

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

SYNTHESIS AND CHARACTERIZATION OF POLYTHIOPHENE DOPED Bi₂O₃ NANOPARTICLES

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ABSTRACT

In the present paper, Bi₂O₃ nanoparticles and polythiophene (PTh) were synthesized using co-precipitation methods and oxidative polymerization method, respectively. An ex-situ approach was adopted for the Bi₂O₃-PTh composites. The confirmation of PTh and Bi₂O₃ samples was examined through X-ray diffraction. Optical properties such as Excitation and Emission of the as-synthesized composites were measured using PL spectroscopy. The photoluminescence (PL) excitation and emission spectra were observed in ranges 200-300 and 300-700 nm. Such type of composites may applicable for different fields of optoelectronics.

Keywords: Polythiophene; nanoparticles; Bismuth-Oxide and composites

I. INTRODUCTION

Among the numerous conducting polymers, polythiophene (PTh) has rapidly become the subject of considerable interest. From a theoretical viewpoint, PTh has been considered as a model for the study of charge transport in conducting polymers with a non degenerate ground state, while on the other hand the high environmental stability of both its doped and un-doped states together with its structural versatility have led to multiple developments aimed at applications such as conductors, electrode materials and organic semiconductors. Polythiophene and its derivatives have the added different advantages of environmental stability and good thermal. Polythiophenes find potential application in polymer, light emitting diode, sensors, electrodes, thermionic devices, solar cells and transistors. Polythiophene (PTh) received attention due to its thermal stability and high conductivity. The conductivity of these materials can be tuned by doping. Dopant anion plays an important role in polymerization [1]. Polythiophene (PTh) can be synthesized by different two types. One is the electrochemical method by applying a potential across a solution of the monomer to be polymerized. Another method is chemically using oxidants or cross-coupling catalysts. The quality of polythiophene thin films prepared by electrochemically method is affected by a number of factors. These include the current density, electrode material, solvent, temperature, electrolyte, presence of water, and monomer concentrations [2]. Polythiophene material can also be modified with many chemical group for the specific applications by fast doping-undoping mechanism [3]. When different inorganic materials such as metal nanoparticles combined with polythiophene, it produced nanocomposites. Polythiophene PTHs have been considered in several reviews devoted to conducting polymers in general or to some of their more specific aspects such as electro-polymerization, electrochemistry, environmental stability and optical properties [4]. The general structure of PTh is as shown in Figure 1.

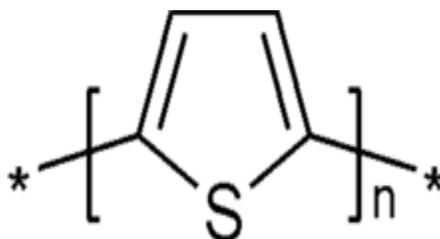


Fig. 1. The general structure of PTH

PTh is a thermally and chemically stable conjugated polymer material with good electronic properties. Polythiophene gives a large and well-behaved chemical properties, making it suitable for efficient modification at

the molecular level that can be used to tailor its physical, electronic and optical properties [5]. Polythiophenes (PTh), as most important intrinsically conducting polymers with an extended p-conjugated system, has shown great promises owing to its unique optical and electrical properties [6]. Native PTh is an insoluble and intractable material, and virtually all reported data for devices based on PTh have been achieved through chemical derivatization of the PTh backbone for solubility and processing. The organic-inorganic hybrid solar cell showed new promises because of several advantages resulting from the introduction of inorganic nanoparticles. These inorganic nanoparticles high electron mobility, physical stability and excellent chemical, size tunability, and complementary light absorption properties. By comparing with other conducting polymers, polythiophene (PTh) and its derivatives have many advantages, for they are easy to process, enhanced stability and versatility which have gained more attentions [7].

