DC conductivity studies of iron decorated polypyrrole

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Abstract. Fe-Ppy was synthesized by in situ polymerization with varying the concentration of oxidizing agent (FeCl3) and green tea extract. As prepared polymer samples have been characterized by XRD, FTIR, SEM and TEM. DC conductivity was measured in the temperature range 303-378 K. Obtained results reveals that, the conductivity slightly increases with increase in temperature. Fe (0.31M)-Ppy-10ml green tea extracted sample exhibited highest conductivity as compared to the other composites. Activation energy found to increases up to Fe-(0.92M)-Ppy 30ml sample and it was maximum for Fe (1.54M)-Ppy 50ml sample.

1. Introduction

Polymers can be shaped, easily processed, do not break easily which is not true for metals/alloys. Conducting polymers possess wide range of electrical properties, these properties & the ease with which polymers can be shaped into the complex multi-polymer architectures are the reasons for industrialists, scientists looking for novel applications and which could be used for electronic applications [1]. In the past three decades conducting polymer nanocomposites have become one of the most extensively studied materials all over the world due to their attractive properties with many applications such as electrical, electronic devices, conductive paints, rechargeable batteries, sensors etc., in conducting polymer nanocomposites [2-9]. Conductivity depends on various factors like polymer morphology, size, concentration of incorporated material & interfacial interaction [10-12]. Literature survey revealed that, more than twenty conducting polymers have been subjected to the academic and research studies, among them polypyrrole (Ppy) has been widely studied and one of the most attractive conducting polymers due to its special transport properties, easy synthesis with low cost, tuneable electrical conductivity and good environmental stability etc., compared to polypyrrole (Ppy), Iron decorated polypyrrole (Fe-Ppy) has exhibited enhanced conductivity [13-15]. In the present work, to improve the conductivity of Fe-Ppy suitable dopants have been incorporated into Fe-
Ppy matrix with high surface area. Conductivity of such composites, changes by the incorporation of nanoparticles into the Ppy polymer. Conductivity of the iron decorated polypyrrole (Fe-Ppy) was measured in the temperature range 303-378 K and the results revealed that, the conductivity has marginally increased with increase in temperature. Composite Fe(0.31M)-Ppy-10ml Green tea extract sample exhibited highest conductivity, compared to other composites. Activation energy of the as synthesized samples was determined using Arrhenius plots for all compositions. Activation energy found to increase up to Fe(0.92M)-Ppy-30ml green tea extract and it was maximum for Fe(1.54M)-Ppy-50ml green tea extract.

2. Materials and Methods

2.1. Materials
Pure Pyrrole (analytical grade) monomer purchased from Merck, Ferric Chloride (FeCl₃) from Nice Chemicals and green tea leaves from Apollo pharmacy used for the synthesis.

2.2. Synthesis of iron decorated polypyrrole
Iron incorporated polypyrrole (Fe/Ppy) was synthesized by in situ oxidative polymerization using suitable oxidizing agent ferric chloride solution and reducing agent as green tea leaves extract in different concentrations. Green tea extract was prepared by using 4.3 g of green tea leaves in 150 ml distilled water boiled till the volume of the solution reduces to 100 ml, it was cooled to room temperature, then filtered to obtain green tea extract which was used for the Fe/Ppy synthesis. Green tea extract contains polyphenol derivatives such as catechin, epicatechin, flavanol etc., which helps for the incorporation of iron particles in polypyrrole polymer matrix. Green tea extract of 10 ml taken in 100 ml beaker and kept for stirring. Then, 1 g of FeCl₃ in 20 ml distilled water was added into the same beaker. Finally, 1 ml of pure pyrrole was added drop wise into the reaction mixture and continued stirring for about 18-20 hours at room temperature, the reaction mixture was filtered through Buckner funnel and kept for drying [16-17]. It was observed that, with the increase in the concentration of FeCl₃ solution and volume of green tea extract, and keeping volume of pyrrole (1 ml) constant, the yield of Fe/Ppy also started increasing. Figure 1 shows the graphical representation of preparations. Figure 2 shows the flow chart of the synthesis process.

