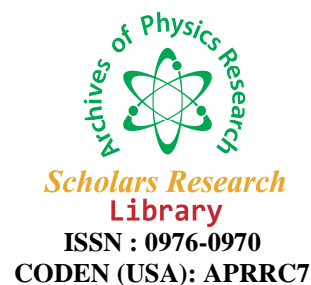




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Optical studies on nano-structured conducting Polyaniline prepared by chemical oxidation method

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ABSTRACT

Nano - structured conducting polyaniline has been synthesized for various reaction periods using in-situ chemical polymerization method. The as prepared Polyaniline are analyzed via structural characterization and absorption spectroscopy using X-ray diffraction (XRD) and UV-Visible spectroscopy (UV-Vis). The XRD results confirm the partly crystalline and amorphous nature of the polyaniline prepared at the reaction period 23h. The average size of the crystallites estimated as 13 nm by Scherrer's formula from XRD data are consistent with particle size estimated from spectroscopic data through Meulenkamp equation. The optical absorption spectrum establishes the formation of polyaniline under nano-regime with the band edge absorption of 1.03 eV.

Key words: Band gap, Chemical oxidation, Hydrogen peroxide, Polyaniline, UV - Visible spectrum.

INTRODUCTION

Conducting polymers have gained great interest and emerged very important class of materials among the scientists worldwide because of their unique electrical, optical and chemical properties [1-4]. One can have tremendous scope for tuning of their electrical conductivity between semiconductor and metallic regime, when they are suitable doped [5, 6]. The unique properties of conducting polymers are the great scope of developing the new models to explain their observed properties, particularly various charge transport mechanism [7]. Among different conducting polymers, conducting polyaniline is the most extensively studied materials due to ease of synthesis, low cost, good environmental stability, unique conduction mechanism and solution processability. The major disadvantage of polyaniline is its infusibility and insolubility in common organic solvents. However, polyaniline is made to soluble by substitution of one or more hydrogen by alkyl, alkoxy, aryl hydroxyl, amino group or halogen in an aniline nucleus [8-9]. Alkyl substituted polyaniline is enabled the stabilization of the charge carriers due to the electron donating effect of these substituent which increases the basicity of imine units [10, 11]. In order the effect of this substituent on parent polymer polyaniline is useful to understand the particle size and semiconducting nature of the materials.

In the present work, conducting polyaniline has been prepared from in-situ chemical polymerization method with the assistant of oxidizing agent hydrogen peroxide at different reaction time (6h, 13h and 23h) and it is characterized by using XRD technique and absorption spectrum in the visible and far away regions from it.

MATERIALS AND METHODS

All the chemicals including aniline, hydrogen peroxide (H_2O_2), ferrous chloride ($FeCl_2$), hydrochloric acid (HCl) and ammonia (NH_3) were of analytical grade procured from Merck and used as received. De-ionized water was used for the preparation and dilution of solutions.

3. Experimental

A calculated amount of 2.79g non aqueous aniline monomer was dissolved in 300 mL of 1 N hydrochloric acid. 0.0064 g of FeCl_2 was dissolved in 75 mL of de-ionized water. The two solutions were mixed in a 500 mL beaker and stirred followed by the drop wise addition of 68 mL (6 wt.%) hydrogen peroxide for 30 min. The reaction period was fixed at different reaction times such as 6h, 13h and 23h at room temperature at constant stirring. Finally the respective solid products at the different reaction times of 6h, 13h and 23h were filtered by the Whatman filter paper (No. 42) followed by washing with de-ionized water. To obtain the polymer in emeraldine base (EB) form, from the dried samples at different reaction time, it was dedoped with ammonia solution for 3h. Then it was washed with de-ionized water and dried well. To obtain the polymer in emeraldine salt form, the EB powder was doped with 1N hydrochloric acid and stirred for 3h and then filtered. The hydrochloric doped PANI at different reaction time were dried and kept in a separate air tight containers for further characterization.

4. Measurements

The powdered X-ray diffraction (XRD) was performed on the samples which prepared different reaction time at room temperature using Philips analytical X-ray diffractometer at the range 10° to 80° at the scanning rate of $5^\circ/\text{min}$. using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). UV – visible spectrum was recorded in the range from 190 to 2500 nm for emeraldine salt form polyaniline powder using a TU-1901 model UV double beam spectrophotometer (Beijing Purkinje Instrument Co, Lt, China).

