## DEVELOPMENT OF ORGANIC CONJUGATED POLYMER MATERIALS FOR ENERGY HARVESTING

#### THESIS

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PHYSICS

BY

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I declare that the thesis on "Development of organic conjugated polymer material for energy harvesting" has been composed by myself and that the work has been submitted only for Partial Fulfillment of the requirements for the degree of Masters of Science in Physics. I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in any submission. I understand that any violation of the above will be cause for disciplinary action by the Institute and can also evoke to penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.



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#### Abstract

The nano fibers of polythiophene has remained equipped by the procedures of insitu chemical oxidative polymerization. The polymer of polythiophene enlarged significant consideration in investigation and industrial extents because it possesses high environmental stability, better thermal stability, and less band gap energy. Moreover, polythiophene is an admirable intrinsic conducting polymer having conjugated double bonds in the backbone. Polymers were pronounced as some of the revolutionary new materials that would lead to the next generation of electronics and optical devices. Various discoveries in the field of polymers would also lead to the birth of polythiophene which entirely improved the enlargement in the field of light-emitting diodes and also for organic transistors. Polythiophenes are also an important class of conjugated polymers that form some of the most environmentally as well as thermally established materials that can be greatly used in electrical conductors, nonlinear optical devices, polymer LEDs, electrochromic or smart windows, photoresists etc.

In the present study, the monomer of thiophene has been prepared from the raw thiophene by adding anhydrous ferric chloride in 1:2 and by adding chloroform to it with the chemical oxidative method, to get the powdered form of polythiophene which has been further used with different compositions to make pelletes with other compounds like GO and PVDF in different ratios with their different compositions. These pellets are further used to characterise to validate the synthesis of polythiophene, to confirm the obtained compound is polythiophene or not. The characterisation of polythiophene is done by using three well known patterns from XRD, FTIR and low temperature conductivity methods. To be concluded the size, shape and structural units of polythiophene the XRD method is used, for the broad spectrum it is obtained through FTIR method and also for variations of conductivity with temperature changes it is obtained by using low temperature conductivity method.

The graphs plotted between Intensity and diffraction angle in XRD method is used to identify the peaks which further confirms the size, shape and structural details of polythiophene. Pure PTH exhibits a broad diffraction peak indicating the amorphous nature of the polymer. For the PTH/GO composite. The graphs plotted between transmittance and wave number in FTIR method is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. The graphs plotted between conductivity and temperature in low temperature conductivity method is used to determine the variation in conductivity. It is concluded from the graph that the conductivity of the resulting composite is 0.01035 Scm–1 at room temperature, which is higher than that of pure PTH.

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### Abbreviations:

PTH: Polythiophene
GO: Graphene oxide
PA: Polyacetyline
XRD: X-ray diffraction
FTIR: Fourier transformed infrared radiations
PV: Photovoltaic
PCE: Power conversion Efficiency
PSC: Perovskite Solar Cell
OSC: Organic Solar Cell
Voc: Open Circuit Voltage
UV: Ultra Voilet
PVD: Physical Vapour Deposition
SCLC: Space Charge Limited Current
CBM: Conduction Band Minima
VBM: Valence Band Maxima
SRAM: Static random access memory
ESA: Excited State Absorption
PIA: Photoinduced Absorption
AFM: Atomic Force Microscopy
MFM: Magnetic Force Microscopy
PL: Photoluminescence
JV: Current density- Voltage
C <sub>v</sub> : Capacitance-Voltage
C <sub>f</sub> : Capacitance Frequency

#### **Organisation of Thesis**

The work presented in the dissertation has been divided in to five chapters as follows:

Chapter 1 deals with the introduction part of the present study and its background.

**Chapter 2** deals with the experimental part having details of material used, measurement to be concluded from the research, synthesis of the polymer polythiophene, how the polythiophene has been formed and the pallet formation from the compound.

**Chapter 3** deals with the characterisation of the compound using available techniques i.e. Fourier transformed infrared spectroscopy, x-ray diffraction and low temperature conductivity.

Chapter 4 deals with the results and discussion concluded from the research carried out.

Chapter 5 deals with the advantages and disadvantages of the conducting polymer.

## CHAPTER 1

#### **CHAPTER 1: Introduction**

#### **1.1 Conjugated Polymers**

Conjugated polymers are basically known as the organic macromolecules that are characterized by a backbone chain of alternating double-bonds and single-bonds. Their overlapping p-orbitals create a system of delocalised  $\pi$ -electrons, which can result in interesting and useful optical and electronic properties

Till the early 19<sup>th</sup> century all the developed polymers were non- conducting. In the year 1976 Alan J. Heeger and his colleagues Alan G. Macdiarmid and Shirakawa discovered the conductive properties of polyacetyline which was comparable to that of a metal. Oxidising the PA using iodine vapour film increases the conductivity of PA greatly ( $\approx$  3000 S/cm) over the undoped material. The consequences of this discovery led to discovery of many more conducting polymers like Polypyrrole, polythiophene, poly (p-phenylene), polyaniline and their derivatives. The key property of conducting polymers was the presence of conjugation i.e. the presence of alternative single and double bond. The property of conjugation is necessary but not enough property to make the polymer conducting, it is where dopant plays in generating charge carriers along the polymer is oxidised polymer chain, this hole allows electron from neighbouring atom to jump due to conjugation thereby creating new hole, the movement of hole along the along the chain of give rise to the current. Some of the conducting polymers are shown in below fig:



#### **Fig.1.1 Conducting Polymers**

#### **1.1.1 Historical Background**

Conducting polymer research dates back to the 1960s, when Pohl, Katon, and their coworkers, first synthesized and characterized semiconducting polymers. The discovery of the high conductivity of polysulfurnitride (SN)x, a polymeric material containing interesting electrical properties, was a step forward for research in conducting polymers. The beginning of conducting polymer research began nearly a quarter of a century ago, when films of polyacetylene were found to exhibit profound increases in electrical conductivity when exposed to halogen vapor. Heeger, Shirakawa and MacDiarmid produced conjugated conducting polyacetylene when monomer of acetylene was doped with bromine and iodine vapor; the resulting electrical conductivity was 10 times higher than the undoped monomers.

