

Novelty and facilitate way for fabrication of microstructure Polyaniline (PANI-EB) thin films

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Abstract: Easiest and chipper only a lone step novelty chemical way for the preparation a conducting polymer of Polyaniline (PANI-EB) emeraldien base has been reported in this paper. This polymer microstructure are characterized with, HR-XRD diffraction, Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM), and UV-vis spectroscopy. Polyaniline (PANI-EB) exhibit amorphous nature as confirmed that from XRD pattern and FESEM analysis study, the formation of the polymer. The presence of characteristic bonds of polyaniline was observed from FTIR spectroscopy technique. Electrical and optical properties explain that p-type conductivity of PANI at room temperature the conductivity of 6.3×10^{-4} (S.cm⁻¹), with tow sharp absorption peak at 426,805 nm has been attributed due to quantized size of polyaniline conducting polymer structure.

Key words: Conducting polymer; PANI-EB; Preparation; Characteristic

1. Introduction

The microstructure materials today have greatest importance in the field of electric and optoelectronics devices. The experimental and theoretical applications has opened new fields of fundamental physics and as researchers can make and study artificial analogs of atoms, molecules and crystals. Polymer materials have been widely used in chemical reactions as catalysts factors due to their flexible applicability. The most commonly studied conducting polymers are polyaniline in emeraldine base form (PANI-EB), also known an air-stable and as highly tunable, organic conducting polymer with good environmental stability, which can be produced as powder, cast films. This, in conjunction with the feasibility of low cost monomer, large-scale production, redox reversibility serves, to further enhance its favorable properties and makes it an ideal candidate in many applications. This could greatly widen its applicability in multi- disciplinary areas such as electrical, electronics, thermoelectric, electrochemical, electro-luminescence (Borole et al., 2006; Jacinth et al., 2011; El Ghanem et al., 2006; Pawar et al., 2009; Chougule et al., 2012a).

The polymer polyaniline can mainly to be found in three modes, including so-called, fully reduced light yellow colored leucoemeraldine (LEB), the partially oxidized dark green-colored emeraldine salt (ES), and fully oxidized dark blue colored emeraldine base (EB). Electrical and optical properties of the polyaniline are varying with the

different oxidation states. It can be converted to conduct across a wide range; from being exactly non-conductive for insulation used to high degree conductive for other electrical purposes (Patil et al., 2012) Emeraldine base form (EB) is more stable state in air at ambient temperature. The available studies explain different methods to fabrication polymer PANI including ectrochemical (Patil et al., 2009); Enzymatic (Kobayashi et al., 2001); solution (Nastase et al., 2005); chemical polymerizations (Jing et al., 2006).

The unnecessary formation of precipitation, waste of material in many of the above works methods that are more of money, time and energy consuming, cumbersome along with needed developed instruments for controlling various parameters may put restrictions on the commercial synthesis of materials. These can be avoided by facility and novelty in situ chemical polymerization method which results into entailed thin film of the deposition at low temperature, (Khuspe et al., 2012). Following reasons strongly portrays our in situ chemical method as easy and efficiently among the other deposition ways. It is relatively simpler and very cheaper method that has emerged as one of the recent chemical solution methods. It is useful due to layer-by-layer growth and contained excellent material utilization efficiency, good control over deposition process along with thin film thickness and specifically convenient for large area deposition on virtually any type of substrate. The in situ preparation of PANI film results in pinholes free and uniform deposits, since the basic building blocks are ions instead of atoms. Corrosion of metallic

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substrates can be avoided as deposition is carried at room temperature (Chougule et al., 2011; Raut et al., 2012b).

In this work, a systematically investigation on the oxidative chemical polymerization of aniline is made as simple as possible by facile in situ chemical way at low temperature, which results in good quality, uniform, well-adherent, porosity structured, semi conducting Polyaniline (PANI-EB) in the thin film form feasible for large area deposition. Our efforts are focused onto development of easiest and cheapest synthesis method for the preparation of Polyaniline (EB) commercially, so that to achieve compatibility in applications. Further, in situ grown films are characterized for study of structural, morphological, optical and electrical properties.