![Figure 1](image1.png)

Figure 1. Synthesis of iron decorated polypyrrole (Fe/Ppy) composite.

| Volume of green tea extract | FeCl₃ Solution (in moles) | Volume of pyrrole | Yield of Fe/Ppy obtained |
|-----------------------------|--------------------------|------------------|--------------------------|
| 10 ml                       | 0.31 M                   | 1.0 ml           | 0.290 g                  |
| 20 ml                       | 0.62 M                   | 1.0 ml           | 0.585 g                  |
Pyrrole Monomer (1.0 ml) + Ferric Chloride (0.31 M – 1.54 M) + Green Tea Extract (10ml – 50 ml) +  
Stirred the resulting mixture about 6-7 hrs at room temperature 
Polypyrrole (Black powder) obtained was filtered, dried in hot air oven at 100°C and powdered. 

**Figure 2.** Flow chart of Synthesis of iron decorated polypyrrole (Fe/Ppy) composite. 

2.3. Characterization
Synthesized Fe/Ppy composites were characterized by X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), Scanning electron microscopy (SEM) and Tunnelling electron microscopy (TEM). 

3. Results and discussion

**Figure 3.** a) XRD spectra of Fe Nanoparticles (Fe-NPs), (b) XRD spectra of pure polypyrrole, (c) XRD pattern of the iron decorated polypyrrole.
3.1. XRD analysis
The X-ray diffraction patterns of iron nanoparticles (Fe-NPs), pure polypyrrole and Fe/Ppy were recorded on X-ray diffractometer. Figure 3a shows XRD Spectra of iron nanoparticles (Fe-NPs) sharp peaks are observed at 2θ = 42° and 49° which are characteristic peaks of Fe-NPs. Figure 3b shows XRD Spectra of pure polypyrrole, broad band at 2θ = 22° to 28° was observed which is a characteristic peak of pure polypyrrole (Ppy), the broad peak in between 22° to 28° reveals that the polypyrrole amorphous in nature, figure 3c shows XRD Spectra of iron decorated polypyrrole, broad band at 2θ = 22° to 28° was observed which is a characteristic peak of pure polypyrrole (Ppy), the peak 2θ at 24° to 28° reveals that the polypyrrole peak and amorphous nature decreases to crystalline nature. The sharp peaks, 2θ value at 42° to 49° reveals the iron nano particles, clearly the XRD pattern reveals the incorporation of iron nanoparticles in Fe/Ppy composite [18-19].

![Figure 4 (a) FTIR Spectra of Iron decorated polypyrrole, (b) FTIR of polypyrrole.](image)

3.2. FTIR analysis
FTIR spectrum of Fe-NPs, pure Ppy and Fe/Ppy, are shown in figure 4, the peaks observed from 974 cm⁻¹ to 611 cm⁻¹ due to =CH vibrations of polypyrrole, broad bands observed at 1397 cm⁻¹ and 1616 cm⁻¹ C-N stretching vibrations of Ppy. The peaks at 762 cm⁻¹ and 974 cm⁻¹ are due to polymerized pyrrole. The band observed at 3411 cm⁻¹ due to N-H stretching, and 1056 cm⁻¹ is N-H plane deformation. The bands observed at 480 cm⁻¹, 1634 cm⁻¹, 2363 cm⁻¹ and 2227 cm⁻¹ are due to iron particle metallic vibrations [20]. Green tea extract were mainly located at 3454 cm⁻¹, 1695 cm⁻¹, 515 cm⁻¹. The presence of peak at 3454 cm⁻¹ indicate the possible O-H stretching vibration of phenol groups, which might be responsible for the formation and stabilization of nanoparticles [21]. Therefore, Fe/Ppy FTIR clearly shows the incorporation of iron nanoparticles on to the Ppy.

