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Polypyrrole doped with phthalic acid- A material with prospects for optoelectronic applications

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Polypyrrole (PPy) have been prepared by chemical oxidative polymerization method. The different dicarboxylic acids such as Oxalic (OA), Adipic (AA), Phthalic (PA) acids were used as dopants. The Prepared polymers were characterized by FTIR, UV-Vis, XRD and Photoluminescence (PL) analysis. FTIR and UV-Vis spectroscopic analyses confirm that the dopants have incorporated into the conducting polymer. The XRD patterns of the samples reveal that PA doped PPy have a significant crystalline nature. On comparing PL emission intensity of the polymers, PPy doped with PA shows better emission.

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1. Introduction

Conducting polymers are important materials emerging with lot of applications in various fields such as sensors, electronic and optical devices, and rechargeable batteries and so on. PPy is an important conducting polymer with high electrical conductivity and appreciable environmental stability [1]. PPy and its derivatives are one of the first conducting polymers used in gas sensors [2]. The conducting and physical properties of PPy depend on the choice of the counter ion, often called dopants [3]. In recent years much research has been conducted on PPy with various dopants. For example, PPy [SO_3H]-DEHS powder showed the highest water solubility and film conductivity of $5x10^{-1}$S/cm [4]. Alkyl benzene sulfonic acid (ABSA) doped PPy exhibits higher conductivity due to short alkyl chain present in the dopant [5]. Dodecyl benzene sulfonic acid (DBSA) doped PPy results better solubility with ammonium per sulphate as an oxidant [6]. The poor solubility of PPy in common solvents, which arises due to strong inter and intra-chain interactions, has limited its practical applications [7-8]. But the dopants having carboxyl group were reported to increase the solubility [9].

However, very little reports have found in the literature on the PL characteristics of the PPy samples.This work aims at the comparison of PL characteristics in PPy samples doped with different dopants, has not been carried out earlier. It has been found that, PPy doped with PA exhibit better PL emission. The above PL investigation has important consequences for practical technological applications, especially for the development of opto-electronic devices.

2. Experimental

2.1Material

Pyrrole (Merck) was distilled under reduced pressure and stored in dark before use. The dicarboxylic acids such as oxalic {HCOOH}, adipic {HOOC $(CH_2)_4COOH$}, phthalic {$(HOOC)_2C_6H_4$} acids and the oxidant ammonium persulfate $(NH_4)_2S_2O_8$ were used as purchased from Merck company.

