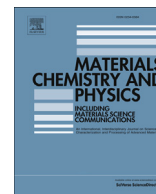




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Electrochemical synthesis of novel polymer based on (4-(2,3-dihydrothieno[3,4-6][1,4][dioxin-5-yl) aniline) in aqueous solution: Characterization and application

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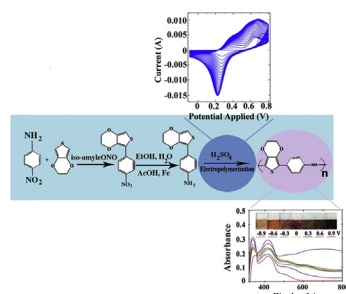
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HIGHLIGHTS

- A Novel monomer comprising aniline and EDOT was synthesized by a simple process.
- Poly (ANI-EDOT) was synthesized and characterized by cyclic potential sweep method.
- The copolymer changes from yellow at -0.9 V to dark green color at $+0.9$ V reversibly.
- Poly (ANI-EDOT)/graphene is porous with electrocatalytic effect on I_3^- reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

4-(2,3-dihydrothieno[3,4-6][1,4][dioxin-5-yl) aniline, an interesting novel monomer was successfully synthesized in which α -carbon on ethylenedioxythiophene was linked to aniline at para position. The structure of the monomer was approved by infrared (IR), gas chromatography-mass spectrometry (GC-MS) and ^1H nuclear magnetic resonance (^1H NMR) spectroscopies. Poly (4-(2,3-dihydrothieno[3,4-6][1,4][dioxin-5-yl) aniline) and its composite with graphene were electrochemically synthesized in aqueous solution by cyclic potential sweep method. The Polymer was characterized by IR and UV-vis spectroscopies, scanning electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy techniques. Electrochemical synthesis conditions were optimized to prepare high conducting and porous polymer so it can be efficiently used as a counter electrode in fabrication of dye sensitized solar cells. Photovoltaic experiments revealed that energy conversion efficiency of the solar cell fabricated using polymer composite (7.52%) is 21% greater than that prepared by Pt counter electrode (6.19%).

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1. Introduction

Development of new emerging technologies necessitates studying the new materials with collection of properties in demand. In past three decades tremendous studies have been devoted

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to synthesis, characterization and application of conducting polymers [1–10]. This great deal of attention is mainly due to versatile properties of conducting polymers which can be well tuned in order to create desired substances applicable in various fields of science and technology [2]. Synthesis of the conducting polymers is mostly limited to the polymerization of a few very well-known monomers such as aniline (ANI), thiophene, pyrrole and their derivatives [11–20]. Therefore, development of new conductive materials with desired properties for employing in fabrication of new devices have conducted several researchers to synthesize new polymers through simple mixing of the conventional monomers [11–15] or via synthesis of new monomers [1,6–8]. Random copolymerization leads to formation the polymers consisting of two or more monomers randomly distributed in polymer chains. It is a simple way to prepare polymers with combined properties of both monomers incorporating in polymer backbone. However, the control of the incorporation of each monomer in formation of polymer chains are significantly influenced by experimental conditions such as monomer feed ratios, reactivity of the monomers, temperature, rate of oxidation and so on [21–23]. Synthesis of the monomers including moieties with desired properties is a good solution to surmount the rarity of the monomers suitable for synthesis of the conducting polymers having alternating structure with synergistic combination of the properties [1,6–8]. By this way, structure of the polymer is not influenced by relative reactivity of two monomers (which is a non-controllable important parameter) and also their fixed 1:1 feed ratio in monomer structure is kept in polymer chains. ANI and ethylene dioxythiophene (EDOT) conductive polymers have been widely used in making of new electrical and optical devices [24–28]. High stability and conductivity, low cost, easy preparation, and electrocatalyzing the reduction reaction of triiodide to iodide make them an attracting candidate as alternatives for replacing the Pt counter electrode in dye sensitized solar cells (DSSCs) [29–51]. Poly (3,4-ethylenedioxythiophene) is a particularly promising organic electrode material, which exhibits a number of desirable properties in the oxidized state, including high conductivity and excellent environmental stability. Also, it has linear chains which block the 3,4-positions of the thiophene ring. This causes the high degree of visible light transmission and high environmental stability in the conducting state, along with a tendency toward multiple redox switching due to its ease of oxidation [12–19]. On the other hand poly aniline (PANI) shows higher electrocatalytic property toward triiodide reduction reaction [29,49]. Then it seems preparation of a copolymer of ANI and EDOT leads to a polymer comprising both properties of high conductivity and good electrocatalytic effect. Several studies have been carried out for random copolymerization of aniline-thiophene, ANI-EDOT and aniline-pyrrole monomers [11–22]. Random copolymerization of the ANI-EDOT has been performed in acetonitrile and also aqueous solutions and the prepared copolymer was characterized and used for making of modified electrode for the purpose of determination of ascorbic acid [12–17]. Since of large difference in oxidation peak potentials of the ANI (0.65 V) and EDOT (0.95 V), copolymerization of these monomers in solution containing a mixture of two monomers is difficult and it is necessary to add a suitable surfactant such as sodium dodecyl sulphate (SDS) to reduce the difference between oxidation potentials of the monomers in order to facilitate formation of their copolymer [12,13]. However based on best of our knowledge synthesis of the 4-(2,3-dihydrothieno[3,4-6][1,4][dioxin-5-yl] aniline (EDOT-ANI; a monomer comprising aniline and EDOT moieties) and corresponding alternating polymer has not been performed at all. In the ongoing study the monomer is synthesized via a simple two step method for the first time. We begin with the para nitro aniline and EDOT as starting materials so EDOT is substituted on the benzene ring and