RESULTS AND DISCUSSION

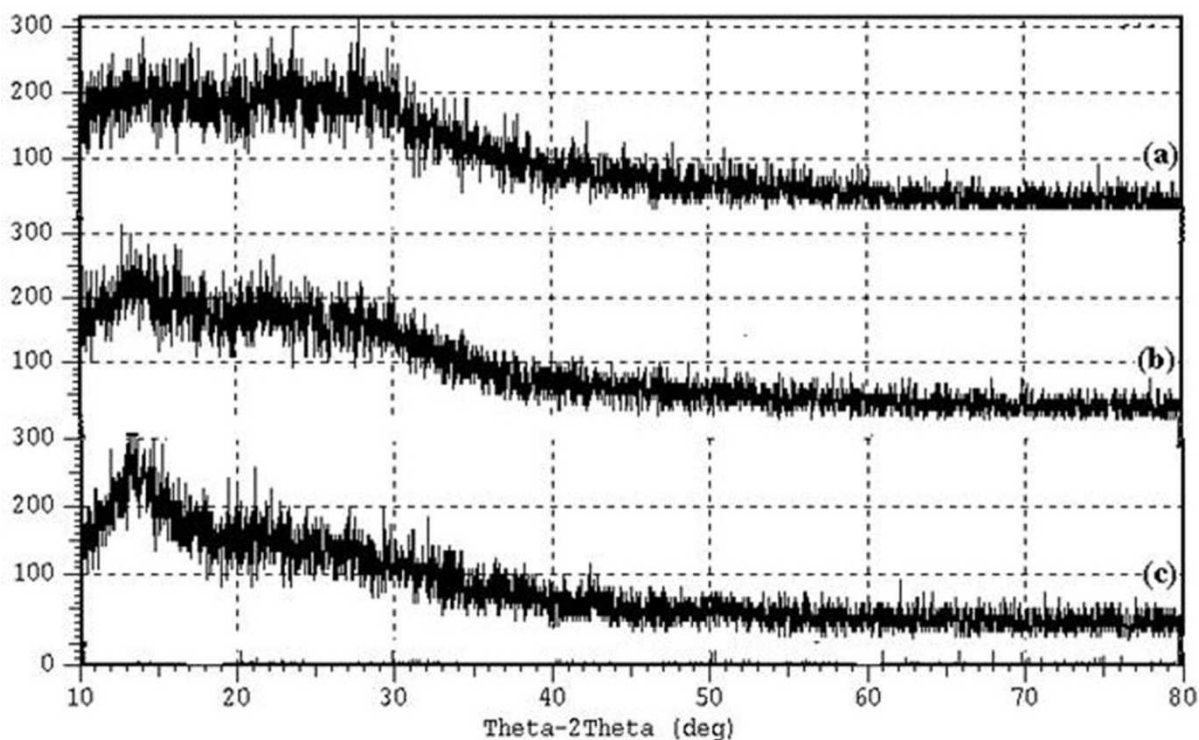


Fig.1 XRD patterns of the nanostructured polyaniline prepared (a) at reaction time 6h. (b) at reaction time 13h and (c) at reaction time 23h.

5.1. Structural studies

XRD results of PANI prepared at different reaction time is depicted in Fig 1 (a, b & c). From the Fig. it is clear that no peaks are observed at the samples of polyaniline prepared at the reaction time of 6h and 13h, but the diffraction pattern for PANI which prepared at the reaction time of 23h is confirmed a characteristic broad peak of 13.90° at 2θ and some other peaks with lesser intensities at $2\theta = 12.22^\circ$, 15.41° and 22.49° . It is also evident from the Fig1(c) that the PANI has several broad peaks with less intensities in the region $15\text{--}30^\circ$, indicating its partly crystalline nature [12]. The average particle size is determined by Scherrer method [13] for the PANI prepared at the reaction time of 23h. The size of the particle is given by the Scherre formula, $D = 0.9 \lambda / \beta \cos\theta$, where λ (1.5406 \AA) is the wavelength of X - ray radiation used, β is the full width at half-maximum (FWHM) and 2θ is the diffraction angle. Evaluations of the particle size of the sample at different peaks were repeated and the average particle size is found to be 20 nm. The estimation of the particle size is tested further by evaluating it with Meulenkamp equation [14]. According to

