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Sonochemical Synthesis and Characterization of PEDOT-ZnO nanocomposite

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Abstract:

Polymer composites are replacing a large number of products due to their high strength to weight ratio. Polymer composites hold a lot much of promise in variety of applications in diverse fields like automobile, healthcare, construction, electronics, etc. which is attributed to their thermal, electrical, optical and mechanical properties. Several methods so far have been employed to synthesize polymer composites. Among conductive polymers, PEDOT [poly(3,4ethylenedioxythiophene)], stands out for its excellent stability and high light transmissivity. In this paper emulsion polymerization technique is used for the synthesis of poly (3,4-ethylenedioxythiophene) (PEDOT) and its composite using ZnO as a filler material. Ultrasound assisted synthesis was preferred over conventional bulk heating process. The process was meticulously followed and optimized so as to develop a stable polymer composite. Synthesis process was investigated based on reaction time, yield and energy efficiency. The PEDOT & its composite with ZnO was characterized for its properties namely porosity, mechanical strength, surface texture and morphology using Conductivity, UV-visible spectroscopy, FTIR and SEM.

Keywords: Composite, PEDOT, Sonication, Morphology, SEM

Introduction:

Polythiophene and its derivatives have been at the center of considerable scientific interest for their superior chemical and physical properties [1]. Among the derivatives of polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), is one of the most

promising conducting polymers because of its low band gap, excellent environmental stability, high electrical conductivity, and transparency in thin oxidized films. Since the advent of PEDOT in 1989, many studies on PEDOT have been undertaken. Many applications like solid electrolytic capacitors, anti-electrostatic agents, transparent electrodes in light emitting diodes, and under-layers for the metallization of printed circuit boards have been reported so far. The synthesis of PEDOT by the electrochemical and chemical oxidative polymerization and organic synthesis of 3,4-ethylenedioxythiophene (EDOT) has also been already done [2-4] with the latter one being most suited for mass production [5]. High-concentration emulsion polymerization of ethylenedioxythiophene (EDOT) in the presence of sodium salt of 2-naphthalenesulfonic acid (2-NaNS) as dopant and ferrous sulfate as oxidant has been reported as a new technique of polythiophene synthesis prescribed by Japanese scientists. The conductivity of PEDOT obtained by this method was 160 S/cm.

3,4-Ethylenedioxythiophene (EDOT) is the most intensively researched monomer in the past decade or so because of high conductivity, and excellent environmental stability of its polymer poly(3,4-ethylenedioxythiophene) (PEDOT) [6-8]. Further, PEDOT and its derivatives have been catching a lot much of attention due to their excellent electronic properties as well. Similarly they are also characterized by low energy-gap values, low oxidation potentials, and high electrical conductivity and stability in the oxidized (p-doped) state. These characteristics make p-doped PEDOT films suitable as electrodes and interfacial hole conducting layers in various types of organic electronic devices, e.g. in light emitting diodes, solar cells, and antistatic or electrochromic coatings [8-10].

Poly(3,4-ethylenedithiathiophene) (PEDTT), as the all-sulfur analog of PEDOT is for the first time reported by Kanatzidis and coworkers in 1995[11]. Much of the research associated with PEDTT has been attributed to its incorporation with other conjugated structures or other functional groups in its structure [12-18]. The PEDTT and its derivatives are potential candidates for applications as electron donor materials in photovoltaic devices [12--16], cathode active materials for rechargeable lithium batteries with better cathode capacity than PEDOT [17]. However, the presence of sulfur atoms in EDTT, in place of oxygen atoms of EDOT, does not exactly justify the very distinct properties exhibited by the two monomers e.g. EDTT has a lower oxidation potential as against EDOT, may be due to electron donating mesomeric effects exhibited by sulfur.[8-19]