One of the most successful PTh is region regular poly-(3-hexylthiophene)₂ (P3HT) which has been employed as the active material in various electronic devices. Some of the highest carrier abilities observed in conjugated polymers have been reported for P3HT, and many of the efficient and stable polymer-based solar cell devices available today are based on this compound. However, new materials are also starting to appear such as low-band-gap materials and carboxy-substituted PTh for increased operational stability of solar cells in both vacuum and air and for transistors in air. There is an increasing focus on the operational stability of devices while the scientific community traditionally has been content with the reports on the achievement of high performance with little or no mention of stability. Methods for improving the operational stability of devices require an understanding of why degradation takes place [8]. PTh has been the subject of considerable interest because of its good environmental stability, unique redox electrical behavior, stability in doped or neutral states, ease of synthesis, and wide range of applications in many fields. Apart from its applications in the electrical or electronic field, PTh has shown promising applications in photo catalytic degradation. The fabrication of a catalyst, metal oxides with PTh, extends the absorption range of the modified composite system, thereby enhancing the photo catalytic activity under UV or visible light irradiation. Substituted PTh, such as alkyl substitution, modifies the electronic properties of the polymer, thereby enlarging the potential for industrial applications. PTh or substituted PTh when combined with metal, metal oxide or a combination of both, can exhibit tailor able photo catalytic properties. The major developments in the field of UV and visible light-assisted photo catalysis are discussed in terms of the parameters that affect the photo catalytic efficiency. On the other hand, some challenges still needs to be investigated experimentally, which are mentioned as the scope for future studies [9]. At the same time PTh doped with numerous oxides materials for examples, Feng et al [10] reported the energy level alignment at interfaces based optimization organic photovoltaic as band offsets of the donor and acceptor materials largely determine the open circuit voltage. The correlation between energy level alignment and photovoltaic properties of a model bi-layer hybrid solar cell incorporating electrodeposited PTH films on ZnO planar substrates. Polythiophene, like other conjugated polymers, has been applied in the photocatalytic area to sensitize metal oxides and develop high performance PTh/metal oxide photo catalytic materials [11]. Wadtkar et al [12] were synthesized polythiophene (PTh) by chemical oxidative polymerization method by using Ferric chloride (FeCl₃) as an oxidant in aqueous medium at room temperature. Jose et al [13] were synthesized by In situ chemical oxidative polymerization for ordered conducting polythiophene nanostructures in presence of dioctyl sodium sulfosuccinate. Alejandro et al [14] demonstrate the organic/inorganic hybrid single nanowire solar cell. The PTh was grafted onto ZnO nanowires to produce p-n heterojunction nanowires. The Individual nanowire solar cell devices exhibited well-resolved characteristics with efficiencies as high as 0.036% short circuit voltage, 0.32 mA/cm² open circuit voltage, 0.4 voltage, and a field factor at 0.28 under AM 1.5 illumination with 100 mW/cm² light intensity. These individual test structures will enable detailed analysis to be carried out in areas that have been difficult to study in bulk heterojunction devices. Das et al [15] was fabricated dye-sensitized thin film hybrid solar cells using by one-pot process using ZnO precursor as electron acceptor, ester-functionalized PTh copolymer as donor and a squaraine dye. Incorporation of slight amount of ester functionality (6%) in the regioregular poly-3-hexylthiophene (P3HT) main chain leads to enhancement in the photoconversion efficiency of the ester functionalized polymer (P3HT-E) from 0.8% to about 1%. Photocurrent associated with both of the P3HT-E and the squaraine dye was observed in incident photon to current efficiency curve of the solar cell.

Therefore, in the present paper we focus on synthesis and studies the different properties of PTh doped with Bi₂O₃ nanoparticles.

II. EXPERIMENTAL

2.1 Synthesis of Polythiophene

The polythiophene (PTh) was synthesized by chemical oxidation method with AR grade chemical without any further purification. In such chemical oxidation method we take polymer as thiophene. The ratio of thiophene taken 1 molar and we used as monomer for PTh with stirrer continuously for 1 hour. Then after add FeCl_3 as oxidant. The same ratio is taken of FeCl_3 and adds directly in thiophene as 1 molar. The chemical solution was stirrer for 12 hours continuously and then we get the black precipitation of PTh materials. Which was dry but again wash it by pure water if some impurity is their then it is removed by using pure water and again the obtained sample was dried at 1000°C for 3 hours; so finely we get pure PTh.