Meulenkamp the wavelength $\lambda_{1/2}$ at which the absorption is 50% of that excitonic peak is directly related to the size of the particle via the fitted expression

$$1240 = \lambda_{1/2} (3.301 + 294/D^2 + 1.09/D)$$

The values of particle size evaluated from Meulenkamp equation is in fair agreement with the values obtained from Scherrer method.

5.2. Optical studies

The transition of charge carriers is analyzed in benzenoid structure and quinonoid ring of the prepared conducting polyaniline using UV – visible spectrum. The characteristics absorption of a conducting polyaniline plays a vital role in the utilization of the materials in the optoelectronic applications. Typically PANI-HCl shows three absorption characteristic peaks in wavelength bands 306-324, 402-420 and 828-835 nm respectively. The peak in wavelength range 306-324 nm is due to the π - π^* transition of benzenoid ring, the peak in wavelength range 402-420 nm is due to polaron - π^* transition and the peak in wavelength range 828-835 nm is due to π - polaron transition. The Fig.2 demonstrates UV – visible absorption spectrum of nano-structured PANI prepared at the reaction time of 23h. In the spectrum, two major absorption peaks and one at less absorption peak are observed at 320 nm and 630 nm and 830 nm. The peak 320 nm is due to the π - π^* transition which is related to the extent of conjugation between the adjacent phenylene rings in the polymeric chain and the peak at 630 nm is owing to the shifting of electron from benzenoid ring to quinonoid ring and the peak at 830 nm is caused by π - polaron transition. These peaks have been assigned to transition from valance band to conduction band at 320 nm and charge transfer between benzenoid and quinonoid rings due to free nonbonding electrons that can absorb relatively low energy radiation and these are well agreed with the results of Xinli Jing *et al.* and Jiping Yang [15, 16].

The valance band or highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbital band (LUMO) are separated by an energy gap is called band gap which is of fundamental important, because the energy gap determines the electrical conductivity and optical absorption character of the polyaniline.

The band gap of conducting PANI has been estimated from the absorbance coefficient data as a function of wavelength using Tauc relation.

$$\alpha h\nu = B(h\nu - E_g)^n$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, B is the band gap tailing parameter, E_g is a characteristic energy which is termed as optical band gap and n is the transition probability index. The probability index has discrete values like 1/2, 3/2, 2 or more depending on where the transition is direct or indirect and allowed or forbidden band gap. The absorption coefficient (α), at the corresponding wavelengths is calculated using the Beer–Lambert's relation.

$$\alpha = \frac{2.303 A}{l}$$

Where l is the path length and A is the absorbance

The plot of $(\alpha h\nu)^2$ versus $h\nu$ is linear function existence of indirect allowed band transition in PANI. Extrapolating of linear dependence of the relation to abscissa yields the corresponding band gap E_g . The value of the optical energy of PANI prepared obtained from Fig.3 is 1.03 eV and this is due to π - π^* transition from valance band to conduction band at 330 nm and the formation of polaron at 830 nm. The measured value is very interesting novelty and less compared with the result of polyaniline prepared with APS as the oxidant with different solvent [17].