After their discovery, research papers dealing with polyconjugated systems were very extensive and systematic. The trend was to understand the chemical and physical aspects, either in neutral (undoped) state or charged (doped) states. According to SCIFINDER, almost 40,000 scientific papers were published in this field of research since 1977. This previously underestimated family of macromolecular compounds turned out to be extremely interesting, from both the basic research and application points of view. In 2000, these three brilliant scientists, founders of the conjugated conducting polymer science, were granted the Nobel Prize in chemistry.[2,3]





#### **1.1.2 Conductive Polymers**

Numerous studies have been done on various conductive polymers to enhance their conductivity and utilize their applicability in various technological areas such as field effect transistors, light diode, organic thermoelectrics etc. A polymer material containing a long chain of molecular structures is first and foremost an insulator. The idea that polymers or plastics could conduct electricity is considered absurd. Their wide application as an insulating material is the reason they are studied and developed in the first place. In fact, these materials are commonly used for surrounding copper wires and manufacturing the outer structures of electrical appliances that prevent humans from coming in direct contact with electricity. Approximately three decades ago, scientists discovered that a type of conjugated polymer called 'polyacetylene' could become highly electrically conductive after undergoing a structural modification process called doping. The polymer is called a 'conjugated polymer' because of the alternating single and double bonds in the polymer chain. Due to the special conjugation in their chains, it enables the electrons to de-localize throughout the whole system and thus many atoms may share them. The de-localized electrons may move around the whole system and become the charge carriers to make them conductive. This polymer can be transformed into a conducting form when electrons are removed from the backbone resulting in cations or added to the backbone resulting in anions. Anions and cations act as charge carriers, hopping from one site to another under the influence of an electrical field, thus increasing conductivity. However, the conjugated polymers are not conductive, since they are covalently bonded and do not contain valence band like pure metal does. It is universally agreed that the doping process is an effective method to produce conducting polymers. Doping allows electrons to flow due to the formation of conduction bands. As doping occurs, the electrons in the conjugated system, which are loosely bound, are able to jump around the polymer chain. Electric current will be produced when the electrons are moving along the polymer chains. Several examples of conjugated conducting polymers are polyacetylene, polypyrrole, polyaniline and polythiophene. In future, conducting polymers or organic metals may replace inorganic metal in several critical areas. Certain aspects of the inorganic metals, such as not being environmentally friendly and having a high toxicity, are the reason why these organic metals have potential benefits as substitutes. The potential applications of these organic metals include corrosion protection, radars, batteries, sensors, as well as electrochromic cells. Much research will be needed before the applications may become a reality, which is very revolutionary since conjugated conducting polymers still have some drawbacks such as not being water soluble, having poor mechanical strength and not being biodegradable. Only time will tell us when the impact of these novel polymers will be as large as their brother's, the insulating polymer. [5,8]

#### **1.1.3 Principle of electrical conduction- mechanism and doping**

Conducting polymers are intrinsic semiconductors in nature. This is due to presence of conjugation of the backbone chain. The overlap of  $\pi$  electrons cloud form delocalized molecular wave function. This delocalization assists in transfer of charge and hence contributes towards conduction. The role of dopant is to add or remove an electron from the chain.

For example, in  $I_2$  doped Polyaniline  $I_2$  extracts an electron from the chain and forms  $I_3^-$  ion, this is an example of oxidative doping, the vacancy created leads to the formation of a radical polaron. The charge is carried along the chain however the counterion ( $I_3^-$ ) associated with the positive charge is entrapped and is immobile. High concentration of polaron is required so that it can move in the field of nearby polaron. Hence higher doping of counterion is required for a highly conducting polymeric species. If the second electron is removed a fresh polaron is created and if the electron from the unpaired electrons of the existing polaron a bipolaron is formed, which moves in a pair. Other type of species formed is solitons, it is like a defect in the chain which can move along the conjugated backbone of the chain but itself doesn't carry a charge.

The formation of the above-mentioned species affects the energy level of the polymers. To electron polaron an electron forms the donating species is added in the upper shell whereas to form the positive polaron the electron from the lowest polaron level is taken and a hole is created. The energy difference between the polaron level and the closest band edge is dependent on the conjugation length and thus, creating the species like polaron, bipolaron and solitons. The doping process is more of a redox reaction where reduction or oxidation of conjugated chain form an anion or cation and which is attached to the counterion by the coulombic force.[3,4]

#### 1.2 Synthesis of conjugating polymers

Conjugating polymers can be prepared by chemical or electrochemical oxidation polymerization or by chemical catalytic synthesis. Conjugated polymer synthesis is to use **chemical reactions of**  $\pi$ -conjugated compounds to linkage them into reciting units to produce the conjugated polymers. Conjugated polymers are organic macromolecules with alternating single and double bonds.

#### **1.2.1 Electrochemical polymerisation**

The electrochemical preparation of the conducting polymers is usually carried out through the oxidative polymerization of their corresponding monomers by constant current, constant potential, or cyclic voltammetry in a potential range. The electro polymerization is performed in an electrolyte solution which contains solvent, electrolyte salt, and the monomer. There are many factors influencing the electro polymerization processes, such as solvents, supporting electrolyte salts, concentration of the monomers, and pH value of the electrolyte solutions, as well as polymerization potential, current, temperature, etc. Among these factors, the polymerization potentials of thiophene and aniline make the electro polymerization of polythiophene and polyaniline easier, and it can be performed in aqueous solutions. Electro polymerization is another coating procedure wherein the conducting polymer is formed and deposited from a monomer solution onto a

conducting substrate. This is usually the method of choice in coating relatively small areas. Care must be taken in choosing the electro polymerization condition, especially the applied potential and current. The applied potential should be high enough to oxidize the monomer and polymerize it, but low enough not to dissolve the metal or induce corrosion. The electrochemical coating is usually done in an electrochemical cell composed of the substrate to be coated as the working electrode and two inert materials as the counter electrode (usually platinum) and the reference electrode (usually Ag/AgCl or SCE). The polymerization solution contains the monomer, solvent, and the supporting electrolyte. This method can be further divided into potentiodynamic, galvanostatic, and potentiostatic electropolymerization.