2. Experimental section

2.1. Synthesis of polyaniline

Polyaniline was synthesized by chemical polymerization of aniline in the presence of hydrochloric acid (HCl) as a reaction stimulating, and ammonium peroxydisulphate (APX) as an oxidant. For the synthesis, we took 50ml beaker, 1M HCl, and 2ml of aniline solution were added into a 250 ml beaker equipped with a Teflon coated magnetic stirrer at about 0C° temperature (ice-bath). Then 5gm of ammonium peroxydisulphate ((NH₄)₂S₂O₈) aqueous solution in 50ml beaker, 1M HCl was drop wise added into the above solution. The polymerization temperature 0C° was maintained for 12 h to complete the reaction. Then the precipitate obtained was filtered. The product was washed successively by 1M HCl followed by double distilled water until the wash solution turned colorless. The product PANI was dried at 60C° for 24h to get powder form, dark green colored Polyaniline pure emeraldine base (EB).

2.2. Characterization and measurements

X-ray diffraction studies were carried out using high resolution an HR-XRD diffractometer (Model:

PANalytical X pert Pro MRD PW3040). The XRD patterns were recorded in the range of 2θ: 10–70° with a step width of 0.02° and a step time 1.25 sec by using (CuKα) radiation (λ=1.5406Å). The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by a JCPDS file. Fourier Transform Infrared (FTIR) spectroscopy (Model: Perkin Elmer Spectrum Gx) of PANI was studied in the frequency range of 400–4000 cm⁻¹. Morphological study of the thin films of PANI was carried out using field effect scanning electron microscopy (FE-SEM) (Model: FEI Nova NanoSEM 450) operating at 20 kV. UV-vis the spectra of the samples, which were dispersed in deionized water under ultrasonic action, which were recorded on a Shimadzu -1800 UV- Vis spectrophotometer.

3. Results and discussion

3.1. Structural analysis

The crystallinity and orientation of conducting polymers have been of much interest because highly ordered systems can display metal-like conductive states, the XRD diffraction pattern of PANI (EB) form Fig. 1 shows a one of wide peak at 2θ=22.68°. The average crystallite grain size is calculated according to Debye Scherer Eq. 1:

$$G_s = K \lambda / \beta \cos \theta \quad (1)$$

Where: K is the shape factor (0.9), G_s is the average grain size; 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 pattern of thin film polymer PANI that shows structure by the study of XRD peaks confirmed amorphous and the semi crystalline nature of the synthesis of the thin film (Huang J X, and Kaner R B, 2004, Deore BA, Yu I, and Freund MS, 2004).

The peak at 2θ = 22.68° may also represent the characteristic distance between the ring planes of benzene rings in adjacent chains (Pouget et al., 1995). The characteristic broadening of the observed peaks implies that the films are Nano crystalline.

Table 1: The XRD parameter of (PANI-EB)

Pos. [2Th°]	d-spacing [Å]	FWHM [°2Th.]	G _s [Å]
22.68	3.93	0.6	2.35

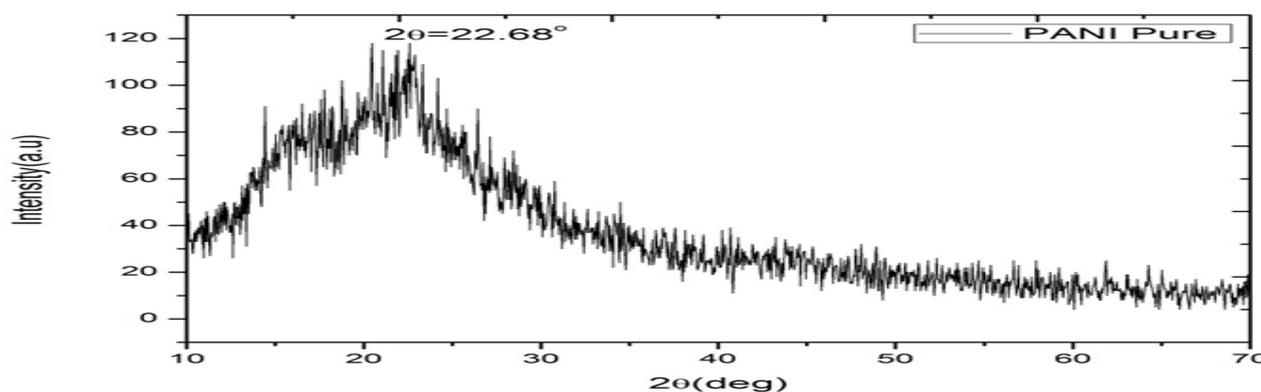


Fig. 1: XRD pattern of Polymer (PANI-EB)

3.2. Microstructure analysis

The tow dimension surface morphology of the polyaniline PANI-EB thin films has been studied by using field emission scanning electron microscopic FESEM images. Fig. 2 shows the FESEM images morphology of PANI thin film. The polyaniline surface at 500nm with highly micro- porous structure is able to increase the liquid–solid interfacial area clearly seen from FESEM images (Matsumura and Ohno, 1997; Xia and Wang, 2002).

