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Synthesis and Characterization of Polythiophene and Polypyrrole

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Abstract - Nanofibers of polythiophene have been made using an in-situ chemical oxidative polymerization technique. Polythiophene production was verified by means of the X-ray diffraction method (XRD) and the Fourier transform infrared analysis (FTIR). Energy dispersive X-ray spectroscopy (EDAX), transmission electron microscopy (TEM), and atomic force microscopy (AFM) were also used to evaluate the synthesized polythiophene nanofibers. The surface charge of the polymer was calculated using the zeta potential technique. Through the use of ammonium persulfate and sodium dodecyl sulfate as surfactants and FeCl3 as an oxidant, a polymer of pyrrole (Polypyrrole) was easily produced. The optimal properties of the synthesized material were achieved by adjusting the synthesis conditions (oxidants, time, temperature, etc.). Polymer structure and morphology were investigated. Polypyrrole production is being investigated using FTIR.

Keywords - Polythiophene, Oxidative emulsion Polymerization, Conducting Polymers

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INTRODUCTION

Conjugated double-bond containing fundamental conducting polymers have been of interest as cutting-edge materials in recent years. Due to their insulating qualities, polymers have been used for a variety of purposes throughout time. In fact, up until recently [1] it was generally thought that the presence of electrical conduction in polymers, which is typically owing to weakly bound ions, was undesirable. Polymers with a large number of conjugated carbon-carbon double bonds are what make them conductive to electricity [2]. Since 1980 [3,] gas sensors' active layers have been made from conducting polymers like Polypyrrole (Ppy), polyaniline (Pani), and polythiophene (PTh) and their derivatives. There are multiple scholarly articles [4] that discuss the synthesis of conducting polymers in great detail. Chemical polymerization, electrochemical polymerization, and photochemical polymerization [5, 6], metathesis polymerization [7], concentrated emulsion polymerization [8], inclusion polymerization [9], solid-state polymerization [10], plasma polymerization [11], pyrolysis [12], and soluble precursor polymer preparation [5] are all methods that can be used to synthesize conducting polymers. The molecular chain structure of conducting polymers is easily modifiable through copolymerization or other structural derivations, and their synthesis is generally thought to be straightforward using chemical or electrochemical procedures [13]. Polypyrrole's excellent conductivity, stability, and enhanced mechanical qualities have garnered a lot of attention. Many other types of sensors, chromatographic stationary phases, and electrical devices could benefit from its use [14]. By using either oxidative chemical or electrochemical polymerization, polypyrrole can be readily produced. PPy's high conductivity, outstanding thermal and environmental stability, and simplicity of synthesis have piqued considerable attention. It is also electroactive in organic as well as aqueous electrolyte solutions [15]. By switching between its oxidized and reduced forms, its characteristics can be altered. Because it is non-toxic, it can be used in a wide range of biomedical contexts without worry. [16]. Because of this, many different methods of synthesizing Polypyrrole have been reported, each tailored to a certain set of needs or uses. Many scientists have reported using a variety of oxidants in the chemical oxidation process to synthesize Polypyrrole, with each approach taking into account the needs of the final product. Iron chloride (FeCl3), for instance, has been utilized as an oxidant in the synthesis of polymer films. [17,18] Conductivity behavior is the main focus of APS (ammonium per sulfate) oxidant usage. Both were employed by some researchers [19] to examine the properties of polymers with different additives. It is important to note, however, that oxidants have an impact on the electrical, morphological, and thermal characteristics of the polymer in its final form. Researchers have reported comparing the efficacy of various oxidizing agents on the final polymer's conductivity, with some even reporting using SDS (Sodium Dodecyl Sulfate) as a dopant. In this study, we synthesized Ppy in five different ways and experimented with different polymerization temperatures and times. The objective was to figure out what kinds of conditions will lead to the best possible end result. Using this document, which can be edited in Microsoft Word 2007 and then saved as a "Word 97-2003 Document" for the PC, authors can adhere to most of the required guidelines for formatting when creating digital versions of their papers. The margins, column widths, line spacing, and type styles are all preset, and samples of each can be found throughout this text (the type styles are noted in italics within parenthesis). Multilevel equations, pictures, and tables are not required, although there are a variety of table text styles to choose from if you'd like to include them.