**Fig.1. 3 Electrochemical Polymerization** 

#### **1.2.2 Galvanostatic Electropolymerization**

Galvanostatic electropolymerization involves the solicitation of constant current to polymerize the conducting polymer at a constant rate. At the establishment of the electropolymerization, the potential rises for a short period and then decreases after a while. It has been clarified that the sudden increase in potential is brought about by the formation of the redox-active charged oligomers in front of the electrode. The subsequent decrease in the potential is brought about by the catalytic effect of the charged oligomers to oxidize the monomers. The measured potential also depends on the temperature which shows the measured potential decreases with decrease in temperature. This can be explained by the decrease of the volume of the solvent, which consequently increases the concentration of the monomer as the temperature decreasing.

#### **1.2.3 Potentiostatic Electropolymerization**

Potentiostatic electropolymerization involves the application of the constant potential. The rate of polymerization thus be controlled and depending on the applied potential. This method is similar to the galvanostatic electropolymerization and is completely different from potentiodynamic electropolymerization because no material is discharged from the dropped film during the coating procedure.

Polypyrrole films are polymerized using potentiostatic electropolymerization (and by galvanostatic electropolymerization) which due to dendritic type and have low connection strength on the substrate required. In contrast, when the polypyrrole is polymerized potentiodynamically, then the resulting film shows shiny black, adheres there super strongly on the surface of the substrate, and has a very smooth and homogenous surface morphology. This has been elaborated as due to the formation of a large number of corresponding nucleation site during the growth process. Poly(3- methylthiophene) films, on the other hand, showed better electrical properties (conductivity, charge mobility, the number of free carriers, and band gap) when polymerized potentiostatically than when polymerized potentiodynamically.

### **1.2.4 Chemical polymerization**

The chemical oxidation preparation of conducting polymers is performed in solution by using oxidants such as  $FeCl_3$  and it is easy to enlarge the production scale with the chemical polymerization. Chemical polymerization is the most important method for the preparation of polythiophene, and it can also be used to produce conducting polypyrole.



Fig.1. 4 Chemical Polymerisation

#### **1.3 Application of conjugated polymers in energy storage devices:**

#### 1.3.1 Supercapacitor

A supercapacitor (SC) are also called as supercapacitor, ultracapacitor (or Goldcap) is a highcapacity capacitor with the capacitance values much higher than some other capacitors (but lower voltage limits) that bridge the gap between electrolytic capacitors and also rechargeable batteries. They typically stored upto 10 to 100 times more than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerate many more charge and discharge cycles than rechargeable batteries.

Supercapacitors are used in applications requiring many rapidly charge/discharge cycles rather than the long term compact energy storage within the cars, buses, trains, cranes and elevators, where they are also used for regenerative braking, short-term energy storage or burst-mode power delivery. Smaller units are used as memory backup for static random-access memory (SRAM). Unlike ordinary capacitors, supercapacitors do not use the conventional solid dielectric, but rather than this they use electrostatic double-layer capacitance and the electrochemical pseudocapacitance, where both of them contribute to the total capacitance of the capacitor, with a few differences:

Electrostatic double-layer capacitors (EDLCs) use mainly carbon electrodes or derivatives with much higher electrostatic double-layer capacitance than electrochemical pseudocapacitance, achieving separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte. The separation of charge is of the order of a few angstroms (0.3–0.8 nm), much smaller than in a conventional capacitor.

The electrolyte forms an ionic conductive connection between the two electrodes which distinguishes them from conventional electrolytic capacitors where a dielectric layer always exists, and the so-called electrolyte (e.g.,  $MnO_2$  or conducting polymer) is in fact part of the second electrode (the cathode, or more correctly the positive electrode). Supercapacitors are polarized by design with asymmetric electrodes, or, for symmetric electrodes, by a potential applied during manufacture. [7,8,9]



Fig.1. 5 Supercapacitor

#### **1.4 Introduction of Polythiophene**

Polythiophene is very familiar electroluminescent polymer. While polythiophenes perform thriving as electrochromic materials, the impenetrability of these polymers pose problems for their practical applications. It has been studied that by replacing the methyl to hexyl substituent and monomers to tune the optical possessions of the resulting polymers. These polymers with different optical belongings can be merged with each other or with poly (3-hexylthiophene) (P<sub>3</sub>HT) to articulate chromic devices. A arbitrary copolymer was produced of 3-octylthiophene and 3-methylthiophene which showed a higher thermal stability.

Direct polymerization of bithiophene and terthiophene with lightly distributed alkyl side chains provided even better stability. Blends have also been verbalized by integrating  $P_3OT$  in a semi-interpenetrating polymer network of partially cross-linked polystyrene. Copolymers and mergers, apart from being able to fine tune the production color can also raise the quantum efficiencies, and the use of heterostructure devices has brought internal efficiencies to 4% and above.

Polythiophene has been considered one of the most promising  $\pi$ -conjugated polymers due to its high stability, ease of structural modification and controllable optical and electrochemical properties. At the beginning the applications of non-substituted polythiophene were very limited because of its insolubility in many organic solvents, due to its extended  $\pi$ -conjugated structure. Furthermore, alkyl chains have been incorporated into the thiophene units in order to obtain functional monomers able to yield soluble polymers. The polythiophene is resulted to be highly processable conducting polymers, whose solubility allowed their full characterization by spectroscopic methods. The stability of polythiophene in the doped state can be performed by introducing alkoxy chains. The incorporation of alkoxy groups into polythiophenes increases significantly their conductivity without decreasing their solubility in many organic solvents.

Among the conducting polymers, polythiophenes are widely utilised in a various engineering applications. Polythiophene and the substituted polythiophenes are currently used as sensors and antistatic coatings because of their controllable electrical conductivity, which is produced due to the existence of an extended  $\pi$ -bonding system. Electrical properties of polythiophene can be manipulated by doping either p or n. In order to explore the use of polythiophenes in various fields, they are prepared by chemical treatment via oxidation.

In this work, polythiophene nanofibers were prepared by in situ chemical oxidative polymerization method and the prepared polythiophene nanofibers were characterized by XRD, FTIR and low temperature conductivity techniques. Zeta potential measurement was used to determine the surface charge of the polythiophene.