FESEM study confirms the embed-connected PANI-EB nanostructure; the nanostructure forming as web-like structure with hollow cavities which are increase micro-porous. The porosity nature of the polyaniline makes it a potential candidate for various.

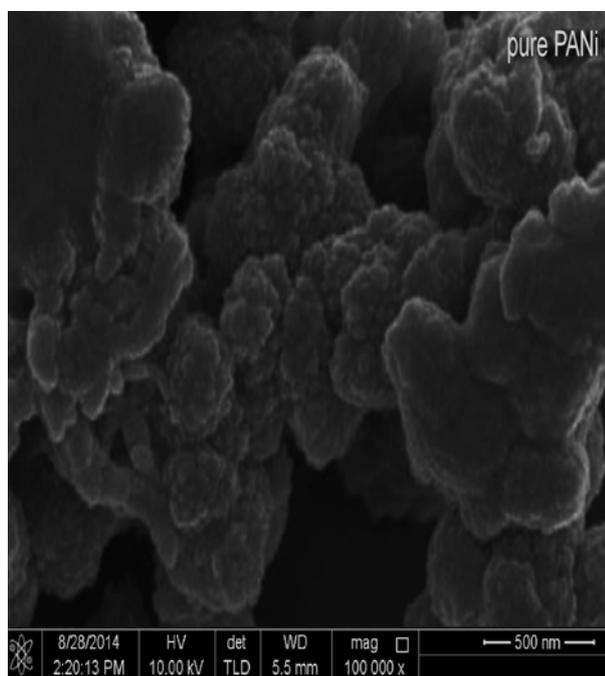


Fig. 2: FESEM morphology of Polyaniline

3.3. FT-IR spectrum analysis

The FTIR spectrum of the PANI-EB show in the Fig. 3 FTIR spectra of the pure PANI-EB, the origin of the vibration bands is as follows: at 3389 cm^{-1} due to the NH stretching band of aromatic amine, at 2936 cm^{-1} due to CH-stretching band, at 620 cm^{-1} due to CH out-of-plane bending vibration. The CH out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. The bands at 1662 and 1486 cm^{-1} are attributed to C = N and C = C stretching mode of vibration for the quinonoid and benzenoid units of PANi. The peaks at 1295 and 1155 cm^{-1} are assigned to C–N stretching mode of benzenoid ring, that of conducting protonated from PANI-EB (Xia and Wang, 2002). The bands at 850 cm^{-1} originate out of the plane C–H bending vibration.

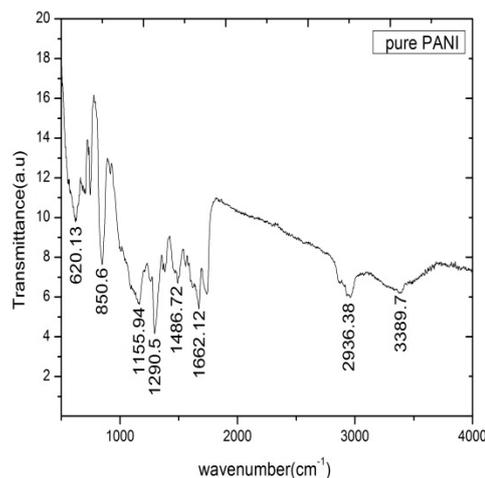


Fig. 3: FTIR Spectrum of pure (PANI-EB)

3.3. Optical absorption studies

The absorption spectrum of the polyaniline pure (EB) film shows in Fig. 4 at the visible spectrum, which is measured on a Shimadzu UV1700 ultraviolet visible spectrophotometer; Shows the variation of optical absorbance with incident photon wavelength of the PANI-EB thin film having thickness of 139 nm. The UV-Vis, absorption spectrum of PANI thin film shows two sharp absorptions: one with maximum at 426 nm with (π - π^*) transition corresponding with benzenoid ring and another at 805 nm with (polaron- π^*) corresponding to molecular exciton transition, this is due to the oxidation states of the polyaniline. The absorbance band approximately at 450 nm has been reported earlier and may be attributed to the excitation to the polaron band (Wang and Herron, 1991). The theory of optical absorption gives by the relationship between the absorption coefficient (α) and the photon energy ($h\nu$) for direct allowed transition can be written as:

