEM images of PANI annealed at 110 °C at magnification of (a) 17 KX, (b) 63 KX and (c) corresponding selected area electron diffraction (SAED) pattern; (ii) TEM images of PANI annealed at 120 °C at magnification of (a)17 KX, (b)63 KX and (c) corresponding SAED pattern; (iii) TEM images of PANI annealed at 130 °C at magnification of (a) 17 KX, (b) 63 KX and (c) corresponding SAED pattern

magnification of 17 KX and 63 KX] as compared to 120 °C (Fig. 5 ii). Selected area diffraction (SAED) patterns of PANI annealed at 110 °C, 120 °C and 130 °C shown in Fig. 5 (i:c, ii:c & iii:c) shows formation of nanorings connecting the discrete diffraction spots which confirms the formation of nanocrystalline polyaniline.

4 Conclusions

Crystalline PANI nanopaticles was prepared by co precipitation method using aniline as precursor and ammonium peroxodisulphate as an oxidizing agent. Synthesis of PANI was confirmed by spectroscopic techniques. XRD result showed that all the prepared samples are crystalline in nature. All the tentative crystalline peaks matches with the JCPDS card no 053-1890. AFM result revealed that the pellets when annealed at temperature more than 110 °C shows crystal growth. TEM analysis revealed various nano rings connecting the characteristics diffraction spots of PANI nanoparticles. The nano rings present in the SAED pattern confirmed that the prepared samples are of nanometer range. Good crystalline growth was observed in pure PANI, which is otherwise amorphous in its natural state.

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