Polythiophene polymer gained significant attention in research and industrial areas because it possesses high environmental stability, better thermal stability, and less band gap energy. Moreover, their interesting properties like semiconducting, electronic and optical activities along with their better mechanical characteristics and ease of processability brought significant attention to the polythiophene composites.

In the recent years, the field of conducting polymers has been one of the most important areas of the polymer electronics research. Owing to the high development of conjugated polymers, it has become possible to control the conductivity of the polymers over the range from nonconductivity to superconductivity. Because of controllable conductivity and resistance to corrosion, conjugated polymers can replace metals in many electronics applications. The synthesis and characterization of polymers containing heteroaromatic rings have been widely studied because of their potential in advanced optoelectronic applications.

In the research field's of energy storage, and more specifically of supplying high powers, electrochemical super capacitors have been used among the most studied systems for many years. One of the possible applications is in electric vehicles. We have been working on electronically conducting polymers for use as active materials for electrodes in supercapacitors. These polymers have the ability of doping and undoping with rather fast kinetics and have an excellent capacity for energy storage. Polythiophene peared to be capable of such a voltage value, as it could be negatively or positively doped. Previous work had shown that negative doping of PTh appeared at very negative potential values, where electrolyte reduction occurred. Due to the ability to form better contact with metal electrodes and their stability at ambient conditions, they are widely used in solar cells. The polythiophene matrix is a better hole transporting polymer, so a combination of polythiophene matrix with n-type semiconducting particles brought new hybrid variety having excellent electrical properties. Also the transparent nature of polythiophene gives notable optical properties. More over, polythiophene is an excellent intrinsic conducting polymer having conjugated double bonds in the backbone. Similarly, in the case of other conducting polymers, the polythiophene matrix can also be changed to a more conducting one by creating polarons and bipolarons in the backbone through either oxidation or reduction.[1,2]

#### Some structures are shown in figure below:-



#### Fig.1. 6 Structure of Polythiophene

#### **1.4.1 General Review of polythiophene**

Polymers have unique properties and therefore attracted towards the scientific and technical interests. Remising the new materials with same interesting electrical, optical and magnetic properties that can be synthesised from these polymers. The organic polymers has same special class and are they are named as conducting polymers that have the special ability to conduct electricity which owing to the conjugation. The conducting polymers also contains contagious sp<sub>2</sub> hybridized carbon atoms. Each of the Sp<sub>2</sub> hybridized carbon atom contains one valance electron in an un-hybridized Pz orbital. The electrons residing in the unhybridized Pz orbitals delocalise over the entire polymer backbone chin via conjugation and thus leads to an one dimensional electronic band with energy gap greater than 2eV. This is higher than thermal conduction to happen, as a result conjugated conducting polymers are usually insulators or semiconductors having conductivity in the range of 10<sup>-10</sup> to 10<sup>-5</sup> Scm<sup>-1</sup>. However, the conductivity in these polymers can be improved upon doping due to some structural changes in the polymer backbone chains. Doping leads to higher mobility of charge carriers and is usually accomplished through oxidation and reduction methods (Redox doping). The discovery of conducting polymers dates back to 1970s, when three scientists namely, Shirakawa, Alan J Heeger and MacDiarmid witnessed significant increase in conductivity of polyacetylene, on treatment with robust oxidizing agents like I<sub>2</sub> vapours. The disclosure alongside broad research in the field of conducting polymers prompted the honour of Noble prize to the three prominent researchers (Shirakawa, Heeger and MacDiarmid) in the year 2000. The revelation prompted a spurt in the field of research in conducting polymers like polyaniline, polypyrole, polythiophene and their derivatives.

Now a day a vast research is being carried out in the field of conducting polymers. Conducting polymers are viewed as potential materials for various scientific applications such as photovoltaic cells, organic light emitting diodes, electrochromic displays, electromagnetic shielding materials, gas sensors, biosensors, charge storage devices and so on. Among various conjugated conducting polymers polypyrrole and polythiophene are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. The monomer unit of PPY and PTh are pyrrole and thiophene respectively. Both Pyrrole and thiophene are five membered heterocyclic aromatic organic compounds with the formula C<sub>4</sub>H<sub>4</sub>NH and C<sub>4</sub>H<sub>4</sub>S respectively. The structure of the monomer units of PPY and PTh. PPY and PTh can be prepared chemically or electrochemically via oxidative polymerization of pyrrole and thiophene monomers. The schematic representation of synthesis of PPY and PTh.

The properties of these polymers depend upon fabrication conditions and preparation techniques used. PPY and PTh have unique electrical properties, significant thermal stability, and oxidation resistance which makes them most promising members for wide range of applications such as optoelectronics, biosensors, electrochromic displays, chemical sensors, field-effect transistors, electroluminescent devices, solar cells, photochemical resists, non-linear optical devices, batteries, diodes, microwave absorbing materials, new type of memory devices, nano switches, optical modulators, DNA detection, transistors ,etc.

PTh belongs to the family of heterocycles and shows striking structural resemblance to PPY in both reduced and doped forms. It has been a subject of great interest during the last four decades for many researchers due to its chromophoric properties, ease of structural modifications that enable one to improve its sensing ability and electrocatalytic properties. PTh and its derivatives exhibit a remarkable color changing properties due to transitions from planar to twisted confirmation of the polymer backbone causing a shift of absorption band to the UV–visible region. This remarkable property makes them excellent prospects to be used in several sensor applications.