Water is a most ideal medium for synthetic chemistry due to its low operational cost, safety, and green nature [20-24] but many organic materials are water-insoluble or only sparingly soluble. To overcome the solubility problem in water, synthetic processes employing surfactant-stabilized emulsions and suspensions have been developed. As a conventional synthetic method, electrochemical polymerization of aromatic heterocyclic compounds with concurrent polymer film deposition has played a very important role in polymer science and it has been proved to be an especially effective method for the preparation of high-quality conjugated polymer film. However, still there is a long way to go to reap up its maximum potential as a “green” pathway. Electrochemical transformations of immiscible materials in aqueous electrolytes have been also investigated.[25-27] Conducting polymers have been

widely studied in aqueous media, such as polypyrrole, polyaniline and PEDOT [28-31]. However, electrochemical polymerization of EDTT was only found to be possible in organic electrolytes [32-33] or ionic liquid [34]. In order to develop new polymerization system and to broaden the application areas of PEDTT, the mild conditions used for electrochemical polymerization in aqueous solution are perfect choice and ideal for incorporation of enzymes, antibodies or even whole living cell. Based on these considerations above, water still seems to be more attractive for the large scale synthesis of PEDTT and their usage in biosensor field than any other solvent from the viewpoint of cost, handling and safety [35-39].

Materials and Methods:

All the chemicals used for experimentation purpose were AR grade (Sigma Aldrich make). For emulsion polymerisation of 3,4-ethylenedioxythiophene (EDOT) semi batch reactor was used. Emulsion polymerization of 3,4-ethylenedioxythiophene (EDOT) was carried out in a 500 ml four necked reaction vessel equipped with sonication probe, thermometer, nitrogen supply and for drop wise monomer addition. Pre-weighed sodium lauryl sulphate (surfactant) and 250 ml of water were mixed in a beaker and the solution was subjected to sonication for complete dissolution to take place at room temperature. Then ammonium persulphate as a initiator was added to the reaction mixture with simultaneous stirring at ambient temperature. Further EDOT (monomer) was added at the rate of 1 drop/sec. The reaction mixture was then sonicated for about 2 hrs. at 275 rpm. Nitrogen was continuously bubbled through the solution for providing inert atmosphere to prevent oxygen from reacting with the radicals generated in the reaction which can otherwise hamper the polymerization process. On polymerization of the product PEDOT black in colour was centrifuged with centrifuge REMI, ω = 15000 rpm, washed by acetone (3 X 15 ml). The polymer thus obtained was then dried by tray drier till final product is obtained. The filler material ZnO was added slowly during polymerization of PEDOT with constant stirring using ultrasound. The experimental set up used for the experimentation purpose is as shown in fig.3.

Results and Discussions:

Fig.1. shows the characteristic structure of the polymer PEDOT. The conductivity of PEDOT film can be enhanced by adding compounds like ZnO. The additive induces a conformational change in the PEDOT chains. Both coil and linear or expanded-coil conformations exist in untreated PEDOT films, whereas the linear or expanded-coil conformation becomes dominant contributing to high conductivity of PEDOT films. This conformational change results in an increase in the intrachain and interchain charge-carrier mobility, so that the conductivity is enhanced [4]. Fig.2. shows the spherical micelle formed by the surfactant, Sodium Dodecyl Sulphate (SDS) is a surfactant which provides a template and each micelle in itself acts as a microreactor for the polymer to form and thus the concentration of emulsifier influences the size of

polymer chain. Fig.3. shows the experimental set up used for the polymerization and composite preparation purpose. For emulsion polymerisation of EDOT semi batch reactor equipped with sonication probe (sonotrode), magnetic stirrer and nitrogen supply was used. The reactor used was a closed vessel with provisions for continuous monomer supply and inserting sonication probe through two inlets of a four necked glass reactor. The product on completion of the reaction followed by centrifugation was dried using heater and tray drier.

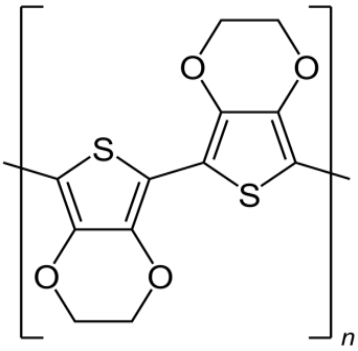

Fig. 1. Poly (3, 4-Ethylenedioxythiophene)