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^{1/2} \quad (2)$$

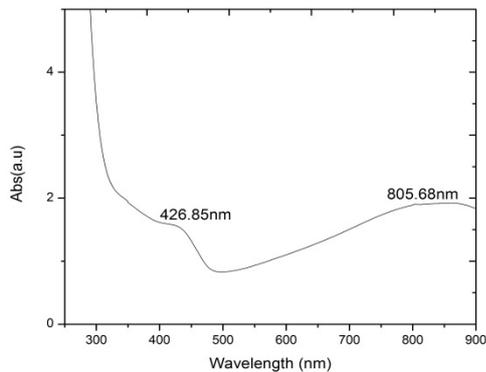
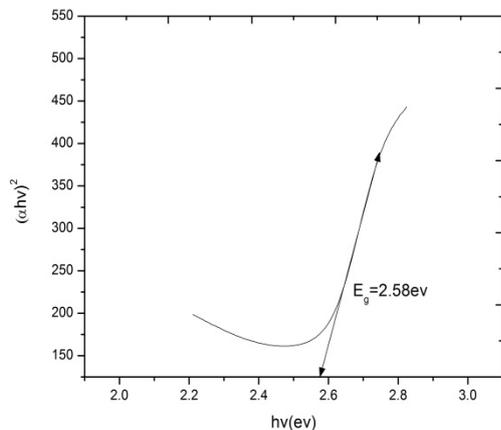
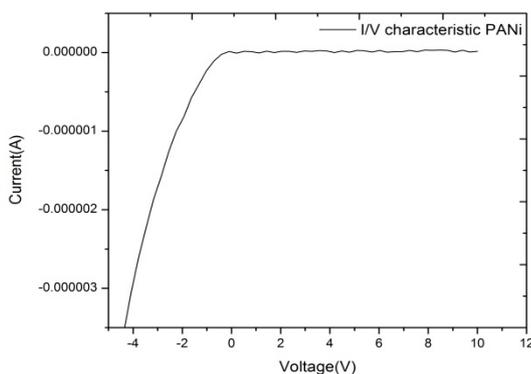
Where: α_0 is a constant; $h\nu$ is the photon energy and E_g is the energy band gap of the material. Inset of Fig. 4 shows the variation of $(\alpha h\nu)^2$ with incident photon energy ($h\nu$), the band gap, E_g , was determined. The band gap was found to be 2.58 eV which is lower than earlier reported (3.65 eV) (Sajeev et al., 2006), and equal to earlier reported (2.5 eV), (Pawar et al., 2011), this is attributed to the size quantization of nanostructure of polyaniline thin films.

Electrical Conductivity

The I/V characteristic shows that in Fig. 6 for device: [Al/Si-N100/PANI/Ag] heterojunctions under simulated solar radiation (100 mW/cm^2) the largest open circuit voltage of 413 mV and short circuit current density (J_{sc}) of 0.0018 mA/cm^2 , with height of conversion power energy at 0.002%.

Table 2: I/V characteristic data of PANi-EB

Structure	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η %
Al/n-Si/PANi(EB)/Au	413	0.0018	2.3	0.002

**Fig. 4:** Absorption Spectrum of pure polyaniline**Fig. 5:** Photon energy vis $(\alpha h\nu)^2$ spectrum of Polyaniline**Fig. 6:** I/V characteristic of Polyaniline (EB)

4. Conclusion

In conclusions, a direct one-step and environmentally friendly simple chipper easy and novelty chemical synthesis method has been developed to produce PANi-EB pure Polyaniline at room temperature. This may be helpful for

commercially synthesis of polyaniline. Study of physical and chemical characteristics with: XRD, FT-IR, FESEM, UV-vis, and electrical techniques confirmed preparation of amorphous microstructure, wide optical band gap and low resistivity of p-type PANi-EB thin film. The in situ chemical method is efficient and constructive for deposition of used nanostructure like PANi films onto substrates of different area with feasibility, at expense of small amount of initial ingredients.

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