PTH biosensors show desirable properties when subjected to optical detection of contaminants present in water such as waterborne parasites, microbes, viruses, nucleic acids, bacteria, proteins, etc.that generate a measurable optical signal. Henceforth it is proved to be time-effective method for the rapid detection of pathogens of water. The PTh structure contains a number of S atoms, bonded to SP<sub>2</sub> hybridized carbons, which exhibit two lone pairs of electrons that are available to interact with other pollutant molecules. Thus it can easily donate the lone pair of electrons to the electron-deficient species, such as heavy metal ions. [8,9]

#### 1.5 Preparation of GO

GO was ready from regular graphite utilizing the technique for Hummers and Offeman.16 KMnO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> were utilized as oxidizing specialists. The item was purged by washing ordinarily with HCH (5%) and deionized water. After purging, the item was ultrasonicated for 1 hand along these lines an all around peeled GO scattering was acquired. GO was ready as per the changed Hummer strategy. Exhaustively, 5 g of graphite and 2.5 g of NaNO<sub>3</sub> were blended in with 108 mL H<sub>2</sub>SO<sub>4</sub> and 12 mL H<sub>3</sub>PO<sub>4</sub> and mixed in an ice shower for 10 min. Then, 15 g of KMnO<sub>4</sub> were gradually added with the goal that the temperature of the blend stayed beneath 5°C. The suspension was then responded for 2 hr in an ice shower and mixed for 60 min before again being blended in a 40°C water shower for 60 min. The temperature of the blend was acclimated to a consistent 98°C for 60 min while water was added persistently. Deionized water was further added so that the volume of the suspension was 400 mL. 15 mL of H<sub>2</sub>O<sub>2</sub> was added after 5 min. The reaction product was centrifuged and washed with deionized water and 5% HCl solution repeatedly. Finally, the product was dried at 60°C

#### **1.5.1 Properties and Applications of Graphene Oxide**

Due to the presence of oxygen functionalities, graphene oxide can easily disperse in organic solvents, water, and different matrixes. This is a major benefit when combining the material with polymer or ceramic matrixes to enhance their mechanical and electrical properties. With respect to electrical conductivity, graphene oxide functions as an electrical insulator, because of the disturbance of its Sp<sub>2</sub> bonding networks.

It is important to reduce the graphene oxide so as to recover the honeycomb hexagonal lattice of graphene, in order to restore electrical conductivity. After a large number of oxygen groups have been removed, it is not easy to disperse the reduced graphene oxide (RGO), because this material tends to produce aggregates.

The properties of graphene can be changed by the functionalization of graphene oxide. The chemically-altered graphenes obtained by this method could possibly be used in several applications. Depending on the intended application, the graphene oxide can be functionalized in a number of ways

One way to ensure that the chemically-altered graphenes disperse easily in organic solvents is to use amines through organic covalent functionalization, for instance. This makes the material better suited to production of biodevices and optoelectronics, and for use in drug delivery. Also, it has been shown that it is possible to attach fullerene-functionalized secondary amines and porphyrin-functionalized primary amines to graphene oxide platelets, to enhance the nonlinear optical performance of the material.

Graphene oxide could potentially be used as an intermediary in the production of single layer or few-layer graphene sheets. To achieve this, an oxidization and reduction process should be developed that can isolate carbon layers and separate then without changing their structure.

In terms of mass production of graphene, the chemical reduction of graphene oxide is considered to be one of the most viable methods. However, scientists have found it challenging to create graphene sheets that have the same quality as those made by mechanical exfoliation on a large scale. [11,12]

#### 1.5.2 Preparation of polythiophene/GO composites

PTH/GO composites of various weight percentages of GO to thiophene (1, 2 and 3%) were prepared by liquid/liquid interfacial polymerization and were labelled as PTGO<sub>1</sub>, PTGO<sub>2</sub> and PTGO<sub>3</sub>. The interfacial polymerization was done as follows. The required amount of GO was dispersed in 20 mL of CH<sub>3</sub>NO<sub>2</sub> (solvent) using an ultrasonicator. Then FeCl<sub>3</sub> (2.44gm) was added to the dispersion and mixed thoroughly. The solution as obtained was added dropwise into a thiophene (0.4 ml) solution in 10 ml of n-hexane and the mixture was continuously stirred for 24 hrs. The product was obtained from the reaction mixture by centrifugation and then washed with ethanol for purification. Finally, the powdery composite was dried at 60°C for 24 hrs.

#### 1.6 Synthesis of conducting polymers

Conductive polymers can be prepared by various methods like chemical oxidative polymerization, metal-catalysed polymerization, photochemical polymerization, solid-state polymerization, plasma polymerization, interfacial polymerization and electrochemical polymerization. Here we discuss chemical oxidative polymerization which is mainly employed during this project.

In chemical oxidative polymerization method, the monomer is first oxidized to form a radical cation series by using a suitable oxidizing methods. This radical cation further rets to form a dimer and subsequently the dimer is oxidized gain and reaction result in a polymerization of the monomer. This methods is widely adapted among researchers to form conducting polymers.



#### Fig.1. 7 Thiophene Plays an important role in adding and removal of electron

#### 1.7 Present and future potential applications

Potential applications for conducting polymers are numerous, since metals be located toxic and can also impairment the background. Below are some potential submissions for conducting polymers.

#### **1.7.1 Corrosion Protection**

The recent methods of the corrosion protection are not very lasting and are coming under increased scrutiny by the Environmental Protection Agency (EPA). As an example, the use of chromium and cadmium for anti-corrosion will soon be banned. Unfortunately, the coatings do not last very long. The oxidized zinc metal is dissolved by water or moisture. For this reason, there are extreme environmental concerns, since toxic metals are being released into the

ecosystem. Barrier coatings, such as epoxy, are employed extensively but are not very durable once a pit or hole in the coating has been formed. A major type of corrosion occurs by oxidation of a metallic surface by a water medium to produce oxides and hydroxides. As these are formed, soluble species are produced, the surface pits increase their surface area, and the rate of decomposition accelerates. One way to provide corrosion protection is to coat the metal with a barrier to prevent the reactive species from reaching the surface.

#### **1.7.2 Sensors and Electromechanical Devices**

Since conducting polymers change properties by incorporation of ions and solvents (the property change easiest to measure is conductivity), it is possible to develop and market ion-specific sensors based upon conducting polymers. Conducting polymers could permit the incorporation of sensors into clothing. There are some challenges involved, such as background noise due to water absorption, lifetime, selectivity, and sensitivity. Conducting polymers also change volume depending on their oxidation state. It is therefore possible for conducting polymers to convert electrical energy into mechanical work.

#### **1.7.3 Batteries**

This field is the first area where conducting polymers promises to have a big commercial impact. Batteries have several key components: the electrodes allow for collection of current and transmission of power. Aside from picking the best conducting polymer available, there are many other issues, not related to conducting polymers, that affect battery performance, such as electrolyte stability and stability of the counter half-cell reaction (which is at least as important as the conducting polymer electrode), and compatibility between the electrolyte and the materials. [7,9]

#### **1.8 Pallets**

The pallets so prepared are strong and compacted enough and they are used further for the characterisations to confirm the size, shape and structure of the polymer. The pallets are formed with the different compositions having mixture of two or more compounds with some different ratios.

