

Adsorption of Iodine on Polyaniline synthesized via green medium and its characteristicsSarun Kumar T.R.¹, Smitha T.R.² and Prema K.H.³

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Abstract

Conducting polymers have unique properties which make them appealing alternatives for specific materials in various fields. In this study we focused on the optical properties of PANI and iodine doped PANI. PANI is synthesized by oxidative chemical polymerization method in green solvent tamarind juice. The sample is characterized by XRD, SEM, IR and TG analysis. It is exposed to iodine vapour in a chamber saturated with iodine vapour to get iodine doped PANI. The optical properties of the samples are studied by UV-VIS spectroscopy and band gap determination. Results revealed that tamarind juice is effective for the synthesis of thermally stable emeraldine form of PANI and iodine doping of PANI by iodine chamber method can be utilized for the optical enhancement for PANI and PANI based compounds.

Introduction

Conducting polymers are polymer materials with metallic and semiconductor characteristics, a combination of properties not exhibited by any other known material[1-2]. They have potential applications at all levels of microelectronics like electrostatic discharge (ESD), electromagnetic interference (EMI) shielding, interconnection technologies, corrosion protection of metals and in devices like diodes, transistors, sensors, biosensors, and actuators[3-4]. In addition, polymeric materials are lightweight, flexible, and can be easily processed which makes them suitable for micro and nanoscale molecular electronic devices. Also, they find application in the detection of single molecule, thus creating future opportunities for high sensitivity sensors and biosensors [5]. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. These enable the electrons to be delocalized over the whole system and so be shared by many atoms. This means that the delocalized electrons may move around the whole system. However, conjugation is not enough to make the polymer material conductive. In addition, the polymer material needs to be doped for electron flow to occur. Doping is either the addition of electrons (reduction reaction) or the removal of electrons (oxidation reaction) from the polymer. An oxidation doping (removal of electrons) can be done using iodine. The iodine attracts an electron from the polymer from one of the bonds. Once doping has occurred, the electrons in the bonds are able to move around the polymer chain. As the electrons are moving along the molecule, electric current occurs. For better conductivity the molecules must be well ordered and closely packed to limit the distance “jumped” by the electrons. The conductivity of conducting polymers can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping and by blending with other polymers [6-8]]. Among conducting polymers, a great deal of researches

have been devoted to polyaniline (PANI) due to its unique electrical, electrochemical properties, high environmental stability, easy polymerization and low cost of monomer [9]. Of the different oxidation states of polyaniline (Figure 1), the emeraldine salt (50% oxidised) is the only electrically conducting form while all other forms are insulating [10-12].

Figure 1. Different oxidized forms of PANI.

Utilization of natural resources in place of laboratory chemicals has great importance in the present environmental situations. In this study we focused on the optical properties of PANI and iodine doped PANI synthesized by oxidative chemical polymerization method in green solvent tamarind juice.

Experimental Materials and methods

All the chemicals used for the synthesis of polyaniline such as aniline, acetone and ammonium peroxydisulphate (APS) were purchased from Merck chemical company and are of high purity. Aniline is used after double distillation.

Polyaniline was prepared by oxidative polymerization of aniline monomer using ammonium peroxydisulphate oxidant in green solvent tamarind fruit extract (pH~2).

Aniline is dissolved in tamarind juice and stirred well using a magnetic stirrer. A solution of APS in distilled water is added drop wise to this reaction mixture with continuous stirring at 0-5^oC (monomer/oxidant ratio=1:1.25). After the complete addition of oxidant, the solution is kept undisturbed for 4-6 hours. The resulting product is filtered, washed with distilled water and the green coloured precipitate of polyaniline is dried in an air oven at 50 ^oC for overnight.

Iodine Doping of PANI by Direct Adsorption Method

The iodine doping is done by the vapor phase method. Pelletized sample of PANI is exposed to iodine vapour in a chamber saturated with iodine vapour. The amount of iodine adsorbed is determined by weight up take of the pellet at regular intervals. After attaining saturation desorption of iodine is allowed from the pellet by placing it in a desiccator and net increase in weight is determined. Finally 6% increase in weight is observed even after the desorption period.

The prepared PANI sample was characterized by FT-IR spectroscopy, X-ray diffraction analysis, Scanning Electron Microscopy and thermogravimetric analysis. The FTIR spectra was recorded on a Thermo Nicolet Avatar (370 Model) spectrophotometer in KBr medium in the region 4000-400 cm^{-1} having DTGS detector. The UV-VIS absorption spectra of the samples were recorded using a Shimadzu UV-VIS spectrophotometer (UV 2600) and the optical band gap of these samples was evaluated from the photon energy absorption plot.

Results and Discussion

X-ray diffraction

X-ray diffraction pattern of the pani is shown in figure 2. The characteristic peaks of PANI at 2θ around 20° and 25° ensure the formation PANI in the emeraldine base form. The broad absorption peaks indicates the amorphous nature of the sample.

