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Studies on Surface Plasmon Resonance in Chemically Synthesized Conducting Polythiophene

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Abstract
In the present work, we studied the surface plasmon resonance in one pot chemically synthesized conducting polythiophene (PTh) using oxidant anhydrous $FeCl_3$. The surface morphology of prepared samples were analyzed through FE-SEM, which shows irregular structure and spongy amorphous morphology.The optical transmission spectra of chemically synthesized PTh samples were recorded by using UV-Vis spectroscopy. The surface plasmon resonance of PTh samples was studied in 200-1100 nm using UV-Vis analysis.

Key words: Chemical polymerization, Conducting polythiophene, Surface plasmon resonance.

1. Introduction

Among the conducting polymers, polythiophene (PTh) is one of the most highly researched polymeric materials because of its extraordinarily electronic optical properties, good processability, environmental stability and ease of synthesis [1-4]. It is in fact also the most frequently used conducting polymer incorporated with various carbon materials [5, 6]. The conjugated conducting polymers are well known for their excellent electrical conductivities in oxidized (doped) state. The recent development in processable conducting polymers has opened the way for large-scale industrial applications.

In recent years, a lot of advancement has taken place in the development of intrinsically conducting polymers such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy) and their derivatives due to their interesting electrical, chemical and physical properties [7]. In addition the conductivity of these materials can be controlled from conducting to insulating range by using different routes of polymerization as well as its surface charge characteristics can easily be modified by changing the dopant species in the material during synthesis [8,9]. Usually, polymerization can be carried out by electrochemical or chemical processes, which provide films with different morphologies and consequently slightly different chemical and physical properties [10]. Now days, these conducting polymers have been widely used as effective materials for the detection of toxic, hazardous and flammable gases due to their ease of synthesis and low cost [11]. The most important advantage of these conducting polymer-based sensors is their room temperature operation and high sensitivity. Among these intrinsically conducting polymers, PTh and its derivatives have attracted considerable attention due to their good environmental and thermal stability, easy polymerization process and high electrical conductivity [12, 13]. PTh can be produced in bulk powder as well as in thin film form [14] and it found wide applications in various fields such as supercapacitors [15], field effect transistors [16], light emitting diodes [17], photoconductive and photovoltaic devices and optical modulator devices [18]. PThs have also found applications in gas sensor field [7]. Soluble PTh derivatives can provide high sensitivity to certain gases, such as NO_2 at small concentration [19] as well as it has been reported that, PTh film showed gas response to ammonia, trimethylamine, acetone, alcohol and toluene at room temperature [7].

In the present study, samples were synthesized by using chemical oxidative polymerization method with anhydrous ferric chloride as an oxidant in deionised water. During polymerization, different concentration of $FeCl_3$ was taken. Prepared samples were characterized through FE-SEM and UV-Vis spectroscopy.

2. Experimental

Thiophene monomers, anhydrous iron (III) chloride ($FeCl_3$) from SD Fine Chemicals (AR-grade) were used in the present study. The thiophene monomer was used as received for synthesis of PTh. The sample was synthesized at room temperature (303 K) by mixing thiophene with $FeCl_3$ in deionised water. H_2O_2 was used to enhance the rate of reaction and also yield. After the rigorous stirring, drop-by- drop monomers was added into the solution. The preliminary polymerization process was identified by the colour change (brown) of the reaction mixture. The polymerization process was allowed to constant stirring for 8 hrs with a magnetic stirrer at 30 °C. The resulting precipitate was collected by vacuum filtration using cellulose nitrate filter papers. The precipitate was washed with copious amounts of triply distilled water until the washings were clear and then kept for overnight at room temperature. Subsequent to this samples were sintered at 60 °C for 30 min. In this way, two samples of PTh were synthesized with different stoichiometric ratios of thiophene and $FeCl_3$ as (90:10) and (80:20) Wt. % [20].

3. Results and Discussion

3.1 FE-SEM

The morphology and structural features of the material report from FE-SEM (JEOL JSM-6360). The surface morphology of PTh powder samples with stoichiometric ratio of thiophene and $FeCl_3$ as (90:10) and (80:20) Wt. % were analyzed by FE-SEM and the micrograph is displayed in figure 1(a-b). The FE-SEM micrograph represents the non-porous and non-uniform structure containing macro-granular structure formed by the aggregation of small globular structures. The nature of particles has irregular in structure which reflects definite amorphous morphology. The micrograph depicts the presence of aggregation up to some extent as well as an agglomeration of particles.