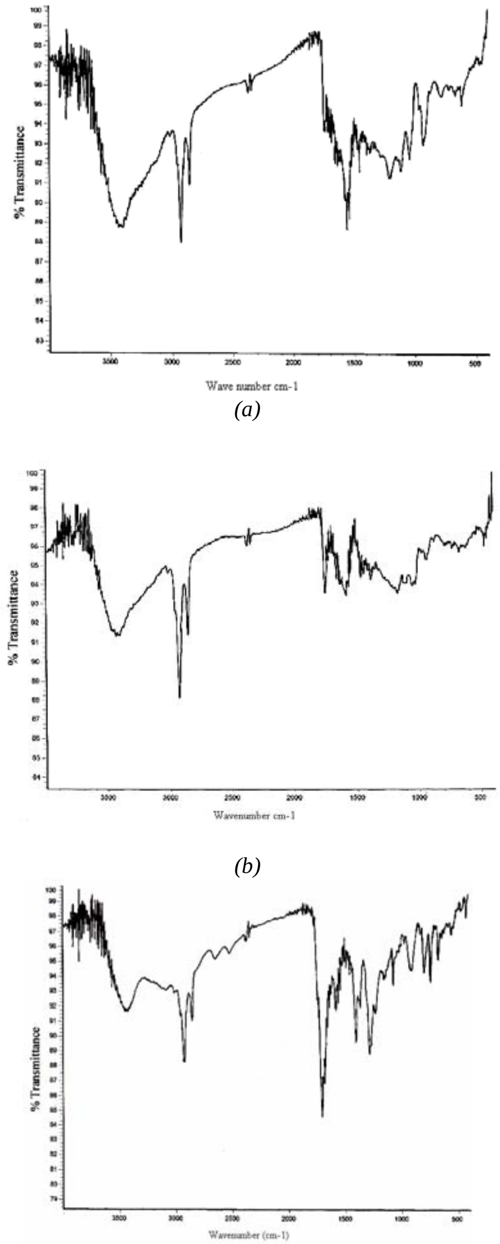
2.2 Chemical polymerization

The chemical polymerization of Pyrrole was carried out in the presence of aqueous dicarboxylic acid solution. Pyrrole (0.2M) was added to polymerization vessel containing dopant acid (0.2M) to make the total volume 100ml. 20ml of aqueous solution of oxidant $(NH_4)_2S_2O_8$ (0.25M) was added to the reaction medium in drop wise fashion in 20 minutes using a dropping funnel. The reaction was carried out for 2h at room temperature (~28°C) with moderate stirring. The precipitated PPy was filtered off and washed with acetone, methanol and de-ionized water. The black PPy powder was dried at 40°C in vacuum.

3. Results and discussion

3.1 FTIR analysis

FTIR spectra of PPy doped with different dicarboxylic acids were taken with KBr pellets using Thermo Nicolet V-200 spectrometer. The FTIR spectrum of the polymer samples were given in Figs. 1(a), 1(b), 1(c).



(a)

(b)

(c)

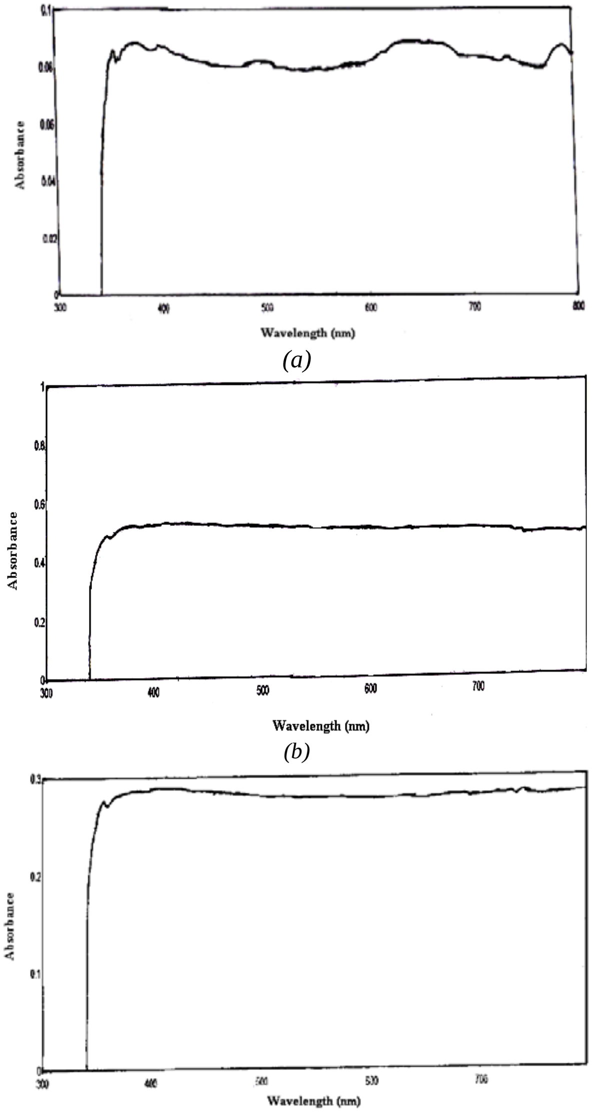
Fig.1. (a) FTIR Spectrum of PPy-AA; (b) FTIR Spectrum of PPy-OA (c) FTIR Spectrum of PPy-PA.

The bands observed at 3568, 3569 and 3567 cm^{-1} in the PPy samples doped with AA, OA and PA are assigned to the N-H asymmetric vibration. And the bands observed at 3399, 3421 and 3448 cm^{-1} in all the cases are characteristics of N-H symmetric vibration. The Strong absorption bands at 2924 and 2925 cm^{-1} in PPy samples are attributed to aromatic C-H asymmetric vibration. The aliphatic C-H asymmetric vibration appears around 2800 cm^{-1} in all the cases. The C=C, C=N vibrations occur at 1559, 1578 and 1579 cm^{-1} in the case of PPy-AA, OA and PA respectively [10].