3.3. SEM analysis
Fe/Ppy SEM images in different resolutions are shown in figure 5a-d. It is observed from SEM images that the spherical shaped particles inserted in the agglomerated Ppy (figure 5a). Incorporation of iron particles in the Ppy matrix, granular grains are observed in the Fe/ppy composite under different resolutions (figure 5b). It is noticed that the incorporation of the iron nanoparticles did not change the morphology of the polypyrrole significantly; iron nanoparticles are inserted in the form of spherical nature of polypyrrole to form multiple aggregated clusters of particles and also some voids, probably
due to weak interparticle interactions (figure 5c-d). The iron nanoparticles incorporation was confirmed in XRD & FTIR spectrum.

![Figure 5](image)

**Figure 5.** SEM images of Fe/Ppy in different resolution.

### 3.4. TEM analysis

TEM images of Fe/Ppy in different resolution are shown in figure 6 (a & b), TEM images shows iron particles incorporated in Ppy matrix. The black-coloured spots in Figure 6(a) and (b) are observed, which indicates that the Fe nanoparticles were effectively incorporated onto the Ppy polymer matrix. Particularly, the Fe nanoparticle was produced and gets distributed on the surface of the Ppy polymer matrix without extra reducing agents through the oxidative polymerization. As the concentration of ferric chloride solution (FeCl$_3$) increased in the synthesis, from 0.31M to 1.54M, the incorporation of Fe nanoparticles on the polypyrrole also increased [22].
3.5. DC conductivity

To analyse the conductivity mechanism of the Fe/Ppy composites, figure 7 shows there is a variation of electrical resistance with temperature. The electrical resistance decreases slightly with increase in temperature which shows almost semiconducting characteristics, also the electrical resistance increases with the increase in the content of the iron particles. The electrical resistance dependence on temperature is studied for varying oxidation and reduction agent’s concentration in the synthesis. Figure 7 shows the decrease in electrical resistance with increasing in temperature indicates the Fe/Ppy composites exhibits semiconducting behavior [23]. It is noticed that resistance decreases slightly with increasing temperature in all five composites. Further, the composite Fe(1.23M)-Ppy-40ml GTE shows high resistance compared to other composites, Fe(1.54M)-Ppy-50ml GTE composite exhibits more resistance compared to other composites whereas rest of the three composites shows almost same resistance with change in temperature [22-25].

Figure 6. TEM images of Fe/Ppy in different resolution.

Figure 7. Fe/Ppy composites of Resistance versus Temperature graph.

The electrical conductance dependence on temperature is studied for varying oxidation and reduction agent’s concentration in the synthesis. Figure 8 shows slight increase in conductance with
increasing temperature. It is noticed that conductance increases slightly with increasing temperature in all five composites. Further, the composite Fe(1.23M)-Ppy-40ml GTE shows lowest conductance compared to other composites. Fe(0.31M)-Ppy-10ml GTE composite exhibited highest conductance [26-30].

The dc electrical conductivity measurement is one of the best tools to understand charge transport mechanism in Fe/Ppy composites. Figure 9 shows the variation of dc electrical conductivity of Fe/Ppy composites of different concentration with varying temperature. It has been observed that the conductivity, not changing uniformly with varying temperature and composition. The conductivity depends on incorporation of nanoparticles on polymer matrix, as the population of nanoparticles increases, conductivity decreases due to increase in band gap. Also, it has been noticed that the conductivity slightly increases with rise in temperature, the composite Fe(0.31M)-Ppy-10ml GTE exhibits highest conductivity, and Fe(1.23M)-Ppy-40ml GTE composite shows lowest conductivity. Further Fe(1.54M)-Ppy-50ml GTE composite conductivity is more compared to (1.23M)-Ppy-40ml GTE composite. The variation in dc conductivity is due to change in the concentration of charge carrier density in the Fe/Ppy composites. The increase in conductivity could possibly be explained based on percolation theory, which predicts that at a certain amount of concentration of conducting polymer a full conducting path is formed for the flow of current and the conductivity rises. This has also been confirmed from SEM micrographs which shows the formation of chain pattern at a particular wt.% of nanocomposite providing an increased conducting path and hence conductivity [31, 32].