- 1. Go polythiophene (1:1)
- 2. Go polythiophene (2:1)
- 3. Go polythiophene (1:2)
- 4. Pure polythiophene
- 5. Pure Go

#### **1.9 Characterization**

The characterisations are further explained:-

1. X – Ray Diffraction (XRD)

X-ray diffraction method (XRD) is used to confirm the formation of polythiophene structure whether the formation is correct or not. These characterisations helps us to know the structure shape, size and variation towards any particular method. By this characterisation we will have the data to plot the graphs with which we can conclude the peaks for the compound.

2. Fourier Transformed Infrared Analysis (FTIR)

Fourier-transform infrared analysis (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. The term Fourier-Transform Infrared Spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum.

3. At Low Temperature Conductivity

The thermal (and electrical) properties of any material are related to the vibrations of its atoms around their equilibrium positions (in a lattice crystal). The amplitude of these vibrations depends on temperature and diminishes as the temperature decreases. Note that these vibrations may propagate within the material at the speed of sound, and are studied as plane waves, with which phonons are associated. Thermal properties also depend on the movements of negative charges (electrons) and positive charges (vacancies) if the material is a conductor.

## **CHAPTER 2**

#### **CHAPTER-2: Experimental details**

#### 2.1 Synthesis of Polythiophene nanofibres

#### **Procedure:**

- Take 1ml of thiophene in 100ml of chloroform and pour it in a round bottom flask and also put a magnetic beat in it, and place the RBF in a chiller's (julabo) lid at the temperature (-22°C)
- After stirring this for several times on a magnetic stirrer add required amount of anhydrous ferric chloride with mole ratio of ferric chloride and thiophene is 1:2 which is approximately 7gms of anhydrous ferric chloride is then added to a mixture in RBF with continued stirring for about 5-6 hrs.
- Then add some amount of methanol in it.
- This mixture is then filtered with the help of de-ionised water by providing vacuum to it. And the brown precipitate of polythiophene is obtained after washing it should be dried in an oven for few hours.



Fig. 2. 1 Julabo



Fig. 2. 2 Obtained Polythiophene

#### **2.2 Materials**

- Round bottom flask,
- Thiophene,
- Chloroform,
- Magnetic beat,
- Ferric chloride
- Deionised water
- Methanol

#### 2.3 Polythiophene Formation

- Polythiophene can be synthesized by foremost two types one that is electrochemically by applying a potential across a solution of the monomer to be polymerized. Another one is chemically using oxidants or cross-coupling catalysts. The quality of electrochemically prepared PT thin films is affected by a number of factors.
- Synthesized by chemical oxidative polymerization technique by drop-wise addition of monomer 3-OT in oxidant FeCl<sub>3</sub> (0.4M) in 100ml CHCl<sub>3</sub> at temperature 253 K. Reaction is carried out in double walled container by constant stirring.



#### Fig. 2. 3 Polythiophene Formation

#### **2.4 Pellets Formation**

- Take a sufficient amount or compound as mentioned in the table for preparation of various palletes.
- Consider for the 1:1 of GO and polythiophene, measure the powdered form of polythiophene and GO and mix it with the help of compound dispenser until very small microbes formed, then add 10% of pvdf in it to bind the compound properly.
- Then with the help of spatula transfer the compound to a beaker and add few drops of chloroform in it. For mixing the compound completely use homogenator for stirring for

about 10-15 minutes. Then after stirring place the beaker having compound in the sonicator for around 30 minutes.

- After sonicating place the beaker in oven until the compound will become dry completely. When the powder form of compound is ready use die to make pelletes and use hydraulic pressure machine to give a compact form to a pellete and then to make pallete strong use annealing machine upto 150°C that provides the sufficient heat and makes the pellete stronger and compacted. And then we have a compacted and a strong pellete of 0.2gm.
- The thickness of obtained pellet is 0.005 cm and area is  $2.80 \times 10^{-5}$



Fig. 2. 4 Flow chart showing Pellet formation



Fig. 2. 5 Instruments used for pellet formation in NPL

S.NO	RGO	POLYTHIOPHENE	PVDF
1.	45%	45%	10%
2.	90%	0%	10%
3.	0%	90%	10%
4.	60%	30%	10%
5.	30%	60%	10%

Table 2. 1 Table showing composition of pellet

#### **2.5 Measurements**

In order to determine the structure and properties of the polythiophene nanofibers, several instrumental techniques, such as XRD (XRD-Smart lab) and FTIR (Spectrum  $RX_1$ ), were employed. Surface charge was determined by using zeta potential measurement (Horiba).

## **CHAPTER 3**

#### **CHAPTER-3:** Characterization

#### 3.1 Techniques Used

In the present study, three characterisation techniques are employed which are:

- X Ray Diffraction Spectroscopy
- Fourier Transform Infrared Spectroscopy
- At Low Temperature

#### 3.2 X - Ray Diffraction Spectroscopy

X-Ray Diffraction Spectroscopy X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analysed material is finely ground, homogenized, and average bulk composition is determined theory Max von Laue, in 1912, discovered that crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths like the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.

These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law (n  $\lambda$ =2d sin  $\theta$ ).



Fig. 3. 1 X-ray Diffraction Phenomenon

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of  $2\theta$  angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

#### **3.2.1 Instrumentation**

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have enough energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being  $K_{\alpha}$  and  $K_{\beta}$ . Filtering, by foils or crystal mono chrometers, is required to produce monochromatic X-rays needed for diffraction. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle  $\theta$  while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 20. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at  $2\theta$  from ~ 5° to 70°, angles that are present in the X-ray.

#### **3.3 Fourier Transform Infrared Spectroscopy**

Fourier Transform Infrared Spectroscopy Fourier transform Infrared spectroscopy (FT-IR) is employed to find the functional groups present in an organic molecule. The instrument uses the infrared spectrum ranging from 4000 to 400 cm<sup>-1</sup>.