SYNTHESIS AND CHARACTERIZATION OF POLYTHIOPHENE

Research into conducting polymers has emerged as a key subject in the study of polymer electronics in recent years. Since a polymer's electrical properties are entirely dependent on the way its structure and properties interact, polymer electronics research focuses primarily on the synthesis and characterisation of conducting polymers. The study of the electrical conductivity of polyacetylene marked the beginning of research into conjugated polymers in 1977. Since then, numerous conjugated polymers have been made for use in electronics, including sensors, rechargeable batteries, and super capacitors, with polypyrrole, polyaniline, and polythiophene being just a few examples. Photovoltaic devices are just one of several engineering applications where research into conducting polymers is ongoing and vigorous. Conjugated polymers have advanced to the point where their conductivity can be manipulated from non-conductivity to superconducting. Many electronic applications previously requiring metals can now employ conjugated polymers instead, thanks to their controlled conductivity and corrosion resistance. Polythiophenes, one type of conducting polymer, sees extensive use in a wide range of technical contexts. The extended -bonding system in polythiophene and the substituted polythiophenes allows for tunable electrical conductivity, which finds application in modern-day applications such as sensors and antistatic coatings. Polythiophene's electrical characteristics can be altered through p- or n-doping. Polythiophenes are prepared for research into their potential applications by undergoing chemical treatment by oxidation. Since thiophene-based conducting polymers are thermochromic and electrochromic, they are an ideal material for theranostic gene transfer. Affinitychromism, Photochromism, and SolvationChromism.

SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE (PPY)

Modern research into polymer applications has shown that this material is increasingly being put to use as an active material with conducting, electromagnetic, and optical properties, in addition to its more traditional passive applications. Magnetic applications [2] and the possibility of energy storage devices [3] are among the other areas where polymer materials have shown promise. Polymers with known electronic or electrical characteristics are the subject of increasing research as of late [4]. Poly-conjugation of the -system in the backbone is a hallmark of conducting polymers' structures [5]. The generation of electrical conductivity in polyaromatic backbone polymers has been the subject of extensive research during the past two decades. Among these, polyaniline (PANi), polypyrrole (PPy), and polythiophene (PT) are among the most promising for use in future conductive polymer-type material development [6]. Polypyrrole (PPy) stands out among conducting polymers because it is more conductive than many others, can be easily synthesized, and exhibits high environmental resilience. Electro-chromic windows and displays, packaging, biosensors [7, 8], gas sensors [9, 10], anti-electrostatic coatings [11], solid electrolytic capacitor [12, 13], wires [14], polymeric batteries, electronic devices, functional membranes, etc. [15–17]. Chemical reactions or electrochemical methods predominate in the fabrication of conducting polymers. The choice between these two approaches to polymer synthesis should be made with consideration for the final use of the synthetic material. Chemical methods typically entail a reactor-based polymerization process of monomer [18]. Since no specialized equipment is needed, this synthesis approach is the easiest, quickest, and most widely used option. After the monomer has been oxidatively polymerized by chemical oxidants in aqueous or non-aqueous solvents, a fine powder is formed, marking the completion of the polymerization reaction. As a result, this method of preparation can be used to produce copious amounts of polypyrrole (PPy). Chemical oxidative polymerization [20], electrochemical, and micro emulsion polymerization are all straightforward methods for producing PPy. Based on the current state of available method development, chemical in situ polymerization stands out as the clear frontrunner for PPy synthesis.