5-(4-nitrophenyl)-2,3-dihydrothieno[3,4-6][1,4]dioxine is synthesized Fig. 1. In second step nitro group is easily reduced to amine functional group and the desired monomer is prepared. The monomer is separated from by-products and unreacted materials and purified using column chromatography. The structure of the monomer is identified and characterized by IR, NMR, and GC-MS techniques. Then it was electropolymerized on the surface of the FTO electrode in 0.5 M H₂SO₄ solution using cyclic potential sweep method. The switching potential was set at 0.8 V which is slightly upper than aniline oxidation peak potential. It is sufficiently low that can cause degradation of the polymer adhered to the surface of the electrode. Subsequently, the polymer coated electrode was used as counter electrode in fabrication of DSSC.

2. Experimental

2.1. Materials

Isopentyl nitrite and 3,4-ethylenedioxythiophene (reagent grade) were prepared from Merck and used without further purification. Aniline (reagent grade) was purchased from Merck and distilled under reduced pressure and kept far from light in refrigerator for subsequent uses. Hexadecyltrimethylammonium bromide (HDTMAB) and other reagent grade chemicals were also purchased from Merck. Conductive glass (FTO glass, sheet resistance 8 Ω sq⁻¹, purchased from South Korea) was used as working electrode and also substrate for deposit TiO₂ porous film. Anhydrous ethanol, iodine (I₂), potassium iodide (KI), hexachloroplatinic acid (H₂PtCl₆), and sensitizing dye (N719) were purchased from Merck and used without further purification. Graphene nanoflakes were prepared by method reported in literature [52].

2.2. Monomer synthesis

Monomer was synthesized via a two-step procedure reported previously by our group for synthesis of 4-(2-furyl) benzenamine [1]. Briefly the steps can be described as follows:

Step A: Isopentyl nitrite (2 mL, 0.008 mol) was added slowly to a solution of 4-nitroaniline (1.38 g, 0.009 mol) in acetonitrile (100 mL (while stirring)). After the color of the solution changed to yellow, EDOT (1.6 mL, 0.015 mol) was quickly added to the mixture and the resulting mixture was stirred for 3 h at room temperature. Then the excess of acetonitrile was evaporated under reduced pressure. The crude product of 5-(4-nitrophenyl)-2,3-dihydrothieno[3,4-6][1,4]dioxine was purified on silica gel column with ethyl acetate/hexane (1:5) as the eluent, and then crystallized from diethyl ether.

IR spectrum for 5-(4-nitrophenyl)-2,3-dihydrothieno[3,4-6][1,4]dioxine, is shown in Fig. 1Sa. Yellow. m.p.: 176–179 °C. IR (KBr) (ν_{\max} , cm⁻¹): 1590, 1477, (Phenyl), 1503, 1335 (NO₂), 1277, 1177, 1063 (C–O–C), 917, 749, 668 (C–S).

Step B: 5-(4-nitrophenyl)-2,3-dihydrothieno[3,4-6][1,4]dioxine (0.2 g, 0.0009 mol) was dissolved in a triple mixed solvent including ethanol (2 mL), acetic acid (2 mL), H₂O (1 mL) and then iron powder (0.3 g, 0.005 mol) was added to the mixture and subjected to the ultrasonic radiation at 30 °C for 2 h. The mixture was filtered and the precipitate was treated with ethyl acetate and the filtered solution was basicified with 20 mL KOH (2 M). The organic phase was separated and the aqueous phase extracted with ethyl acetate, then solvent was evaporated under reduced pressure and the residue was purified on silica gel column with ethyl acetate/hexane (1:6) as eluent and then crystallized from diethyl ether.

IR, ¹H NMR and GC-MS spectra of 4-(2,3-dihydrothieno[3,4-6][1,4][dioxin-5-yl] aniline are shown in Figs. 1Sb, 2S and 3S, respectively. Brown powder; m.p. 227–230 °C. IR (KBr) (ν_{\max} , cm⁻¹): 1617, 1485, (Phenyl), 3410, 3520 (NH₂), 1262, 1166, 1066 (C–O–C),

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