It is being observed that the even a simple molecule can give complex spectrum and by matching peak by peak we can identify the no. of functional group present. Two compounds except for enantiomers cannot have same IR spectrum. IR spectrum can also be used to check the differences in the various groups formed and lost during chemical reaction by comparing with the spectrum of the reactants. Infrared frequency less than 100 cm<sup>-1</sup> is absorbed and

converted into rotational energy in organic molecules. This is shown in the form of discreet lines as this energy is quantized.

Infrared radiation ranging from 10000-100 cm<sup>-1</sup> is absorbed and converted by organic molecules in the form of vibrational energy. This energy is also quantized but vibrational energy appears in the spectrum as bands rather lines because a vibrational energy change is accompanied by many rotational energy changes. We are only concerned in vibrational rotational energy belonging to the spectrum ranging between 4000 and 400 cm<sup>-1</sup>. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

Band positions in IR spectra is defined by wavenumbers whose units is reciprocal cm. This unit is proportional to the energy of the vibration and instrument are linear in reciprocal cm. Band intensities can either be defined by transmittance or absorbance.

Transmittance is the ratio of radiant power transmitted by the sample to the radiant power incident in the sample. Absorbance is the low to the base 10 of the reciprocal of the transmittance;  $A = \log 10(1/T)$ .

There are two types of vibration stretching and bending, in stretching the bond length increases or decreases with constant vibrations whereas in bending the bond angle changes. Only those vibration that results in rhythmically change in dipole movement of the molecule are observed in IR.

#### **3.3.1 Instrumentation**

For many years, and infrared spectrum was obtained by passing an infrared beam through the sample and scanning the spectrum with diffraction grating. The spectrum was scanned by rotating the diffraction grating, the absorption areas were detected and plotted as frequency v/s intensity. Over the past decade Fourier transform infrared (FT-IR) spectrometry has been extensively developed providing several advantages. Radiation containing spectrum form 4000-400 cm<sup>-1</sup> is split in to two beams one is of fixed length and other is of variable length. The varying distance between two path lengths result in a sequence of constructive and destructive interferences and hence variations in intensities: an interferogram. Fourier transformation converts this interferogram form time domain into frequency domain. Smooth and continuous variation of the piston varies the path length of beam B by adjusting the position of the mirror B. Fourier transform at successive points throughout this variation gives rise to complete IR spectrum. The schematic diagram of working of FT-IR spectrometer is given in

figure 3.1. There are number of advantages to FT-IR method. Since a monochromator is not used, the entire spectrum of radiation if passed through the sample simultaneously and much time is saved. FT-IR have much high resolutions.

Also, since the data undergoes analogue to digital conversion it is easier to manipulate, results of several scans can be combined to average out random absorption artefacts and excellent spectra from very small samples can be obtained.

Samples can be used in solid, liquid or gases. The spectra of gases or low boiling liquids may be obtained by expansion of the sample into an evacuated cell. Gas cells are available in length of a few centimetres to 40m. Liquids can be examined neat or in solutions, neat liquids are examining between salt plates. Solid or gel form can be examined by ATR assembly which was used at NPL for FTIR characterization. Sometimes the KBr pellets are also used but the use of KBr pellets is mostly avoided because it is very less likely to make good pellets.



Fig. 3. 2 Instruments used for FTIR



Fig. 3. 3 FTIR steps

#### **3.4 Conductivity at low temperature**

Polythiophene is also highly conductive (its conductivity usually exceeds 100 S/cm) and possesses thermal and chemical stability. And further functionalization could enable its sensing selectivity and improved electrocatalytic properties. Polythiophenes could be fabricated as the recognition units of biosensors by the direct polymerization of monomers or the substitution of the prepared polythiophene backbones. The latter approach is also used for the immobilization of enzymes or aptamers into polythiophene layer. For example, Floch et al. fabricated an electroactive, cationic, water-soluble polythiophene transducer. In this work, the neutral peptide nucleic acid (PNA) capture probes on the gold electrodes would not bind to the electroactive polythiophene. Instead, polythiophene transducer can interact strongly with the negatively charged backbone of the complementary oligonucleotide bound to the PNA probes. The interaction allowed the transduction of room-temperature hybridization into electrical signal, enabling a specific and sensitive detection of unlabeled DNA targets. [1,3,7,9]

# **CHAPTER 4**

#### **CHAPTER 4: Results and discussion**

#### 4.1 Pattern Observed

The patterns obtained from the present study is shown in the form of graphs in subsequent sections of this chapter. The experimental results obtained from three characterization methods mentioned above is as follows:

#### 4.2 X-Ray Diffraction Spectroscopy

It is elaborated from the graph that only one broad peak centred at near 20 value of 21.5°. This diffraction peak strongly associated with the  $\pi$ - $\pi$  stacking structure in polythiophene chains indicating the amorphous nature of the polymer. The XRD patterns of GO, PTh/GO composite and pure polythiophene are presented in Fig.5.1. The XRD pattern of GO (Fig. 4(e) shows a strong peak at  $2\theta = 11.4$  corresponding to reflection peak. Pure polythiophene exhibits a broad diffraction peak at  $2\theta = 22^{\circ}$  (Fig. 5.1) indicating the amorphous nature of the polymer. For the PTh/GO composite, the characteristic broad peak of polythiophene appears at  $2\theta = 23.5^{\circ}$  (Fig. 5(b, c, d) indicating the presence of PTH in the composite. Also a peak appears at  $2\theta = 21.6$  which indicates the presence of GO in the composite. Thus the XRD analysis indicates the interactions between GO and polythiophene.

Intensity v/s Diffraction angle graph is obtained from the experimental data and is shown below:



Fig. 4. 1 Variation of Diffraction angle Two Theta (degree) with change of intensity (counts) for (a) Pure Polythiophene, (b) GO polythiophene (1:2), (c) GO polythiophene (2:1), (d) GO polythiophene (1:1) & (e) Pure GO respectively.

