



Electrochemical and morphological analysis on novel phthalocyanine grafted conductive polymeric nanofibers



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ABSTRACT

Metal free phthalocyanine grafted polypyrrole and cobalt metallated phthalocyanine grafted polypyrrole nanofibers were prepared by electrospinning method. The electrospun PPy and phthalocyanine grafted polypyrrole fibers were coated on indium tin oxide electrode surface for a proper investigation of the electrochemical activity of the fibers. Different methods were used to characterize the obtained fibers. Fourier-transform infrared spectroscopy, Scanning electron microscope and polarized optical microscope were used for their morphological characterization, while electrical behaviors of the nanofibers were characterized by direct current and electrochemical impedance spectroscopy measurements.

The synthesis and characterization results showed that the incorporation of phthalocyanine metal chelate affected the electrical behavior of the fibers. The electrical conductivity of the Polyvinylpyrrolidone fiber was improved by grafting cobalt metallated phthalocyanine to the polypyrrole main chain, while the unmetallated phthalocyanine showed an unforeseen electrical property.

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1. Introduction

Nanofibers possess exclusive physical, chemical, and electronic properties. Although different methods are known [1,2], electrospinning has been used with an increasing impact because of the ease of proceeding and the use of a wide range of polymeric materials [3,4] in the production of nanofibers. This electrostatic technique consists by the propulsion of a polymer solution through an electrostatic field created by a high voltage applied syringe and an oppositely charged collector where the fibrils are formed. The applied electrical field, the collector distance, and the assets of the polymer solution had an immense effect on physical and morphological properties of the fiber such as the diameter, the surface area per unit mass and the pore size [5].

On the other hand, conductive polymers have displayed a great impact in the last two decades because of the mutual electrical properties of organic polymers and metals characteristics. The fabricated nanofibers prepared with conductive polymers have found usage in the construction of nanoelectronic [6,7], electrochromic devices [8], active coatings [9], sensors [10], and actuators [11]. The good electrical conductivity and thermal stability of the five-membered heterocyclic ring structured polypyrrole (PPy) conjugated conductive polymer makes it a good candidate among

other conductive polymers for the synthesis and characterization of nanoscale materials in diverse applications [12–15].

Phthalocyanines were known as dye and pigment agents during a long period. They are known nowadays for their nonlinear optic applications and also electroactive behavior procured with the incorporation of a transition metal on its structure [16–18]. Phthalocyanines are composed by four pyrrole ring and are used as electron donor or acceptor according the addition of substituted groups [19]. Because of the thermal, chemical and optical stability and the formation of an aligned crystalline film phthalocyanine derivatives have found applications as photovoltaic cells, solar cells, sensor electrodes, drug release systems, gas detectors and electroactive devices [20–23]. Their copper, nickel and cobalt incorporated chelates are known for their relatively high conductivities [23–27]. Along with that, cobalt phthalocyanines have usage in a variety of field such as air purifier [28], ion selective sensors [29] and optoelectronics [30].

Challenging efforts are given to incorporate metallic groups to improve the conductivity of carbon based polymeric fibers [31–33] in various applications. In this investigation, we report the synthesis and characterization of electrospun solution mixture of PPy and PVP acting as carrier in order to improve PPy processability to obtain nanofibers and also by incorporating a grafted metal phthalocyanine [34] to stabilize the metallic ion in the fiber structure instead of the only addition of metal salts and by this way improve electrochemical properties.

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The conductivity and the evaluation of the charge transport behavior of electrode material at the electrode/electrolyte interface were analyzed with the widely used electrochemical impedance spectroscopy (EIS) method [35,36]. In EIS the system under study is subjected to perturbations by applying a sinusoidal voltage of small amplitude (10 mV) with variable frequency (0.01 Hz–10 kHz) recording the imaginary component (Zim) of the impedance and the real component (Zre) as a function of the frequency. The Nyquist plot conferring the imaginary component against the real component is fitted to simple equivalent circuits and important information on the electrode–electrolyte interface, such as electron transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and Warburg element (W) are collected.

The compositions optical, morphological and topographical structures of these fibers were determined by Fourier transform-infrared (FT-IR) spectroscopies. Their structural and topographic properties were also determined by polarized optical (POM), and scanning electron (SEM) microscopic methods.

2. Experimental

2.1. Materials

The monomer, Pyrrole (Py; Sigma–Aldrich, Germany) and Polyvinylpyrrolidone (PVP; Sigma–Aldrich, Germany) were used without further purification. Phthalocyanine (Pc) complexes were synthesized in the MAMARG laboratory facilities. Ammonium persulphate (APS; Sigma–Aldrich, Germany) was chosen as initiator. Acetonitrile (ACN; Sigma–Aldrich, Germany), tetrahydrofuran (THF; Merck, Germany), dimethylformamide (DMF; Merck, Germany) and dimethylsulphoxide (DMSO; Fluka, Germany) were chosen as solvents.