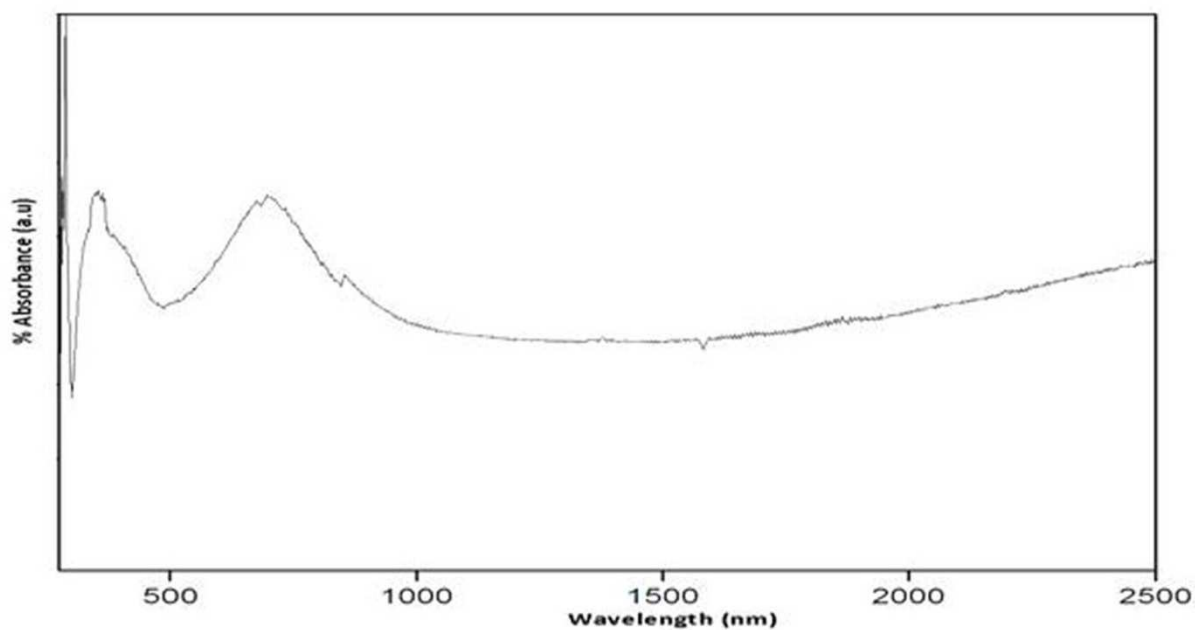


Fig. 2. UV – visible spectrum of powdered form of conducting Polyaniline prepared at 23h.

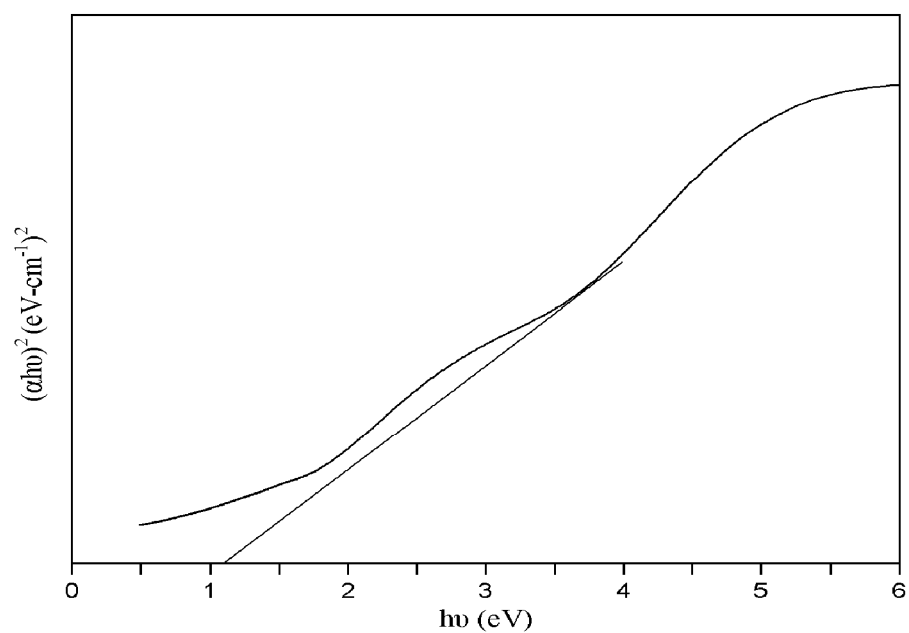


Fig.3. Relation between $(\alpha h\nu)^2$ and $h\nu$ for the conducting Polyaniline.

CONCLUSION

The optical transmission spectra of conducting polyaniline prepared through in - situ chemical polymerization method using hydrogen peroxide as oxidant at room temperature at 23h, illustrates some characteristic peaks in various optical regions and show less band gap. The variation of the crystallite size at the reaction time of 23h from Scherrer formula is in fair agreement with change of particle size calculated by Meulenkamp equation.

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