Figure 8. Fe/Ppy composites of conductance versus temperature. Figure 9. Fe/Ppy composites of conductance versus inverse temperature.

3.6. Activation energy

Activation energy is determined by plotting fit linear curve for various polypyrrole composites as shown in table 2, activation energy (Ea) (the lowest energy needed to start conduction by charge carrier mechanism) ‘k’ Boltzmann constant. Using the below formula, the change in dc conductivity (‘σ’) with variation temperature is explained by Arrhenius equation, i.e.

\[ \sigma_{dc} = A e^{\frac{E_a}{kT}} \]

where ‘A’ is the pre-exponential factor, and T is the temperature in K. The Ea activation energy is estimated from the slope of Arrhenius plot of log(σ) against (1/T),

\[ E_a = -Slope \times k \]

In the above equation slope is negative and the activation energy is positive. Figure 10 shows the Activation energy is lowest for Fe (0.31M)-Ppy-10ml GTE-PVA and increases up to Fe (0.92M)-Ppy-
30ml GTE-PVA then decreases for Fe (1.23M)-Ppy-40ml GTE-PVA but shows highest $E_a$ for Fe (1.54M)-Ppy-50ml GTE-PVA composite [33].

Table 2. Activation Energy of different polypyrrole composites.

| Sample code                  | Slope     | Activation Energy ($E_a$) (in eV) |
|------------------------------|-----------|-----------------------------------|
| Fe (0.31M)-Ppy-10ml GTE-PVA  | -108.00452| 9.3x10^{-3}                       |
| Fe(0.62M)-Ppy-20ml GTE-PVA   | -121.47402| 10.476x10^{-3}                    |
| Fe(0.92M)-Ppy-30ml GTE-PVA   | -319.15015| 27.526x10^{-3}                    |
| Fe(1.23M)-Ppy-40ml GTE-PVA   | -144.03400| 12.420x10^{-3}                    |
| Fe(1.54M)-Ppy-50ml GTE-PVA   | -660.93064| 57.005x10^{-3}                    |

Figure 10. Fe/Ppy composites of Conductance versus inverse temperature graph.

3.7. EMI Shielding Effectiveness
The Electromagnetic interference shielding effectiveness (EMISE) is the attenuation of propagating EM waves produced by the composite films (prepared by using different composites in polyvinyl alcohol solution), shielding material. Shielding is the direct loss of EM waves which has been absorbed by the composite films. EMI Shielding (power loss) can be measured by placing the samples in the wave guide for different frequencies ranging from 2 GHz to 3 GHz in signal generator. To obtain power loss by the samples, subtract the EMISE (dB) of empty wave guide with EMISE (dB) for respective frequencies. Finally, graph was plotted for different samples as shown in figure 11. EMISE can be expressed in dBm, Fig 11 shows samples from Fe(0.31M)-Ppy-10ml GTE- PVA to Fe(0.31M)-Ppy-10ml GTE-PVA shows different power loss at different frequencies (2GHZ to 3GHz) [34-43].
4. Conclusions
The Fe/Ppy composites were prepared successfully by using in-situ polymerization. As obtained iron decorated conducting polymer composites were confirmed by X-ray Diffraction pattern, Fourier Transformation Infra-Red spectrum, and scanning electron microscope and tunnelling electron microscopic techniques. Conductivity was found to increase slightly in the temperature range 273–378 K and the experimental results showed that a marginal reduction in dc conductivity in the composite materials, when compared to their counter base polymers. Such polymeric nanocomposite materials could find applications as the dielectric materials in capacitors and as a better base insulation material for Printed Circuit Boards (PCB). They can be used as conductive in situ precoat materials for the metallization of PCB patterns. Particularly, Fe/Ppy is a good conducting polymer composites for sensors, solar cells, ultra-capacitors, and electro chromic displays etc.

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