2.2. Analysis and characterization techniques

Polypyrrole, phthalocyanine and Polypyrrole-grafted phthalocyanine fiber samples were analyzed and characterized by using Fourier transform infrared spectroscopy (FTIR), polarized optical microscope (POM), direct current (DC), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements. FTIR spectra of the samples were recorded on Perkin Elmer Spectrum One (FTIR-reflectance, Universal ATR with diamond and ZnSe) spectrometer. Optical micrographs of fiber samples placed between two lamellae were taken with a Leica DM-2500P model polarized optical microscope under bright field and cross-polarized light (at 90°) conditions. The morphology of the samples was studied by scanning electron microscope JEOL/JSM-6335F. All the samples used for DC conductivity measurements were placed between two identical Pt electrodes in a conductivity cell. The slope reciprocal of the potential versus current plot in the range of 1.0–10.0 V yields the conductivity (Keitley picoammeter Model 6487).

For the voltammetric measurements, ITO coated fibers were chosen as working electrode, Pt wire was used as the counter electrode, and a silver (Ag) wire as the pseudo-reference electrode were used for all electrochemical characterizations in ACN + 0.1 mol/L TBAClO₄ (Tetrabutylammonium perchlorate) system using a Gamry 600 potentiostat. All fibers were doped before analysis at 1.5 V for 10 min. The conductivities of the materials were calculated from the data obtained by EIS in the frequency of 10 mHz to 10 kHz. Equivalent circuit was used to fit the experimental data, with the help of the ZsimpWin v3.10 software. The bulk conductivities were calculated from the bulk resistance value obtained from the complex impedance diagram.

2.3. Preparation of PPy homopolymer

Polypyrrole homopolymer was synthesized using APS as initiator for the oxidative polymerization of the brown colored pyrrole monomer in acidic media and 5 °C, to improve yield. The mixture was magnetically stirred for 24 h. The obtained black-colored precipitate product was filtered and washed several times with methanol and toluene, until no unreacted chemical were left. The obtained black powder product was dried under vacuum at room temperature to constant weight [37].

2.4. Preparation of phthalocyanine complexes

Carboxylic acid substituted 2(3), 9(10), 16(17), 23(24) – Tetrakis (carboxymethylsulfanyl) cobalt (II) phthalocyanine molecules were synthesized for this purpose. Cobalt (II) phthalocyanine was synthesized according to conventional method with 4-(4-carboxyphenoxy) phthalonitrile in the presence of CoCl₂ in n-pentanol at 140 °C for 24 h by cyclotetramerization. The obtained product was precipitated and filtered in n-hexane. The obtained green colored product was purified by column chromatography, then characterized by FTIR and NMR [38] and labeled as CoPc. To compare the electrochemical effect of cobalt, an unmetallated phthalocyanine was synthesized in the same synthesis conditions in the absence of CoCl₂, and was labeled as H₂Pc. A single symmetrical phthalocyanine product with a carboxylic acid functional group is obtained.

2.5. Preparation of phthalocyanine grafted polypyrrole

Polypyrrole was dispersed in DMF solution. Phthalocyanine was added at 10.0 wt% with respect to the polymer. The mixture was kept under constant temperature in N₂ atmosphere and magnetically stirred for 96 h at 60 °C, until the formation of phthalocyanine grafted polypyrrole was realized. The obtained precipitated product was filtered and washed until no reactant was left. The obtained product was dried under vacuum at constant temperature to constant weight. A schematically presentation of the grafting process is given in Scheme 1. As seen from the FTIR spectrum in Fig. 2, the presence of phthalocyanine –OH peak after the reaction process confirms the presence of unreacted phthalocyanine carboxylic acid groups.

2.6. Preparation of ITO/PPy and ITO/PPy-g-Pc nanofibers electrodes

Pristine PPy molecular weight is not high enough to form fibers on its own through the electrospinning process [39]. Therefore, it has to be electrospun as a mixed solution containing other high molecular weight polymers such as polyvinylpyrrolidone (PVP); unfortunately this lowers the conductivity. The PPy and PPy-g-Pc fibers were prepared by electrospinning a solution of PVP (10 wt/v%) and PPy (or PPy-g-Pc) (at 0.1 and 1.0 wt /v%) blends in DMF using a magnetic stirrer for 24 h at room temperature. Although, polypyrrole is known to be insoluble in DMF, it dispersed up to 1.0 wt/v% in the presence of PVP which acted as a stabilizer and/or dispersion reagent [40]. Blend solutions were poured into a syringe and delivered at a constant flow rate to a needle with a blunt tip connected to a high voltage power supply producing a voltage of 15 kV. With the applied voltage, the solvent was evaporated and charged polymers were deposited on the ITO-PET electrode placed on an aluminum foil collector in the form of nanofibers (Fig. 1). The obtained nanofibers were thermally cured by heating at 150 °C under vacuum to obtain crosslinked PVP which is insoluble by definition, and be described as polyvinylpolyrrolidone (PVPPP). To get rid of confusion the obtained ITO/PVPPP/

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