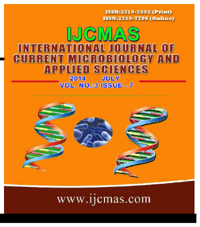

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Original Research Article

Synthesis and optical studies of pure polyaniline film

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ABSTRACT

Keywords

XRD,
SEM,
FTIR,
UV-visible,
PL,
polyaniline film

Inherently conducting polymer, polyaniline (PANI) has been synthesized by a chemical oxidative polymerization method. Ammonium peroxydisulphate was used as an oxidizing agent dissolved in aqueous media. The polyaniline film was prepared by dip coating method and its characterizations were done by XRD (X-ray diffraction), SEM (scanning electron microscopy), UV-Vis (ultra-violet visible spectrophotometer), PL (Photoluminescence spectrophotometer) and FT-IR(Fourier transform Spectroscopy). From the SEM image of PANI film, it has been observed that interfacial polymerization offers the agglomeration of grains having spherical morphology and its particles size were found to be 300 nm. FTIR study shows several absorption peaks centred at around 920 cm^{-1}, 1220 cm^{-1}, 1487 cm^{-1} and 1594 cm^{-1}. Photoluminescence spectrum exhibits mainly two emission peaks cantered ~381 nm and 391 nm.

Introduction

In the few past decades inherently conducting polymer (ICP), polyaniline (PANI) has been paid considerable attention because of its high electrical conductivity (LiW and Wan M, 1998), thermal stability (Jing X et al., 1995), ease of preparation, and good environmental stability (Genies E et al., 1990). This polymer was found to be the most promising candidate for technological applications (Pouget J et al., 1991; Mac Diarmid A and Epstein A, 1994) especially in light-weight batteries and sensors (Ogura K et al., 1997; Kulkarni M and Viswanath A, 2005). Polyaniline (PANI) is a very well-known conducting polymer which has attracted a lot of attention due to its promising applications (Kang E Tet al., 1998) in anticorrosion coatings (Wessling B, 1994; Lu W K et al., 1995), electrodes in secondary batteries (MacDiarmid A G et al., 1987), active components in LEDs etc (Wang H L et al., 1996; Chen S A et al., 1996). The ease of synthesis, reasonably high electrical conductivity and good environmental stability make it a potential candidate for use in organic electronic devices (Neoh et al., 1990). Indeed, PANI is a dynamic block copolymer consisting of reduced benzoid units and oxidized quinoid units (Shimano J Y and MacDiarmid A G, 2001). It can exist in several oxidation states. The approach of chemical synthesis method and the use of functional dopants in the polymer matrix as an inherent part of the doping is more attractive, as it eliminates the use of volatile dopants. Recently, new types of protonic acids have been used, such as polyacids and functionalized acids, to dope chemically synthesized polyaniline in order to improve the selected properties, in particular, solubility, processability, and electrical conductivity (Cao Y et al., 1993; Santos Jr et al., 1995).

Materials and Methods

Aniline hydrochloride (2.59 g) was dissolved in distilled water in a volumetric flask to make 50 mL solution. Ammonium peroxydisulfate (5.71 g) was dissolved in water also to make 50 mL of solution. Both the solutions were kept for 1 hour at room temperature. They were then mixed with a brief stirring at room temperature and left at rest to polymerize. The solutions turned to dark green within few minutes. Film was prepared by dip coating method. The glass slide was dipped in 100 mL solution and kept in it for one day. The next day the glass slide removed from the 100 mL solution in volumetric flask and kept the film in oven for annealing at 100 ^{0}C for 1 hour.

Results and Discussion

XRD analysis

XRD pattern provide information in relation to the nature and structure of the sample Fig.1 shows X-ray diffraction of PANI thin film prepared by chemical-oxidative polymerization method at room temperature. Diffraction pattern of PANI has abroad amorphous scattering peak at about 2θ = 22.55°, which is a characteristic peak of PANI (Tarachiwin L et al., 2002; Kiran Kumari, 2011), which confirms that PANI has been synthesized.

Scanning electron microscopy

The morphology of PANI was studied by using scanning electron microscopy (SEM). The typical morphology of PANI indicates that the particle size of PANI have 300 nm with small spherical morphology. The obtained morphology of the PANI shows that many nanostructures are loosely entangled without any particle-like impurities. The morphology of the as-synthesized PANI nanostructure film (see Fig.2), which in the form of matrix and agglomeration of grains has spherical morphology. This type of morphology of PANI film indicates strong conducting behavior.

FTIR studies

FTIR spectra of the sample of pure PANI was obtained in the transmission range 500–4000 cm^{-1} as shown in Fig.3. As shown in Fig. 3 the IR spectra of PANI film, the peaks are approximately presented at 920, 1053, 1220, 1325, 1487, 1594, 1732, 1952 cm^{-1}. IR spectra of sample of pure PANI shows strong absorption bands, in the region 900–1700 cm^{-1}, which correspond to the characteristics of polyaniline. The peak at frequency 920 cm^{-1} is observed in PANI film that is because of N–H out-of-plane bending (Hieu et al., 2009). The absorption peak at 1053 cm^{-1} may be attributed of C-H of 1-4 trisubstituted aromatic rings. The C–N stretching vibrations mode in the polymer chain gives rise to peak at 1162 cm^{-1} similar peak at 1155 cm^{-1} is earlier reported by Bairi et al (Bairi et al., 2012). The peak at 1325 cm^{-1} may be attributed to the C–N stretching mode.

