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Investigation on Optical, Morphological and Thermal Properties of Spray Coated Polypyrrole Film

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Abstract: Soluble polypyrrole has been synthesized by In-situ chemical oxidative polymerization method in aqueous solution of pyrrole monomer. The solution contained dodecyl benzene sulfonic acid (DBSA) as a dopant and ammonium persulfate (APS) as an oxidant. The reaction temperature was 20°C for 24 hours. The prepared polypyrrole was dissolved in m-cresol solvent. The solution was coated on glass substrate by spray coating technique at 200°C for 5 minutes. The attachment of sulfonic group is confirmed in the pyrrole structure by FTIR spectroscopy. The absorption of PPy film at 360 nm and 600 nm was confirmed by UV spectroscopy. The emission wavelength of the film was found at 415nm as well as the direct band gap of the polypyrrole was 2.8eV. XRD study shows the crystalline nature of the DBSA doped polypyrrole film. SEM graph reveals globular morphology and the presence of functional acid on PPy film surface. TGA graph shows good thermal stability of the film.

Keywords: Spray coating method, Photoluminescence, Scanning electron microscope, X-ray diffraction, Thermal analysis.

1. Introduction

Conducting polymer films found various applications in electrochemical devices, rechargeable batteries, sensors, solar cells and light emitting diodes [1]. Among the conducting polymers, Polypyrrole is most attractive one because it has high conductivity, excellent environmental stability and easy preparation [2]. One of the obstacles for its practical applications is its poor solubility in common solvents due to strong interactions between polymer chains. This solubility problem made it difficult to investigate the optical properties of polypyrrole and which can be removed by inducing counter ions into the polymer backbone by doping Protonic acids, such as dodecylbenzene sulfonic acid (DBSA) and butyl naphthalene sulfonic acid (BNSNA) [3-4]. In the present study, soluble polypyrrole was prepared by chemical polymerization method at 20°C. Polypyrrole powder was coated on glass substrate maintained at 200°C for 5 minutes by spray pyrolysis technique dissolved in m-cresol and softer. Not much has work done in this area.

2. Experimental

2.1 Materials

Pyrrrole and dodecylbenzene sulfonic acid (DBSA) (Sigma-Aldrich, India) were purified by using distillation plant. Ammonium Persulphate (APS) obtained from Loba chemicals, methanol and acetones (Merck) were used for synthesis.

2.2 Preparation of DBSA doped Polypyrrole

0.15 mol of dodecylbenzene sulfonic acid (DBSA) and 0.3mol Pyrrrole was dissolved in 500ml of de-ionized water. After 10 minutes, 0.06 mol of ammonium per sulfate (APS) was prepared in 100ml de-ionized water and added drop wise into solution mixture. The solution was stirred for 24 hours in an ice bath maintained a constant temperature at 20°C. The solutions become dark brown color. Methanol was added to solution to stop the reaction. The precipitate was collected and washed with de-ionized water, methanol and acetone and dried at 30 °C for 12 hours in Vacuum oven.

2.3 Polypyrrole film preparation by Spray coating technique

20mg of Polypyrrole powder was taken in 5ml m-cresol solvent. It was stirred for 24 hours. The obtained solution was put into 100ml burette. Commercial glass substrate was cleaned, with acetone and isopropylalcohol respectively. Then the prepared solution was sprayed on glass substrate kept at 200°C for 5minutes and was annealed in air for 30 minutes. Polypyrrole film was formed on glass substrate. The Optical, structural and morphological studies were carried out for the prepared film samples.