The bands of C-H in plane bending are situated at 1120, 1096, 1114, 1071 cm^{-1} in the spectrum. The Peaks at 1637, 1743, and 1735 cm^{-1} are common to all samples, are corresponds to carboxyl groups of dopants used [11]. The bands at 1543 and 1542 cm^{-1} in the case of PPy-AA is related to C-C vibration in the pyrrole ring [12]. The bands at 931, 939 and 905 cm^{-1} in the case of PPy-AA, OA and PA are related to C-H out of plane deformation. Therefore the FTIR spectrum confirms the presence of monomer and functional dopants.

3.2 UV-Vis analysis

The UV-Vis spectra of the PPy samples was recorded employing Jasco V-530 dual beam spectrophotometer in m-cresol solvent and the UV-Vis spectra are depicted in Fig. 2 (a), (b), (c).



(a)

(b)

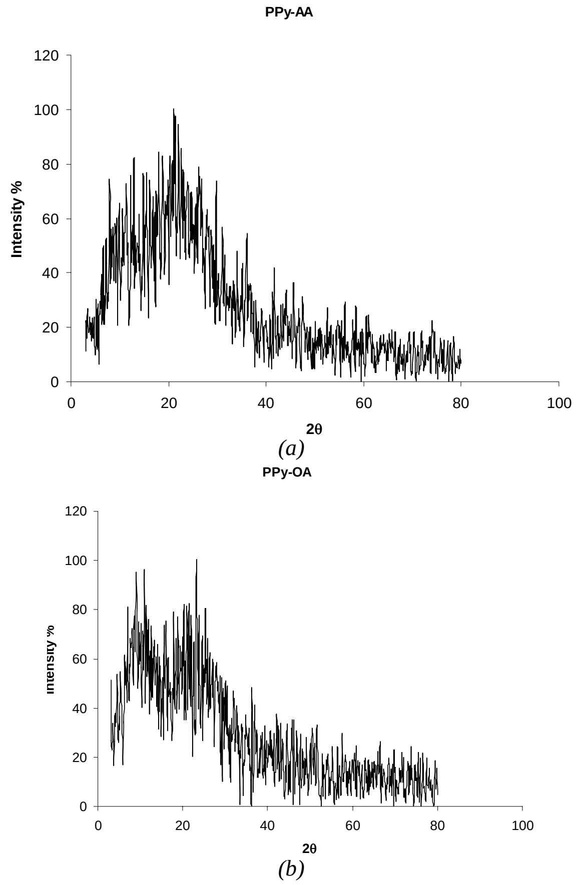
(c)

Fig. 2. (a) UV-Vis Spectrum of PPy-AA; (b) UV-Vis Spectrum of PPy-OA (c) UV-Vis Spectrum of PPy-PA.

The absorption band at 648nm in PPy doped with AA, corresponds to π-π^* transition. But PPy doped with OA and PA bring forth the absorption bands at 413 and 411nm respectively due to π-π^* transition. PPy-AA inherently allows more polaron, bipolaron generation by inducing anionically charged carbonyl groups in the polymer chain, which results pronounced bathochromic shift(red shift) of the π-π^* band to longer wavelength(648nm). The λ_{max} shift to higher wavelength indicates the gradual increase of the charge mobility and intrinsic conductivity [13]. Therefore PPy doped with AA is expected to have higher conductivity than other samples.