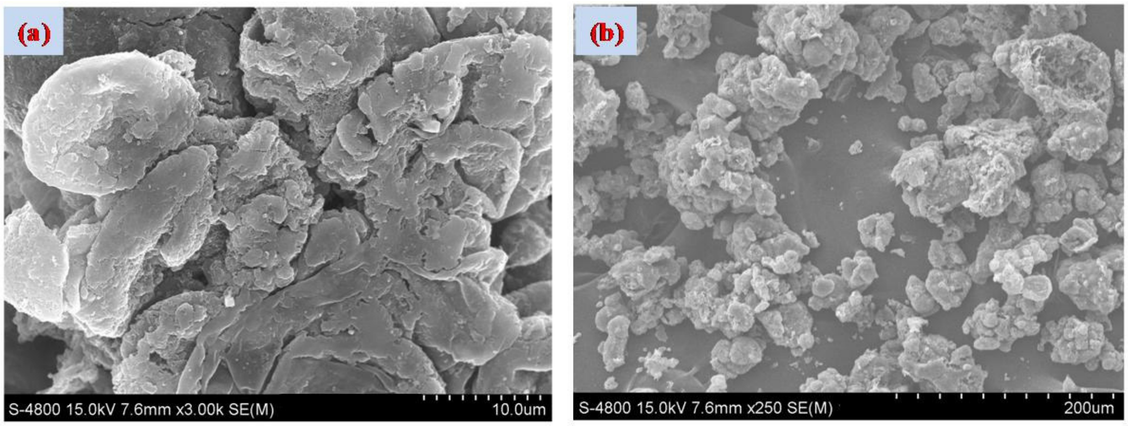

Fig. 1. FE-SEM micrograph of PTh with stoichiometric ratio of thiophene and $FeCl_3$ as (90:10) and (80:20) Wt. %.

3.2 UV-Vis Spectra

UV-Vis absorption spectrophotometer is frequently used to investigate the surface plasmon resonance phenomenon. Figure 2 (a-b) shows the UV-Vis spectra of PTh samples synthesized with different stoichiometric ratios of thiophene and $FeCl_3$ as (90:10) and (80:20) Wt. %. In this case, the transmission observed in the range 200-1100 nm. The transmission peaks of PTh samples are listed in table 1. The collective oscillation frequency of conduction electron is termed as plasmon's frequency. The characteristic frequency of plasmon's is given by equation (1) [21].

$$\omega_p = (Ne^2/m_e)^{1/2} \qquad (1)$$

where, ω_p is the plasma frequency, N is the conduction electron density, e is the charge on electron, m_e is the electron effective mass and is the vacuum dielectric permittivity.

In the present work, plasmon frequency found to be increased with decrease in transmission wavelength. Also, the conduction electron density increases with decrease in transmission wavelength. According to the Fermi liquid model, plasmon can be satisfactorily described as a negative charged electron cloud displaced from its equilibrium position around the lattice made of positively charged ions, in analogy to factual plasma.

Table1. Values of Transmission wavelength, plasmon frequency and conduction electron density.

Sample (Wt. %)	Transmission Wavelength (nm)	Plasmon frequency (ω_p) (MHz)	Conduction electron density (N) (m^{-3})
S_1	276	0.1089	2.0137×10^{34}
S_2	274	0.1094	2.0174×10^{34}

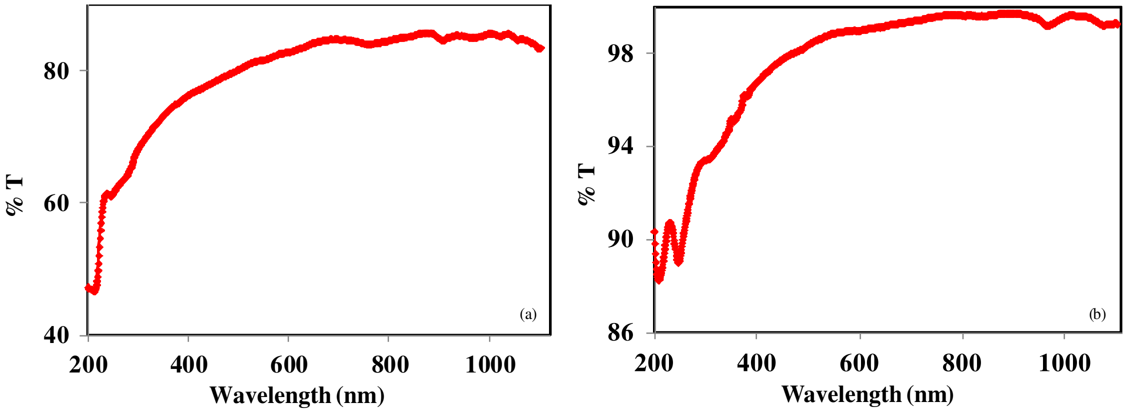

Fig. 2. UV-Vis spectra of PTh with stoichiometric ratio of thiophene and $FeCl_3$ as (a) (90:10) and (b) (80:20) Wt. %.

4. CONCLUSIONS

In the summary of present work, the samples were synthesized by using chemical oxidative polymerization method with anhydrous $FeCl_3$ as an oxidant in aqueous medium at room temperature. The amorphous nature of as-synthesized material confirmed through FE-SEM analysis. The UV-Vis is a very simple technique to study the surface plasmon resonance. The characteristic frequencies of plasmon resonance in PTh were found to be increase with decrease in transmission wavelength. The conduction electron density is easily computed from this method.

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