EXPERIMENTAL

Materials

The product of two distillations, thiophene (Sigma-Aldrich), was put to use. Both chloroform and anhydrous ferric chloride (FeCl3) came from Merck. All materials were of an AR quality. De-ionized water was used in this study.

Measurements

In order to determine the structure and properties of the polythiophene nanofibers, several instrumental techniques, such as XRD (XRD-Smart lab), FTIR (Spectrum RX1), EDAX (FESEM-SUPRA 55), HRTEM (JEOL 3010) and AFM (NTMDT, Ireland) were employed. Surface charge was determined by using zeta potential measurement (Horiba).

Synthesis of polythiophene nanofibers

One milliliter of thiophene was added to one hundred milliliters of chloroform in a round-bottomed flask and the mixture was agitated for several minutes. The aforesaid mixture was kept stirring while the necessary amount of anhydrous FeCl3 was added (the mole ratio of FeCl3/thiophene was 1:2). A brown polythiophene precipitate was formed after the dispersion was filtered and stirred for 12 hours. After 12 hours of extraction with methanol, this precipitate was obtained. The resulting precipitate was then washed and dried at 70 degrees Celsius for five hours.

RESULTS AND DISCUSSION

XRD

X-ray diffraction (XRD) analysis was used to look into the crystalline structure of polythiophene nanofibers. Figure 1 displays the XRD pattern for polythiophene. Only one large peak is visible, with its center located close to the 2 value of 21.5°. The - stacking structure in polythiophene chains is significantly correlated with this diffraction peak. In general, the XRD spectrum showed that polythiophene nanofibers are semi crystalline.

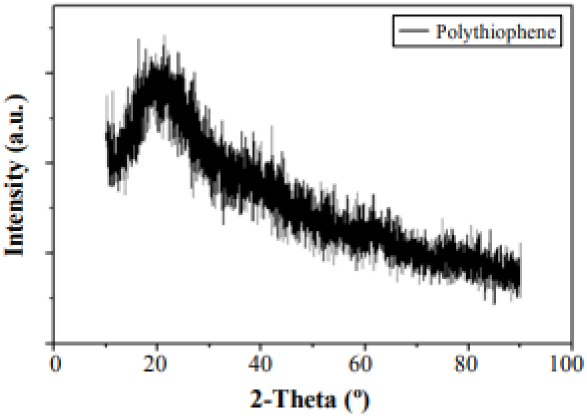

Fig. 1: XRD pattern of polythiophene nanofibers

FTIR

The Furiour transform infrared spectrum of polythiophene prepared with oxidant FeCl3 in the region from 4000 to 400 cm-1 is shown in Fig. 2.

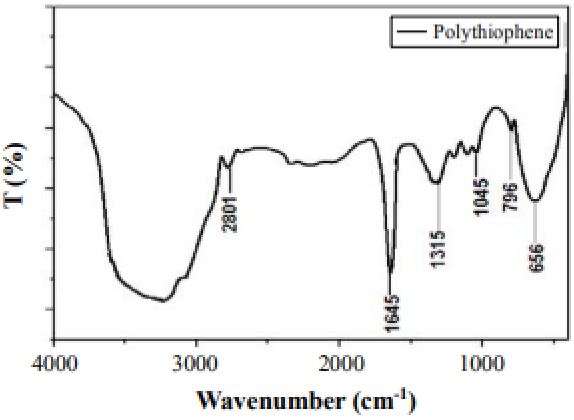

Fig. 2: FTIR spectrum of polythiophene nanofibers

In Fig. 2 we see the FTIR spectrum, where the unique absorption bands of polythiophene nanofibers stand out. Polythiophene's C-H stretching is reflected in its spectra by a band at 2801 cm-1. The C=C signature peak is at 1645 cm-1, where a band can be seen. The 1045 cm-1 and 796 cm-1 band are characteristic of C-H deformation and stretching in and out of plane, respectively. The C-S thiophene stretching peak is located around 656 cm-1. All of the typical peaks of polythiophene were seen in the fingerprint area (600-1500) of the FTIR graph.