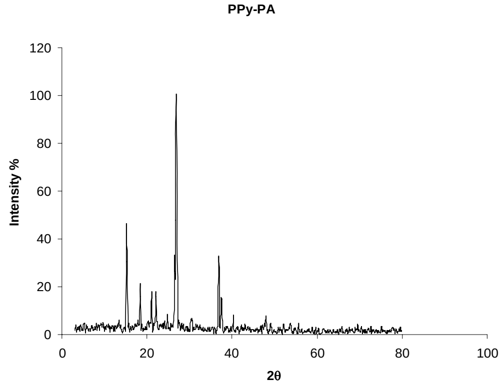
3.3 XRD analysis

X-ray diffraction (XRD) pattern of the PPy samples was obtained using Bruker AXS 5 D8 advance diffractometer with monochromatic Cu Kα radiation. The XRD spectrum of PPy doped with different dicarboxylic acids is given in the Fig. 3 (a), (b), (c). PPy doped with PA shows a crystalline sharp peak at 2θ=26.885°. The peaks shown by AA and OA doped PPy at the same position are amorphous peaks. Additionally, PA doped PPy shows sharp peaks at 2θ=15.255° and 36.897°. The appearance of sharp peaks in PA doped PPy may indicate considerable degree of crystallanity in the polymer. The peaks at 2θ=29.774° and 24.14° in OA doped PPy are less sharp and reduced in intensity.



(a)

(b)



(c)

Fig. 3. (a) XRD Patterns of PPy-AA; (b) XRD Patterns of PPy-OA; (c) XRD Patterns of PPy-PA.

XRD patterns show that PPy-PA has a better crystallanity than PPy doped with other three acids and it indicates doping PA into PPy molecular chains, could improve the crystallanity of the resulting polymer. Accommodating large size dopant ions demand greater rearrangements of bonds along the polymer back bone, which also leads to better crystallanity [14]. The crystalline size is calculated using the Scherer's formula $D=K\lambda/\beta\cos\theta$, where, D is the crystalline size of particle, λ=1.54Å being the X-ray wavelength, K is the shape factor (0.89), $\cos\theta$ the cosine of the brag angle, β the full width at half height of angle of diffraction in radians. The average particle size is 41 nm by considering the intense characteristics peaks at 2θ=26.885°, 15.255°, 36.897° in PA doped PPy.

3.4 Photoluminescence analysis

The PL emission spectrum of the PPy samples was obtained using a FP-6500 spectroflurometer. The PL emission spectrum of the three powdered samples is depicted in the Fig.4. The wavelength of excitation chosen for all the samples was 370nm. For the three samples, the maximum PL emission was observed at 425nm. But PPy doped with PA shows the highest PL emission intensity followed by PPy doped with AA and OA.

The better crystallanity in PA doped PPy favors the highest PL intensity, which is evident from its XRD spectrum. There is another reason for the observed better PL emission in PA doped PPy, as the conjugation length increases during excitation [16]. PPy-AA also shows better emission due to enhanced π-electron mobility in the polymer chain. The optical band gap energy is calculated using the formula $Eg=hc/\lambda e$, where h is the plank's constant (6.626×10^{-3}), c is the velocity of light (3×10^{8}), λ is the PL emission wavelength, e is the charge of the electron (1.602×10^{-19}). The band gap energy calculated is 2.91eV.

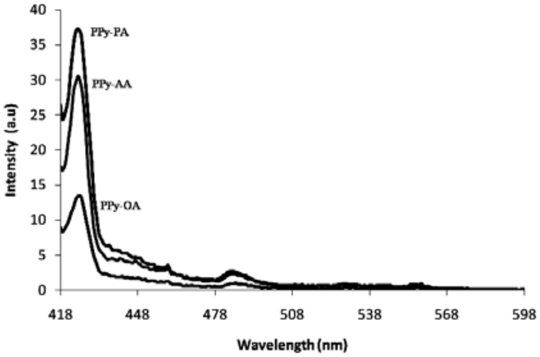


Fig. 4. PL emission Spectrum of PPy doped with different acids.

4. Conclusions

PPy was synthesized by chemical oxidative polymerization method. FTIR spectra confirm the presence of carboxyl groups of dopants in the polymer. The λ_{max} in UV-Vis spectra of AA doped PPy demonstrates the longer wavelength shift of the $\pi - \pi^*$ band which enhances the polymer conductivity. X-ray diffraction pattern of PA doped PPy indicates substantial degree of crystallanity .The average particle size is found to be 41nm. The PL studies predict that the PPy doped with PA exhibits the highest PL emission intensity, making it suitable for various optoelectronic applications.

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