Fig 1: X-ray diffraction pattern of pure PANI synthesized by chemical-oxidative method.

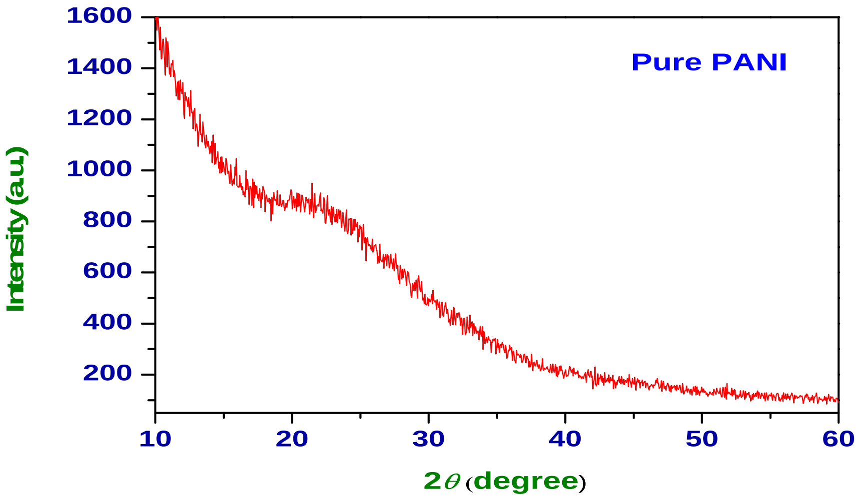


Fig 2: Scanning electron microscopy of pure PANI synthesized by chemical-oxidative method.

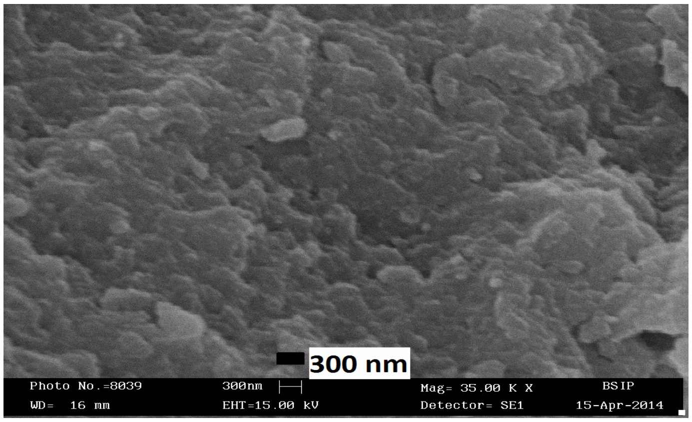


Fig 3: FTIR spectrum of pure PANI synthesized by chemical-oxidative method.

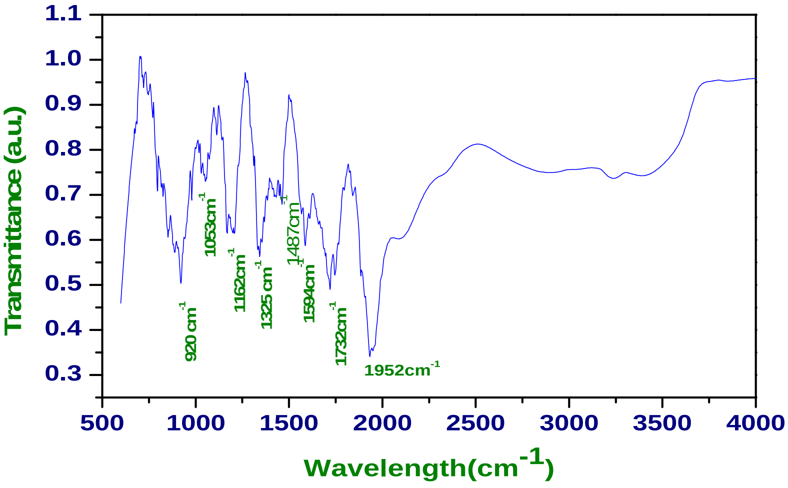


Fig 4: UV–Vis transmission spectrum of pure PANI synthesized by chemical-oxidative method.