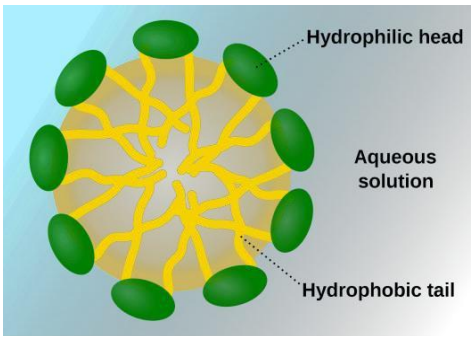

Fig. 2. Micelle Structure

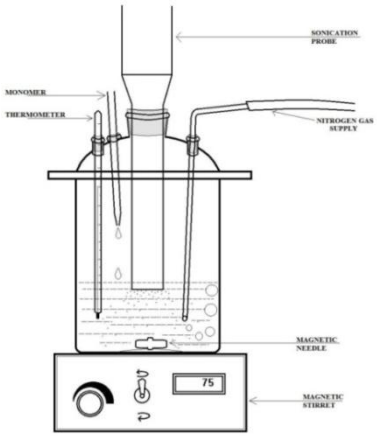

Fig. 3. Experimental set up

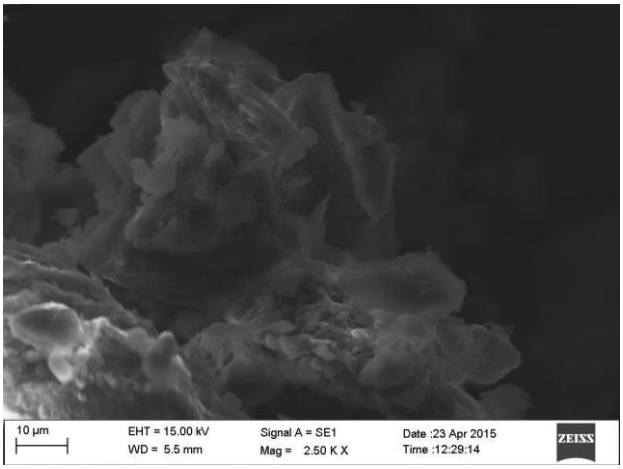

Fig. 4. SEM image of PEDOT

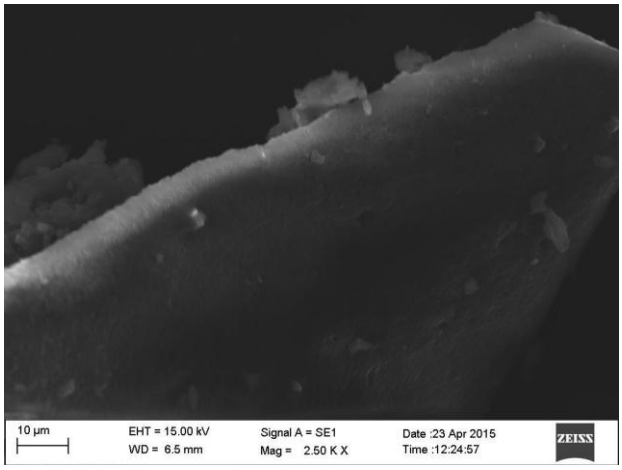

Fig. 5. SEM image for PEDOT-ZnO composite

FT-IR spectrum of synthesized polymer shows the peaks at 1525 and 1330 cm^{-1} (C-C and/or C=C stretching vibrations in the thiophene ring), 1197 cm^{-1} (for C-O-C bond), 991, 850 and 690 cm^{-1} (ν(C-S) and δ(C-H)) [6]. Thus one can conclude that emulsion polymerization product is PEDOT. Thus the characteristics same as that shown in the earlier literature, namely by Lei Y. et al. [5]. It was proposed that PEDOT has lamellar or sheet structure, in each of them PEDOT chains are lying parallel to one another with doping agent ZnO embedded in the form of inclusion in the body of PEDOT. The composite is washed with milli Q water to purify it which brings about increase in conductivity from 1 S/cm to approx.150 S/cm. Fig. 4. Shows the SEM-image of PEDOT wherein shapeless flat but lamellar structural formations. In order to enhance PEDOT conductivity heating of it is proposed which can lead to its postpolymerization resulting into comparatively more regular structure. Fig.5. is meant for SEM image of the nanocomposite of PEDOT with ZnO which shows the

latter one being distributed in the body of PEDOT in the form of inclusion which add up conductivity to the former one.

Conclusions:

Emulsion polymerization has been successfully used as a innovative, cheap and simple synthetic method for PEDOT leading to obtaining a better conductivity product of the order of 150 S/cm which furthers on adding ZnO as a filler material. The polymer PEDOT obtained has got a lamellar or flat sheet like structure which has irregularity in terms of shape or morphology but heating can bring in reasonable regularity in the structure of the polymer and nanocomposite in turn. The properties and structural aspects exhibited by the polymer, PEDOT are in tandem with that reported in the earlier literature.

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