EDAX

Table 1 gives the results of elemental analysis using EDAX experiment. Weight percentage of these elements of polythiophene was calculated within experimental error limit of 1%. The EDAX data confirmed that the polymer synthesized is polythiophene.

Table 1: Weight percentage of various elements obtained through EDAX analysis

Elements	C	O	S	Fe	H
Weight %	62.05	5.3	29.75	0.25	2.65

TEM

Many researchers have studied polythiophene morphologies with TEM, although the vast majority of nanofibers have been generated via the electro spinning method. Polythiophene nanofiber use has already paved the way for advancements in organic nano electronics. Transmission electron microscopy (TEM) was used to capture images of chemically produced polythiophene at the nanoscale.

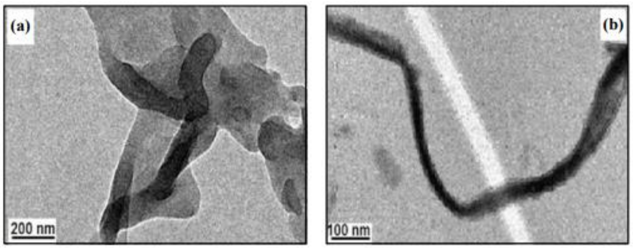

Fig. 3: TEM images of polythiophene nanofibers (a) scale bar 200 nm, (b) scale bar 100 nm

In contrast to AFM phase imaging, here we focused on the analysis of short range morphologies (at a scale bar of 100 nm) for manufactured polythiophene. Transverse electron micrographs unmasked the growth of nanoscale polythiophene fibers, each measuring around 25 nm in thickness. Figure 3 (a & b) shows transmission electron micrographs of chemically produced polythiophene nanofibers at two different scale bars (200 & 100 nm).

AFM

The topography and roughness of polythiophene were imaged using AFM on glass slides that had been coated with the material. The AFM images were captured with a device manufactured by NTMDT in Ireland. All imaging was performed in ambient room temperature air. The 2D AFM picture of polythiophene nanomaterials is shown in Fig. 4a with a resolution of 3 x 3 m. Figure 4b displays the 3D surface topography of polythiophene. Polythiophene films have a shape resembling a structure of tiny globules, with sizes ranging from 100 nm to 200 nm. Here, the globules' structure is a hybrid of long- and short-range morphologies, the former because of the globules themselves, the latter because of the regions within them. Fig. 3a and b are TEM pictures of a polythiophene nanofiber, which show its short-range shape. The tiny size and low intensity of the surface imperfections are seen in Fig. 4 (a and b). Surface roughness of nanoscale polythiophene is characterized by the parameters Sq and Sa. For polythiophene film, we get average (Sa) and root mean square (Sq) roughness values of 17.027 and 22.927 nm, respectively (Table 2).

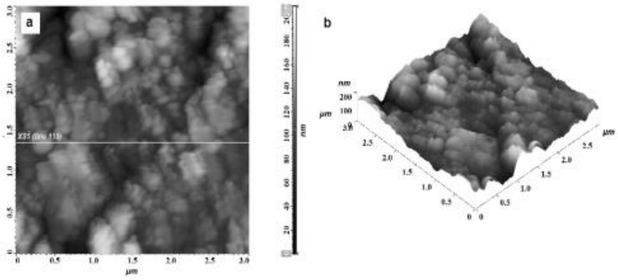

Fig. 4: AFM micrographs of a polythiophene nano material (a) 2D image, (b) 3D topographic image