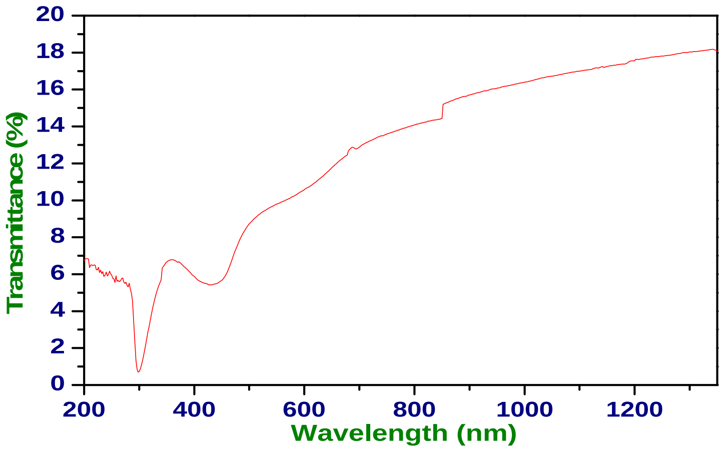
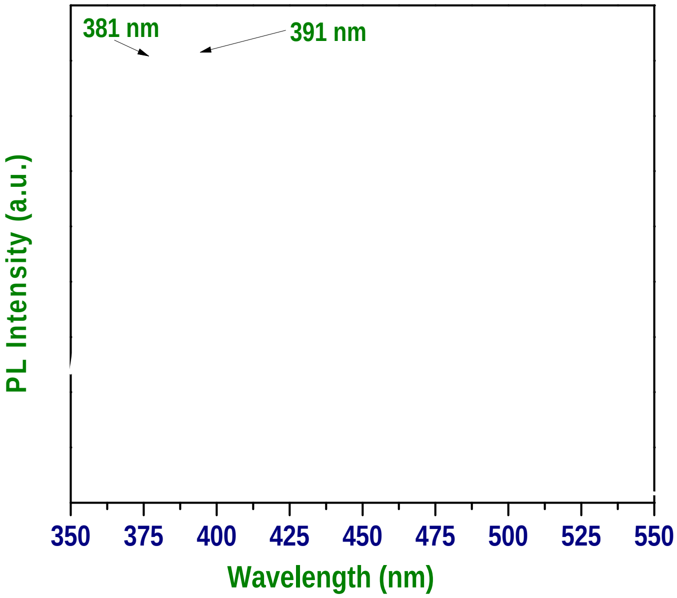


Fig 5: PL spectrum of pure PANI synthesized by chemical-oxidative method.



The peak amplitude characteristic of the absorption upon a stretching vibration of quinoid ring at 1594 cm^{-1} is found quite close to that corresponding to the absorption of a benzene ring at 1487 cm^{-1}, which is a characteristic feature of the conductive form of polyaminoarenes (C. Mayyoso et al., 1995; R. Murugesan and E. Subramanian, 2002). The absorption peaks at 1952 cm^{-1} is in the form of cyclopentanes.

UV–Visible transmittance

The UV–vis transmission spectrum of the PANI film was recorded at room temperature by using spectrophotometer between the wavelength range 200–1200 nm as shown in Fig.4. The UV-visible transmission spectra have been recorded with base line correction. The UV-visible transmission spectra can significantly determine the interaction. The PANI film shows three peaks at around 293 nm, 440 nm and 695 nm. The peak at 293 nm which correspond to л–л* band transitions (Akhilesh Tripathi et al., 2013). There are two visible region bands one at 440 nm and other centred on 695 nm. The peak centred at around 440 nm is attributed to *π*–polaron band transitions (Smritimala Sarmah and A Kumar, 2013). And the peak at around 695 nm for transition between benzenoid → Quinoid rings. Normally, the change of second peak is due to the change in degree of polymerization, while the change in position of first peak is due to degree of oxidization. For example BB → B → BB absorbs at 333 nm while BB → Q → BB at 310 nm (Wang et al., 2002) Comparing the obtained results from resulting peaks; it is found that both the transitions are observed at 292 nm and 663 nm with shifts in the peak positions. This will be probably due to unique chemical structure and degrees of ionization (S.K. Shukla et al., 2010). The absorption bands that have been obtained from the UV-Visible spectra are in good agreement with that reported in the literature.

Photoluminescence studies

Photoluminescence of organic molecules are a new class of compounds with interesting properties. They undergo emission over a wide range from the violet to the red. They can also be combined in several different forms to produce white light. One category of organic material with photoluminescence properties is conjugated organic polymers. The photoluminescence (PL) of semiconducting nanoparticles, which is strongly dependent on their surface energy states, can be easily modified by passivation with various organic molecules. The range of PL spectrum is 350 nm - 550 nm as shown in Fig. 5. The wavelength of excitation chosen for the PANI film is 343 nm, this is because of π-π* transition of the benzenoid unit is responsible for PL in PANI. The PL spectra of the PANI Film show peaks at 381 nm and 391 nm. The centred peaks around at 381 nm and 391 nm are lies in UV Visible region, which is specified in the wavelength scale of violet light. The presence of distinct peaks in the PL spectra indicates the possibility of the existence of multiple electronic states participating in the photo-excitation process (Sharma M et al., 2006) The direct band gap of the film was calculated by using this formula E= hc/λ, where h is the Planck constant, c is the velocity of light and λ is the emitted wavelength in photoluminescence spectrum. The direct band gap energy of the film is found as 3.26 eV and 3.18 eV. We suggested that the soluble poly-aniline film has better luminescence than other solvents.

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