3. Characterization techniques

The PL property of the soluble polypyrrole film was studied using FP-6500 Spectrofluoro meter- 67 at room temperature at 30°C. FTIR analysis was done in the range 500 to 4000cm⁻¹ using thermo Nicolet V-200 FTIR Spectrometer. AJEOL JSM -5610 scanning electron microscope was used to study the surface morphology of the Spray coated polypyrrole film. X-ray diffraction patterns of DBSA doped Polypyrrole film were recorded using an X-ray diffract meter with CuK α radiation ($\lambda=1.54\text{\AA}$) to identify crystalline nature of the samples. The UV-visible spectrum of Polypyrrole film sample was recorded employing Jasco V-530 dual beam spectrometer. TGA measurements were utilized to investigate the thermal stability of PPy by employing perkin Elmer model thermo gravimetric analyzer in N₂ atmosphere between 40 to 1100°C at a heating rate of 20°C/min.

4. Result and discussion

4.1 Photoluminescence spectrum of Spray coated PPy film

Photoluminescence spectrum of soluble DBSA doped PPy film coated by spray pyrolysis technique is shown in fig (1). Already PL property of soluble polypyrrole film has been studied and reported with various solvents like DMF, NMP, THF and Chloroform. The PL intensity of DBSA doped PPy was found to have higher luminescence than DMSO, Chloroform and THF in m-cresol solvent. The broad emission wavelength of the film was found at 415nm.

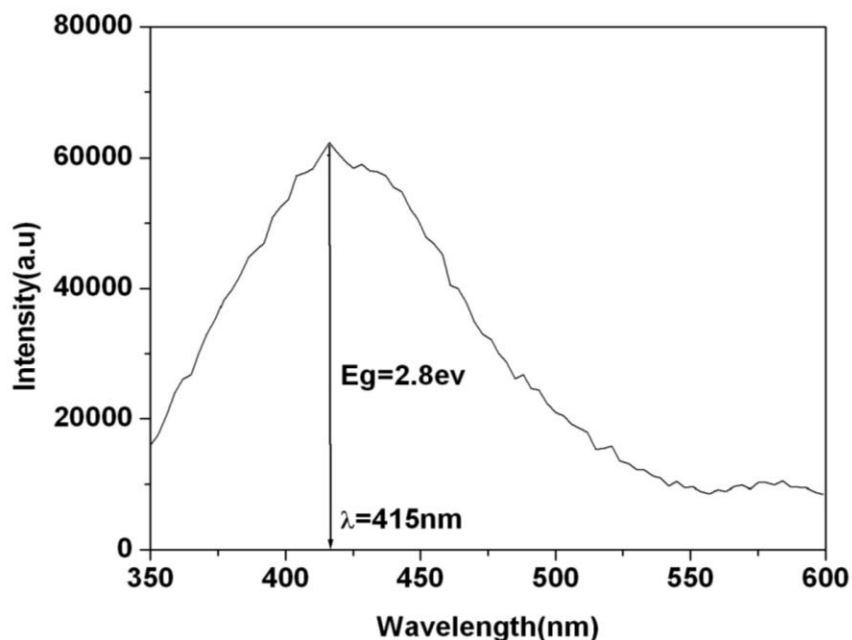


Figure 1: Photoluminescence spectrum of DBSA doped Polypyrrole film

The direct band gap of the film was calculated by using this formula, $E_g = hc / \lambda$, 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 2.8eV. We suggested that the soluble polypyrrole film has better luminescence than other solvents.

4.2. FTIR spectrum of Spray coated PPy film

Fig.2 shows FTIR spectrum of DBSA doped Polypyrrole film. N-H symmetric stretching appears at 3500 cm^{-1} . The peak at 2900 cm^{-1} corresponds to S=O and C-H stretching mode, which indicates the presence of benzenoid, ring in the DBSA molecule [9]. The small peak at 1580 cm^{-1} is due to C=C stretching vibration. The broad peak at 1300 cm^{-1} shows C-C and C-N vibration modes. The bands at 700 and 500 cm^{-1} are due to S-O, C-S stretching vibration [5]. The FTIR spectrum confirms the attachment of sulfonic group to the pyrrole ring.

