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The evaluation of Temperature effect on Peak-to-Peak Line Width ($\Delta H_{pp}$) of conjugating polymer Polypyrrole (Ppy)

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Abstract. The magnetic properties of the neutral and doped polymer polypyrrole (Ppy) nanostructure has been successfully synthesize via chemical method. The nanostructurated powder was investigated using electron spin resonance (ESR) measurements. The board ESR signal was attribut to the existence of unpaired electrons. The $g$-factor of pure Ppy decreased with increasing temperature while that of doped (Ppy) was found to increase linearly from 1.9504 to 1.9925 within a temperature range of 298K - 473 K. This could be due to polaron species formation. The current results demonstrated that polypyrrole (Ppy) could be considered as a good candidate for many applications especially in organic photovoltaic and gas sensors.

1. Introduction

Polypyrrole (Ppy) is one of the most promising conjugated polymers, because, is it has a good physical and electrical properties, easy to synthesis, high electrical conductivity and stable in conductive oxidative state compared to other conjugated polymers. (Ppy) is easily prepared by chemical and electrochemical polymerization. In chemical oxidative polymerization of Pyrrole (Py) monomers, many oxidants have been used such as ferric chloride, ferric per chlorate, ammonium peroxydisulfate and others [1-3]. In this article we focus on conjugated polymer mainly polypyrrole (Ppy) electron spin relaxations as function of dopant concentrations and temperature depended. Electron Spin Resonance (ESR) spectroscopy is a very useful to study polymer samples that involve unpaired electrons, thus it be a complementary and quantitative tool for the analysis of optical spectra [4]. Electron spin relaxation behaviors of conducting polymers are studied using a pulsed of electron spin resonance spectroscopy (ESR) technique, in order to estimate the line width and $g$-factor variations [5].
Polypyrrole (Ppy) in both its natural-insulating and oxidized-conducting states exhibits a strong ESR signal, various studies investigated polypyrrole (Ppy) g-value, signals occurred in the g = 2 region, line width and intensity corresponding to oxidation concentration and electrochemical behavior [6]. The ESR line width extremely increased as a result of increasing temperature this behavior dependence of the ESR line width provide through Elliot relaxation mechanism for metallic characteristic[7]. All the results exhibited the lorentzian line shape, which confirm that chlorine and arsenic atoms are irrelevant to the line width [8]. The objective of this paper is to show the effect of dopant concentration ESR line spectra as function of temperature dependence.

2. Material and Methods

Pyrrole (Py) C₄H₄HN, (Fluka) 98%, ferric sulphate Fe₂(SO₄)₃ and sodium dodecyl Sulphate (SDS) CH₃(CH2)₁₁OSO₃Na (Sigma-Aldrich) were used as a starting material while, distilled water was used as solvent. All the chemicals were used in their original form except the Pyrrole (Py) which was purified by vacuum double distillation at 404 K then kept at 277 K in order to avoid degradation. 0.2M from freshly prepared Pyrrole (Py), were dissolved in 20 cm³ of distilled water then stirred for 10 minutes furthermore, 0.2 M ferric sulphate was dissolved in 80 cm³ distilled water then stirred for 10 min. One hundred cm³ of water was added to solution and stirred for 6 h at 25°C. The same procedure was repeated with adding various concentrations of sodium dodecyl Sulphate (SDS) as dopant agent, which are marked as: Ppy (0) for pure, Ppy (5%). The Precipitated powder was filtered, washed, dried at 50°C for 36 h then the ground powder inserted in 5 mm diameter tube. The ESR spectra through different temperature (25-200) °C were recorded on a JOEL JES-FA200 EPR spectrometer (JOEL, Tokyo, Japan). The g-value was estimated directly from ESR recording data.

3. Result and Discussion

As shown in Fig.1 the Ppy particle diameter can be directly achieved from TEM image using equation [9-10]:

\[
D_n = \frac{\sum N_i D_i}{\sum N_i}
\]

(1)

Where Di, is the diameter of individual particle, Ni, the numbers of (Ppy) nanoparticle small size of (Ppy) particle size reduce from 105 nm to 86 nm as the (SDS) ratio increase from 0% to 5% SDS respectively thus the shape and size can be controlled through the variation of sodium dodecyl sulphate (SDS) This is attributed to small size of micelles [11-12].