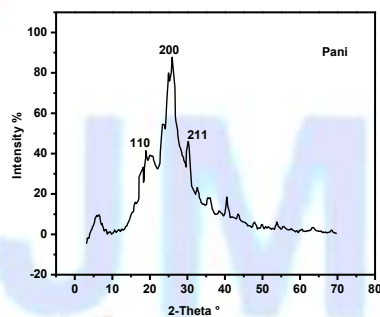


Figure2. X-ray diffraction diagram of PANI

2. Thermal analysis of PANI

The result of TGA of the sample is depicted in figure 3. Generally PANI shows three stage degradation processes. The first stage is due to the loss of moisture, which ends at 139°C . The second one starts at around 153°C and ends at around 295°C is due to the dopant evolution and the final one in the range of $342\text{-}689^\circ\text{C}$ is due to the degradation of PANI chain. About 70% of the weight loss occurs during this degradation. From TG curve it is found that the sample prepared using green solvent is thermally stable.

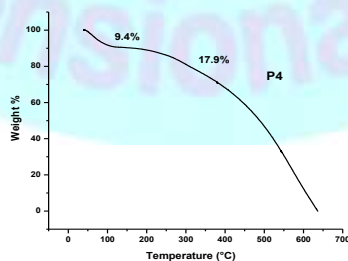


Figure 3. TGA curve of PANI

1. Scanning electron microscopy

The surface morphology of the sample was studied using scanning electron microscope and is represented in figure 4.

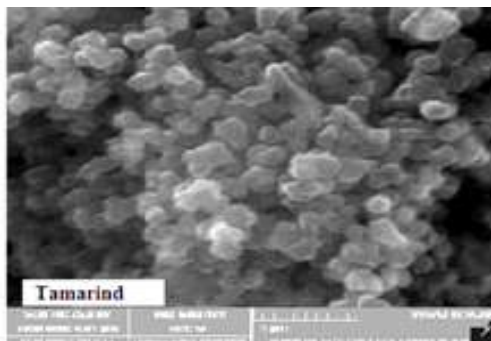


Figure4. SEM image of PANI at K 30000 magnification

Size and homogeneity of the particles are dependent on the type of the medium of preparation as the solvent affects the rate of polymerization. As shown in the figure the sample gives well uniformity to the particles. Spherical particles with an average particle size of about 200nm are found to be uniformly distributed. Surface morphology has great role in many of the properties of PANI.

5. IR absorption studies of PANI and PANI doped with Iodine

IR spectra of PANI and PANI doped with iodine are depicted in figure 5 and 6. The bands corresponding to stretching vibrations of N-B-N (benzenoid) and N=Q=N (quinoid) structures appear at 1485 and 1571 cm^{-1} respectively in the IR spectrum of PANI. The presence of these absorption bands confirms the formation PANI in the most conductive emeraldine form. A strong band appears at 1078 cm^{-1} has been explained as an electronic or a vibrational band of nitrogen quinone, an inplane bending vibration of imino-1,4-phenylene, and has been reported to be associated with the electrical conductivity of PANI. A visible change in the IR absorption of iodine doped PANI is observed in the range 1485-1571. This is due to the oxidation of PANI chain structure. The peak due to quinoid structure is shifted to higher wave length. All these confirm the chemisorption of iodine to the PANI chain. Peak at 1289 cm^{-1} is due to N-H bending vibration. The broad band observed at 3435 cm^{-1} is due to N-H stretching. In the iodine doped PANI intense peak is observed in this region that may be due to the existence of I^{3-} anion associated with the protonated $-\text{NH}^+$ of PANI chain.