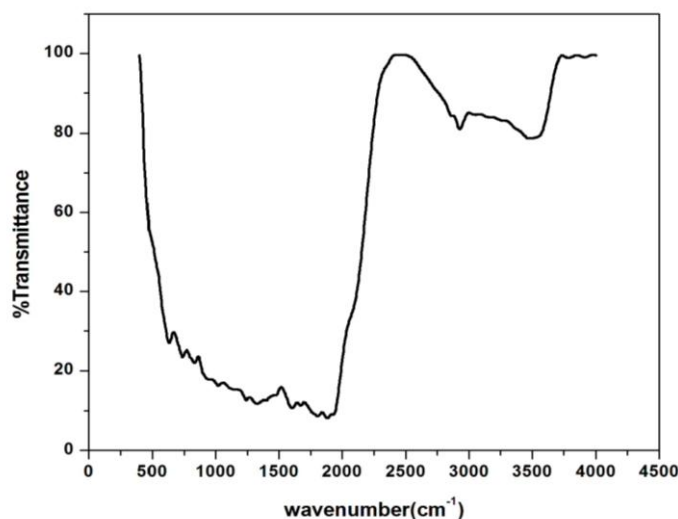


Figure 2: FTIR spectrum of DBSA doped Polypyrrole film.

4.3 Morphological properties of Spray coated PPy film

Fig (3) shows the SEM image of the DBSA doped soluble polypyrrole film prepared by spray pyrolysis technique. No cracks and pin holes are found in the morphology. The morphology of the polypyrrole film is globular [6], which is the characteristics of the functional acids used as dopants [7]. We confirmed that the presence of functional dopant in the polypyrrole film surface.

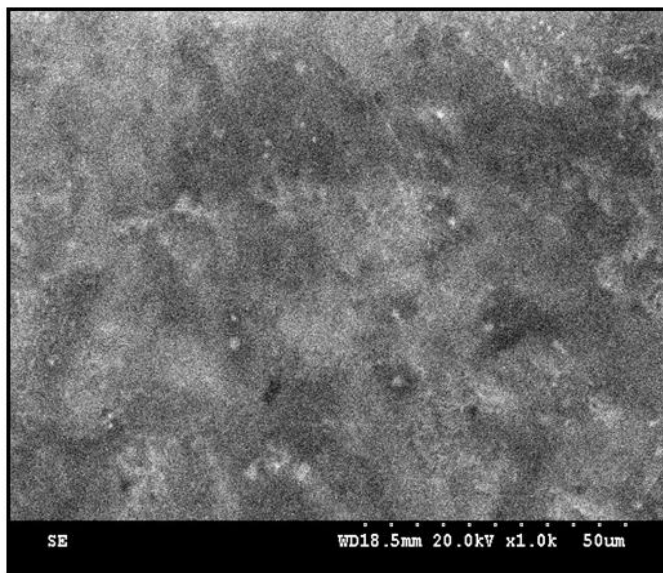


Figure 3: SEM image of DBSA doped Polypyrrole film

4.4.X-ray diffraction pattern of Spray coated PPy film

The X-ray diffraction pattern of Spray coated PPy film is shown in the Fig (4). The peak at $2\theta = 22^\circ$ reveals the crystalline nature of DBSA doped polypyrrole film. It corresponds to (101) plane value. The peak at $2\theta = 22^\circ$ describes the periodicity perpendicular to the polymer chain [8]. DBSA doped polypyrrole has better crystallinity compared to HCl and H_2SO_4 doped PPy [9]. The XRD result shows that the crystalline nature of DBSA doped polypyrrole.