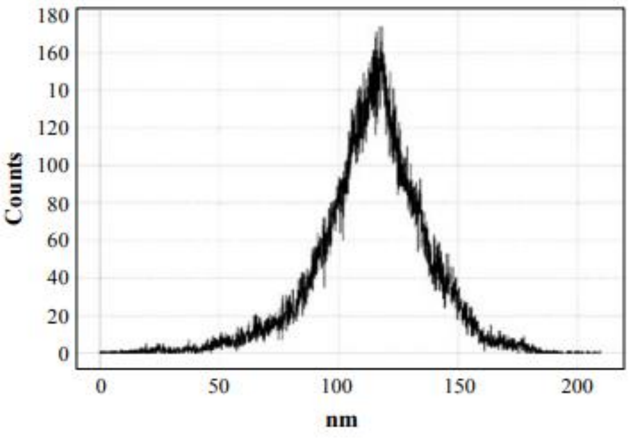

Fig. 4c: Histograms corresponding to AFM images

Table 2: Results of roughness analysis from AFM experiment

Results of roughness analysis	
Amount of sampling	65536
Max	209.449 nm
Min	0 nm
Peak-to-peak, Sy	209.449 nm
Ten point height, Sz	104.025 nm
Average	113.871 nm
Average Roughness, Sa	17.0277 nm
Root Mean Square, Sq	22.9273 nm
Second moment	13492.2
Surface skewness, Ssk	-0.482209
Coefficient of kurtosis, Ska	1.55895
Entropy	9.86969
Redundance	-0.281188

Zeta potential

Suspension stability is a function of the net surface charge of particles in a given liquid. Zeta potential readings provide the effective surface charge. Changing the zeta potential of a suspension can make it more stable. Horiba SZ-100 nanopartica dynamic light scattering system was used to detect the surface charge of polythiophene nanofibers in deionized water. To get the sample ready, we mixed 1 gram of polythiophene nanofibers with 100 milliliters of distilled water. An electric field was created by injecting 1 mL of the material between two electrodes in a zeta cell. Polythiophene nanofiber motion was detected after an electric field was applied. This test was conducted using a 25 C temperature and a 100 V applied voltage. In distilled water, the sample concentration was 1mg/mL. Dispersion of polythiophene nanofibers, as shown by their zeta potential distribution in Fig. 5.

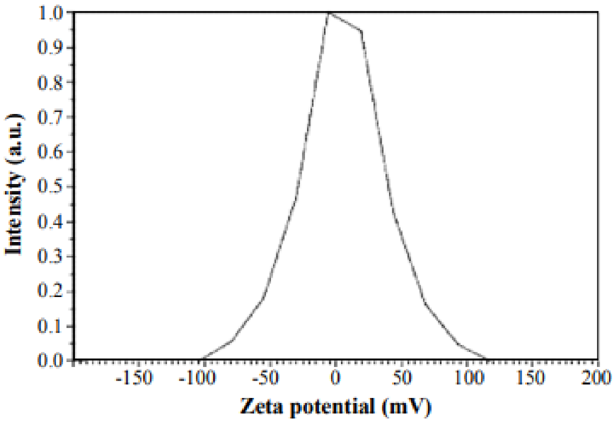

Fig. 5: Zeta potential distribution for polythiophene nanofiber dispersion

CONCLUSION

The electronic, electrical, mechanical, and industrial engineering communities all make extensive use of standard polymeric materials. Depending on the intended use, various fillers can be added to these polymers to enhance their already impressive list of capabilities. In addition, our study has unlocked the door for the facile polymerization-based synthesis of a wide variety of hybrids. Using a chemical oxidative polymerization technique, polythiophene nanofibers were successfully produced. The produced compound was identified as polythiophene using XRD, FTIR, and EDAX studies. We used TEM and AFM to investigate the polythiophene's morphologies. Nanofibers, as seen by transmission electron microscopy, make up polythiophene's short-range morphology. Polythiophene's long-range shape, as shown by atomic force microscopy, is characterized by a globules-like structure. In a zeta potential experiment, the surface charge of polythiophene nanofibers was determined. The outcomes demonstrated that polythiophene nanofibers have a positive surface charge.

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