As presented in Fig .2 the FESEM images for pure and doped (Ppy) through 30X magnification shows a typical granular morphology with cauliflower shape. The grain size of pure (Ppy) without (SDS) is mainly 196 nm meanwhile, the (Ppy) particle size reduced to 152 nm at 5% (SDS). The surface morphology of Ppy shows uniform spheroid particles with average size about 100 nm because the ionic surfactant (SDS) prevents agglomeration and control the particle size. This results in agreement of study [13].

The ESR spectrum of conjugated polymer polypyrrole (Ppy) in the temperature range 25-200 °C (298 - 473) K. were measured through different molar ratios 1 MR and 2 MR doped with 5 % of Sodium Dodecyl Sulphate(SDS) as shown in Fig. 3 to 5.

ESR spectra of (Ppy) samples exhibited spectral boarding with different intensity and sharpness as shown in Fig 3 to 5. The ESR line width increases as a result of increased molar ratio within same temperature range, mostly for all 1 MR and 2 MR at 5% SDS dopant concentration. Meanwhile, pure Ppy at room temperature 250C through 1MR and 2 MR showed reduced line width thus the peak-to-peak Line Width (ΔHpp) decreased as temperature increased. This characteristic feature is in agreement with [14-17].
Polypyrrole (Ppy) samples mentioned below exhibited a different behavior especially, with in the temperatures ranges 323 K to 473 K this attributed to the strong coupling region that related to metallic nature [18].

We now discuss temperature dependence of ESR intensity, as shown in Fig 3 and Fig 5. For, 1 to 2 molar ratios, the relative intensity of Ppy decreases as temperature increased, which is attributed to partial transitions from polaron and bipolaron [19]. Polaron is a radical action induced after the introducing of dopant in conjugated polymer. This charge carrier is characterized by a charge \( \pm|e| \) and a spin \( 1/2 \) which give rise to ESR spectra. Two polarons may combine to form a bipolaron which has a charge \( \pm|e| \) and zero spin, where ESR signal is no longer observed. This results in agreement with [20], which confirm the possibility of polaron-bipolaron transformation. As sown in Table 1 and 2. The \( g \)-factor of pure Ppy decreases as temperature increased while, the \( g \)-value of doped (Ppy) increased linearly from 1.9504 -1.9925 in a temperature regime (298-473) K, and this may be due to the formation of polaron species.

4. Conclusions

In current study, ESR measurements have been achieved on the neutral and doped polypyrrole (Ppy), polypyrrole-sodium dodecyl sulphate (SDS) respectively. A narrow Lorentzian line is observed in doped samples; highly conducting polymer, the characteristic of (Ppy) ESR signal with stronger intensity was produced due to the formation of polaron and bipolaron. The current results demonstrated that conjugated polymer polypyrrole (Ppy) could be an excellent, attractive and of highly thermal stability, conducting polymers due to the free sulphate ions which are thermally active with less degradation and easily synthesized.

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Table 1: variation of polypyrrole (Ppy) g-value through different temperature

| Samples | 30 °C | 50 °C | 80 °C | 110 °C | 140 °C | 170 °C | 200 °C |
|---------|-------|-------|-------|--------|--------|--------|--------|
| Ppy(0)  | 1.9951| 1.9951| 1.9950| 1.9950 | 1.9950 | 1.9951 | 1.9951 |
| Ppy(1)  | 1.9925| 1.9952| 1.9952| 1.9951 | 1.9951 | 1.9951 | 1.9950 |

Table 2: variation of polypyrrole (Ppy) g-value through different temperature

| Samples | 30 °C | 50 °C | 80 °C | 110 °C | 140 °C | 170 °C | 200 °C |
|---------|-------|-------|-------|--------|--------|--------|--------|
| Ppy(0)  | 1.9948| 1.9946| 1.9945| 1.9946 | 1.9946 | 1.9947 | 1.9948 |
Fig. 1: TEM image of Ppy at different SDS concentrations (a) 0 % (b) 5 %

Fig.a: Pure Ppy 0% SDS

Fig.b: Ppy at 5% SDS
Fig. 2: FESEM Image of Ppy (a) 0% (b) 5%

(a) Ppy pure 0%  (b) Ppy at 5% SDS

Fig. 3: peak-to-peak ESR line width of Pure Ppy (1 MR) from RT to 200 °C

RT
500C
800C
1100C
1400C
2000C
1700C

ESR Intensity(a.u)
Magnetic Field(mT)
322 329 336
Fig. 4: peak-to-peak ESR line width of 5% SDS Ppy (1 MR) range from RT to 200 °C

Fig. 5: peak-to-peak ESR line width of Pure Ppy (2 MR) from RT to 200 °C