2.2 Synthesis of Bismuth Oxide

The Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and hexamethylenetetramine (HMT, $\text{C}_6\text{H}_{12}\text{O}_6$) were used for the synthesis of Bi_2O_3 nanoparticles. In a typical synthesis, 1 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was mixed with 1 M $\text{C}_6\text{H}_{12}\text{O}_6$ in 20 ml deionized water under magnetic stirring for 30 min at room temperature. Subsequently, obtained product kept for a centrifuge operating at 3000 rpm for 30 min. After this procedure, solution was separated into two gradations. At the bottom a yellowish layer of Bi_2O_3 nanoparticles observed and over it more transparent and dispersed layer appeared. This centrifuged precipitate was collected through cellulose nitrate filter paper. The filtrate was dried at room temperature for 24 hours in vacuum chamber and then sintered at 500 K for 24 h. After sintering the synthesized material appears yellowish colored powder in visible light. For the composites the weight percent ratio was applied. The 5 wt % and 10 wt % PTh doped Bi_2O_3 composites were prepared using weight percent ratio formula.

The PTh and Bi_2O_3 were characterized through XRD and recorded using a Rigakuminiflex-II diffractometer with $\text{CuK}\alpha$ radiation in 2θ range 10° - 80° . The PTh, Bi_2O_3 and PL excitation and emission recorded using fluorescence spectrophotometer HITACHI, F-7000.

III. RESULTS AND DISCUSSIONS

3.1 XRD Analysis:

Figure 2 shows the XRD pattern of the Bi_2O_3 nanoparticles and polythiophene (PTh) in 2θ range between 10° - 80° . The Bi_2O_3 nanoparticles shows the broaden peaks. The broadening in XRD peaks of Bi_2O_3 materials shows the prepared material is in nano range. The prominent at peaks at 27° is characteristics peak of Bi_2O_3 nanoparticles. In case of PTh the broad hump was appear in range between 10° - 80° . The small sharp peaks on this hump were clearly shows the materials was polymer. The highest and sharp peak in PTh spectrum at $2\theta = 41.78^\circ$ indicates a highly organized structure of prepared PTh. The XRD pattern of PTh presents a diffraction peak at $2\theta = 40.86^\circ$ with an interlayer spacing of 0.36 nm, which can be indexed to the (002) peak of PTh structure of carbon.

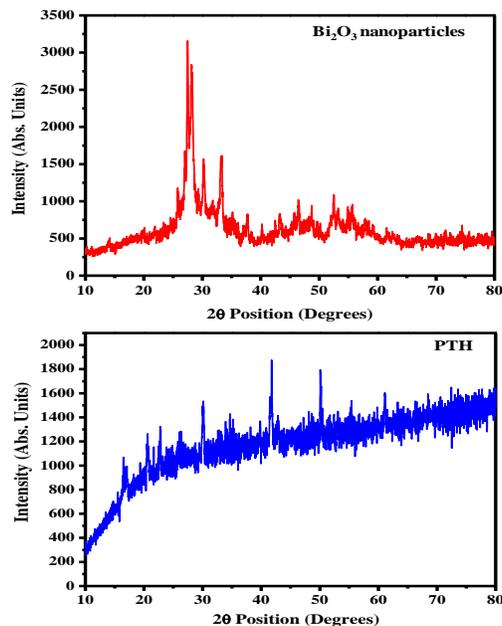


Fig. 2. XRD pattern of Bi_2O_3 nanoparticles and polythiophene (PTh)

The lower intensity of highest and sharp peak in PTh spectrum at $2\theta = 41.78^\circ$ assigned may be to a lower degree of crystallization and the presence of defects. In the XRD pattern of polythiophene, a typical diffraction peak is broadening, indicating smaller crystalline size of polythiophene. This may be due to adsorption of oxygen molecules with amorphous carbon inside the PTh.