#### 4.3 Fourier Transformed Infrared (FTIR) spectroscopy

Graph between Transmittance (%) v/s wave number is plotted and it is concluded from the graph that GO shows a broad peak at 3409 cm<sup>-1</sup> for O-H stretching and a peak at 1719 cm<sup>-1</sup> which can be assigned to the carbonyl stretching vibration. The peak at 1066 cm<sup>-1</sup> for C–O stretching vibration appears due to the presence of the epoxide group in the GO layers. The peaks at 1236 and 1411 cm<sup>-1</sup> can be ascribed to the C-OH stretching vibration and O-H deformation, respectively. The band at 1167 cm<sup>-1</sup> is assigned to C-H (in-plane) bending vibration of thiophene. A band at 790 cm<sup>-1</sup> appears due to C–H (out-of-plane) bending vibration of thiophene units indicating the  $\alpha$ -position linkage between the thiophene rings. Moreover, the bands at 830 and 692 cm<sup>-1</sup> may be assigned to C-S stretching and C-S-C bending vibrations indicating the presence of thiophene rings. The FTIR spectrum of GO shows a broad peak at 3409 cm<sup>-1</sup> for O-H stretching and a peak at 1719 cm<sup>-1</sup> which can be assigned to the carbonyl stretching vibration. The peak at 1066 cm<sup>-1</sup> for C–O stretching vibration appears due to the presence of the epoxide group in the GO layers. The peaks at 1236 and 1411 cm<sup>-1</sup> can be ascribed to the C-OH stretching vibration and O-H deformation, respectively.21 The FTIR spectrum of PTh/GO composite shows almost the same bands as that of polythiophene; however, the bands are shifted to longer wavelength. Also a peak near 1720 cm<sup>-1</sup> for the carbonyl stretching vibration appears in the spectrum of the composite which is absent in that of pure polymer.

Transmittance v/s Wave No. graph is obtained from the experimental data & is shown below:



Fig. 4. 2 Variation of transmittance (%) with change of wave number for (a) Pure Polythiophene, (b) GO polythiophene (1:2), (c) GO polythiophene (2:1), (d) GO polythiophene (1:1) & (e) Pure GO respectively.

#### 4.4 Low temperature conductivity

Graph between Conductivity & Temperature is plotted and it is concluded from the graph that the conductivity of the resulting PT/GO composite in 1:1 is  $1.30012 \times 10^{-4}$  S cm-1 and 1:2 is  $6.68957 \times 10^{-5}$  and for 2:1 is  $4.1563 \times 10^{-5}$  room temperature, which is higher than that of pure polythiophene that is 0.01035 S/cm. The DC conductivity values of the composites are seen to increase with increasing GO content. The conductivity of GO is  $8.32152 \times 10^{-7}$ . This increase in conductivity may be attributed to the increased electron mobility arising from the  $\pi -\pi$  stacking between the GO layers and polythiophene within the composite system. And the conductivity is decreasing with the increase in temperature.

Conductivity v/s Temperature graph is obtained from the experimental data & is shown below:



Fig. 4. 3 Variation for Conductivity(S/Cm) with change of Temperature 1000/T (K-1) for (a) Pure Polythiophene, (b) GO polythiophene (1:2), (c) GO polythiophene (2:1), (d) GO polythiophene (1:1) & (e) Pure GO respectively

## **CHAPTER 5**

## CHAPTER 5: Applications, Advantages & Disadvantages and Conclusion 5.1 Applications

Polythiophene nanocomposites have been used for many applications due to their chemical, mechanical, optical and electrical properties. Their semiconductor properties allow conjugated polymers to be used particularly in a large area, such as electrochromic devices (EDCs), rechargeable batteries, light-emitting diodes (LEDs), field-effect transistors (FETs), photovoltaic cells and chemical Sensors.

Owing to the various advantages like low density, low cost, flexibility of design, ease of fabrication, low energy and labour requirements for fabrication and processing etc. Conducting polymers have been exploited for various applications in different fields like polymer battery electrodes, rechargeable batteries, EMI Shielding and solar cells etc. The applications of conducting polymers can be summarised in three main groups which are based on the three main properties i.e. conductivity, electroactivity and semiconducting nature of conducting polymers. This is depicted in scheme 1.





#### 5.2 Advantages

- No pollution associated with it.
- It must last for a long time.
- No maintenance cost.

#### **5.3 Disadvantages**

• It has high cost of installation.

- It has low efficiency.
- During cloudy day, the energy cannot be produced and also at night we will not get solar energy.

#### **5.4 Conclusion**

It is concluded from the above graph that the formation of the polythiophene has been confirmed. Both FTIR and XRD results indicate the incorporation of GO in the polymer matrix. The polythiophene/Graphene oxide composites exhibited an improved thermal stability compared to pure polythiophene. Both optical and electrochemical band gaps of the composites were calculated and found to decrease dramatically on incorporation of GO into the polymer matrix. Electrical conductivity of the composites was found to be higher for PT/GO than that of pure polythiophene. The composites showed reversible electrochemical response and a good cycling stability even up to 100 cycles. A specific capacitance value of 99 F  $g^{-1}$  (scan rate of 50 mV s<sup>-1</sup>) was obtained for the PT/GO composite. The present work shows that the PTh/GO composites prepared using the interfacial polymerization method possess great promise for a range of potential applications in batteries and optoelectronic devices. The cycling performance of the composites was estimated by repeating the CV tests for 100 oxidation and reduction cycles at a scan rate of 10 mV s<sup>-1</sup>. The curves show clear redox peaks for the first cycle and, as the cycling increases, the peak shape becomes weaker and broader. Polythiophene which restricts the change of network structure during cycling. Thus the composites exhibit good potential for application in capacitors and rechargeable batteries. Polythiophenes remain one of the most versatile conjugated polymer systems. Owing to the ease of synthesis of PT derivatives, the number that can be engineered as new materials is limited only by the imagination. Polythiophenes will continue to lead the way to new unique sensory materials, to highly stable and efficient all-polymer transistors, to very highly conductive plastics, and to new nanoelectronic and nano optical materials. New advances in the synthesis of region regular polythiophene and the discovery of selfassembly in regioregular polythiophene provide welldefined building blocks that have increased the importance of polythiophene among conducting polymers. As well-defined materials become more readily available, new structure property relationships will continue to unfold through systematic studies of structure/physical property correlations. This will allow chemists, physicists, materials scientists, and engineers to have a better grasp on the development of new technologies. The ease and low cost of processing these polymers can then be exploited for future technologies and continued commercial applications.

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