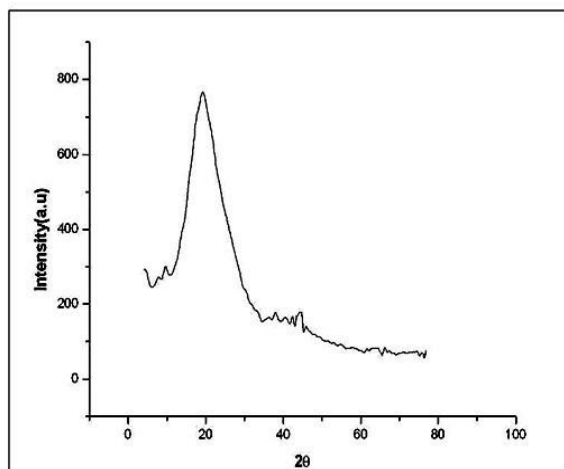


Figure 4: XRD pattern of DBSA doped Polypyrrole film

4.5 UV-Vis absorption spectrum of Spray coated Polypyrrole film

Fig.5 shows absorption spectrum of Spray coated PPy film. The sharp peaks at 360 nm and 600 nm are assigned to the $\pi - \pi^*$ transition of the benzoid rings. The UV-vis spectra were observed, which

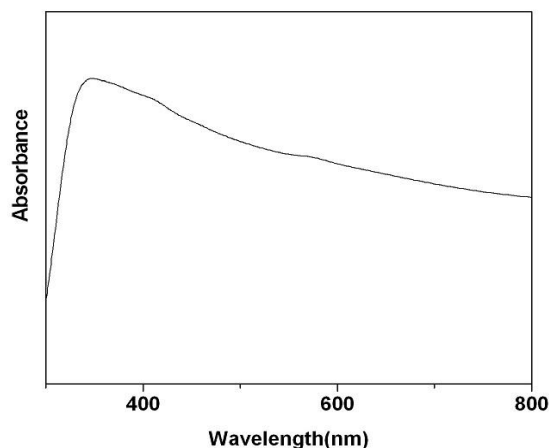


Figure 5: UV-vis absorption spectrum of Spray coated PPy film.

correspond to absorption bands of the $\pi - \pi^*$ transition, polaron and bipolaron respectively. The additional band at 600 nm shows extension of conjugation in the polymer chain. We confirmed the electron transition of spray coated PPy film.

4.6. Thermal analysis of spray coated PPY film

Thermo gravimetric analysis of soluble spray coated PPY film was recorded in the temperature range 50°C to 1000°C under nitrogen atmosphere at 20.00°C/min. Fig.7 shows the TGA spectra of soluble spray coated polypyrrole film. The initial weight of the sample was 3.039 mg. The first weight loss was observed between 100–280°C. This indicates the evaporation of physically absorbed water and the loss of surplus DBSA on the product surface. Then the sample starts to degrade above 300°C. It is observed that the DBSA doped PPY possesses a good thermal stability.

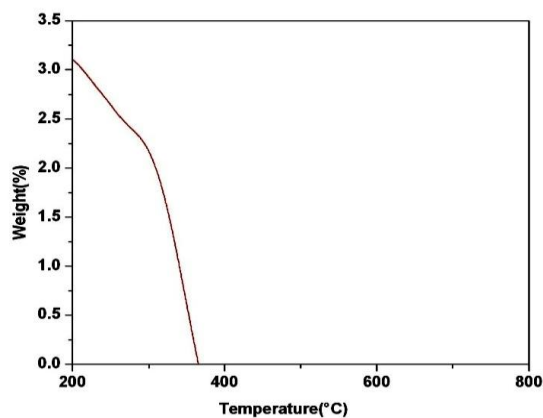


Figure 6: Thermal analysis of spray coated PPY film

4. Conclusions

Soluble polypyrrole was prepared by chemical oxidation method at 20°C. polypyrrole was dissolved in m-cresol solvent. Then the prepared solution was coated by spray coating technique at substrate temperature 200°C. FTIR study confirms the presence of sulfonyl groups combined with carbon ring. DBSA doped PPy gives higher luminescence. The emission of the film is found at 415nm. XRD study confirms crystalline nature of the DBSA doped polypyrrole film. SEM image reveals globular morphology of Polypyrrole film. UV-Study shows the π - π^* transition of DBSA doped polypyrrole film. Thermal study reveals the good thermal stability of the film.

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