3.2 Fluorescence Spectroscopy (PL) Analysis

Figure 3 shows the photoluminescence (PL) spectrum of Bi_2O_3 nanoparticles, polythiophene (PTh), 5 wt % and 10 wt % Bi_2O_3 -PTh composites in wavelength range between 300-700 nm with the excitation wavelength of 254 nm. All the prepared materials show good and broad emission peak. The broad PL emission spectrum in composites is useful investigation to study and the efficiency of charge carrier trapping, immigration, transfer and to understand the electron-hole pairs inside the materials. The Bi_2O_3 nanoparticles show maximum PL intensity as compared to PTh material. The PTh material shows maximum PL intensity as compared to 5 wt % and 10 wt % Bi_2O_3 -PTh composites.

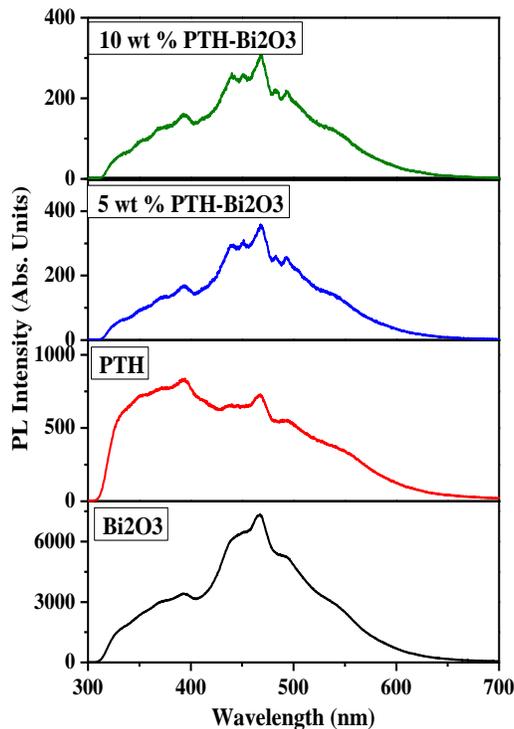


Fig.3. PL emission spectrum for Bi_2O_3 , PTh, 5 wt % Bi_2O_3 -PTh and polythiophene and 10 wt % Bi_2O_3 -PTh composites

The relatively lower in intensity of emission band in UV-Visible region for 10 wt % Bi_2O_3 -PTh composite as compared Bi_2O_3 nanoparticles, PTh and 5 wt % Bi_2O_3 -PTh composite show lower recombination rate of presented electrons and holes and higher separation efficiency under light irradiation in composite than Bi_2O_3 and PTh materials. Hence, we could reported that PTh interact with Bi_2O_3 , leading to enhanced electron transport of the photo-induced electrons inside the composite materials. Furthermore, it is observed that inhibit the recombination of the photo-induced electron-hole pairs inside the composites. It is reported that presence of PTh due to its excellent conductivity in the Bi_2O_3 sample might be effective for different application.

IV. CONCLUSIONS

In this work we developed of PTh doped Bi_2O_3 nanoparticles by using chemical precipitation and modified chemical oxidation method using FeCl_3 as oxidizing agent. The phase and structure purity analyzed by XRD and showed the formation of Bi_2O_3 and PTh materials. The photoluminescence (PL) excitation and emission spectra were observed in ranges 200-300 and 300-700 nm. The obtained results clearly show that this method is low cost and very effective for synthesis of Bi_2O_3 nanoparticles. The prepared materials can be proposed as a suitable candidate for fields of optoelectronic devices.

V. ACKNOWLEDGEMENT

Author G. V. Chavan is very much thankful to Head, Department of Physics, SGBAU, Amravati for providing the necessary facilities for this work.

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