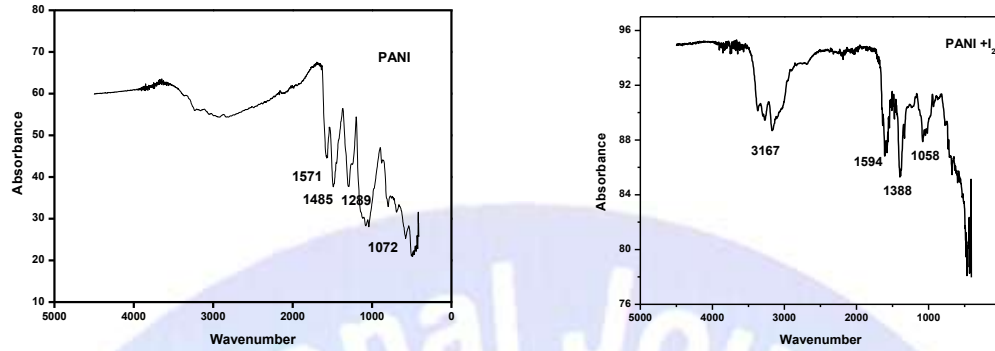


Figure 5 and 6. IR spectrum of PANI and PANI + I₂

6. Optical Properties PANI and Iodine doped PANI

UV-VIS spectra of PANI and PANI+I₂ are shown in figure 7 and 8

Three absorption peaks are observed in the UV-VIS spectrum of PANI and iodine doped PANI. The band at 270 nm is due to π - π^* transition of carbonyl group which proves the presence of acid in the matrix of the polymer. The π - π^* transition is seen around 385nm and the band due to polaron- π^* transition at 560 nm. π - π^* transition due to carbonyl group and polaron- π^* transition is not much shifted in doped PANI. The π - π^* transition in the ring structure is shifted to higher wavelength in the iodine doped sample which indicates an increase in extensive conjugation the polymer back bone.

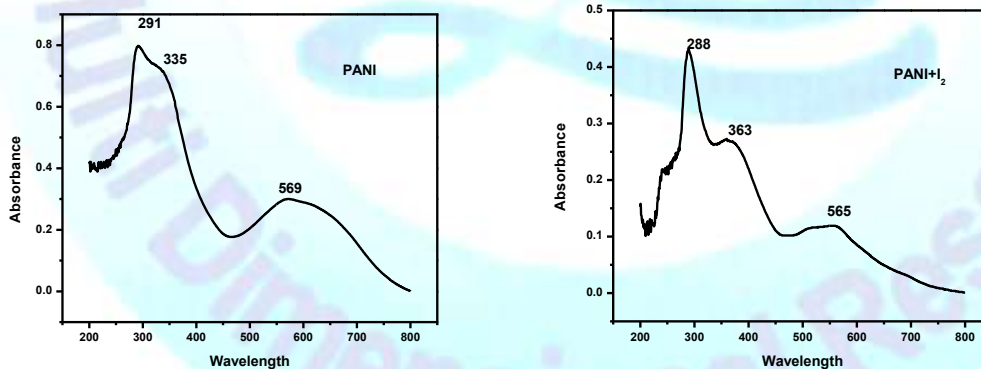


Figure 7 and 8. UV-VIS spectra of PANI and PANI+I₂

Band gap energy is calculated using the Tauc relation, $\alpha h\nu = A(h\nu - E_g)^n$, where A is a constant and n is $\frac{1}{2}$ for direct band gap semiconductor. Figure 9 and 10 shows the plots of $(\alpha h\nu)^2$ against $h\nu$. Extrapolation of the straight line portion to the $h\nu$ axis gives the band gap energy.

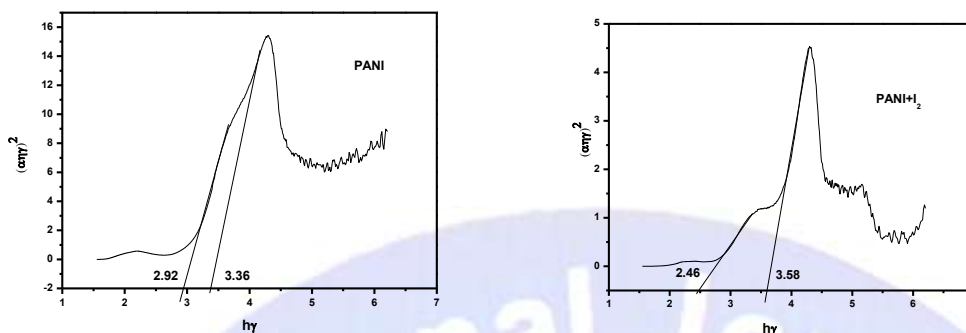


Figure 9 and 10 Band gap calculation of PANI and PANI+I₂

Band gap energy calculated corresponding to the wavelength absorption in the region 335 and 363 nm of PANI and doped PANI is found to decrease from 2.92 to 2.46 eV respectively. This clearly indicates the improvement in the optical absorption of PANI doped with iodine. Band gap energy corresponding to λ_{max} below 200 nm is found to increase with doping. This clearly indicates that some of the doped iodine molecules exist as I³⁻ anion. As this absorption is due to the $\pi-\pi^*$ transition of the carbonyl groups of the associated anion in the protonated chains of PANI. In the doped samples these may be replaced by the I³⁻ anions hence the absorption shifted to higher energy regions.

Conclusions

The results revealed that tamarind juice is effective for the synthesis of thermally stable emeraldine form of PANI. Iodine doping of PANI can be effectively done by direct adsorption method. The iodine can attach to the surface of the PANI due to physical adsorption as well as due to electronic interactions (charge-transfer type interactions) based on the doping mechanism observed for conducting polymers. Band gap energy for optical absorption can be decreased with iodine doping. Effective and easy method of iodine doping of PANI by iodine chamber method can be utilized for the optical enhancement for PANI and PANI based compounds.

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