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Poly (dithienylpyrrole) / Keggin type $(n\mathrm{Bu_4N})_3[\mathrm{PW_9O_{34}}(t\mathrm{BuSiOH})_3]$ hybrid material: Enhanced optical and electrical properties of conjugated polymers via polyoxometalates

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ABSTRACT

Conductive polymers with unique optical and electrical properties are ideal matrices for redox active inorganic materials in the development of flexible, easily processable conductive materials for promising applications. Polyoxometalates (POMs) are a class of inorganic materials consisting of soluble, anionic metal oxide clusters of transition metals exhibiting enormous versatility in their structural features and properties. The properties as well as the processability of POM clusters can be enhanced by combining them with conducting polymers, either electrostatically or covalently, resulting in organically modified POMs, which have found extensive applications in diverse fields. For this purpose, we electrochemically incorporated a Keggin type POM anion, $(n\mathrm{Bu_4N})_3[\mathrm{PW_9O_{34}}(t\mathrm{BuSiOH})_3]$, into a dithienyl pyrrole based conducting polymer (pDOB). Obtained organic-inorganic hybrid composite film has superior optical and electrical properties when compared to PDOB. Also composite film with advantages such as high optical contrast, low response time, long-term stability etc. is promising to meet the requirement for constructing smart windows, supercapacitors and electrochromic devices.

1. Introduction

Polyoxometalates (POMs) are novel inorganic metal oxide clusters that attracts the scientists attention for the last years [1–7]. They can be defined as metal-oxo cluster anions that include a large range of structures in terms of elemental composition and size.

One of the most important characteristics of the polyoxometalates (e.g. Keggin-, Dawson- and Finke-type POM anions) is their ability to accept electrons, which makes them very attractive for use in the preparation of organic inorganic hybrid polymer in electrochemistry [8,9]. Due to their interesting optical and electrical properties, POMs have been investigated in different fields such as, materials science [10,11], medicine [12], different sensors application [13,14], capacitors [15], catalysis [16], optical devices, molecular electronics and corrosion protection [17–19]. One important class of hybrid materials containing POMs is POM/polymer hybrids. Polymers are among the most widely used materials and the incorporation of POM clusters into polymers is believed to improve their functionality and hence widen their scope of applications [20].

There are several procedures based on electrostatic interactions, electrochemical deposition, entrapment into polymeric matrices or layer-by-layer (LbL) self-assembly techniques, for the design modified electrodes by POM derivatives [21–28]. The most widely investigated conducting polymers used in electrode modification are polypyrrole or polyaniline which can be doped with anionic species such as redox-active Keggin-type polyoxometalates [29–39]. Furthermore, polythiophene derivatives have been investigated as host materials for heteropolyanions, incorporating phosphometalates and silicometalates [15,40].

In this study, a hybrid composite of tungsten-based Keggin type POM and amide substituted dithienyl pyrrole derivative conductive polymer has been electrochemically synthesized in order to improve the optical and electrical properties of conductive polymers for technological applications. For this purpose, firstly the POM derivative $(n\mathrm{Bu_4N})_3[\mathrm{PW_9O_{34}}(t\mathrm{BuSiOH})_3]$ was obtained by condensation reactions of tungsten (VI)) hydroxide complexes in acidic medium. After that, electroactive monomer *N*-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)-4-(dodecyloxy) benzamide (DOB) was synthesized as the amide-substituted dithienylpyrrole derivative. The electroactive monomer was polymerized electrochemically by optimizing the synthesis conditions and

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monomer feed ratios in the solution containing POM. Thus, POM anions incorporated in the conducting polymer structure to form a hybrid composite structure via theirs interaction with cationic polarons and bipolarons in polymer structures formed during the electrosynthesis. Conducting polymers modified with POM are promising to meet the requirement for developing flexible displays and electrochromic devices in term of long-term stability, high optical contrast, suitable response time and low operation potential.

2. Experimental section

2.1. Chemical and equipment details

All chemicals and reagents were used as commercial products without any purification. For the electrochemical deposition, electrically conductive and optically transparent indium tin oxide (ITO) coated glass slides from Delta Technologies (7 × 50 × 0.5 mm thickness and 8–12 ohm.sq^{-1}) was used as a working electrode. (nBu$_4$N)$_3$[PW$_9$O$_{34}$(tBuSiOH)$_3$](POM) was synthesized according to literature [41]. Synthesis procedure of *N*-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)-4-(dodecyloxy) benzamide (DOB) was carried out according to published literature [42]. ^{1}H and ^{31}P NMR spectra were measured on Varian 400 NMR spectrophotometers. Ivium Compactstat electrochemical potentiostat/galvanostat was used for electrochemical polymerizations and characterizations. Electrochemical deposition of composite film on ITO electrode was carried out in a three-electrode set-up using an Ivium Compact stat with the platinum wire as a counter electrode, and Ag wire as a reference electrode. Spectroelectrochemical measurements were recorded on an Agilent 8453 UV–vis spectrophotometer and electrolyte solutions were prepared using 0.1 M in the acetonitrile–lithium perchlorate (ACN/LiClO$_4$) couple. For the surface characterization, NT-MDT (Ntegra Solaris) model AFM and Zeiss (EVOLS10) model Scanning Electron Microscopy (SEM) were used.

2.2. Synthesis of POM and DOB

N-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)-4-(dodecyloxy) benzamide (DOB) [42] and POM [41] were synthesized as in literature (Scheme 1).

2.3. Preparation of POM doped pDOB films

POM doped pDOB films were synthesized by electropolymerization method in POM and DOP containing electrolyte solution. For electropolymerization process, cyclic voltammetry technique was used at a scan rate of 100 mVs^{-1} and indium tin oxide (ITO) (surface area = 1.2 cm^2) was used as the working electrodes. 5 mM DOB and 0.25 mM POM have been dissolved in 0.1 M LiClO$_4$/acetonitrile for electrochemical polymerization medium. In order to have the same characteristics of the prepared POM/pDOB films, the cyclic voltammetry experiments were fixed to 6 cycles. Oxidation–reduction behaviors of POM/pDOB were examined by cyclic voltammetry (CV) in 0.1 M LiClO$_4$/ACN.

2.4. Investigation of electrochemical and spectroelectrochemical properties

The electrochemical behaviors of DOB and POM were investigated using a three-electrode cell. All electrochemical measurements were performed at room temperature on an Ivium Compactstat Potentiostat. Polymerization was carried out by mixing at different ratios POM and DOB in 0.1 M LiClO$_4$ / ACN electrolyte solution to determine optimum POM/pDOB ratio. It was determined that the best optical and electrical properties were obtained in a mixture of 0.25 mM POM and 5 mM DOB, and all electrochemical studies were performed using this ratio. The total charges (Q$_d$) of composite films were calculated from the integrated area under the cyclic voltammetry curves as in literature [43]. Spectroelectrochemical properties of the composite film was examined by an Iviumstat model potentiostat-galvanostat and an Agilent 8453 model UV–vis spectrophotometer in monomer free solution.

3. Results and discussion

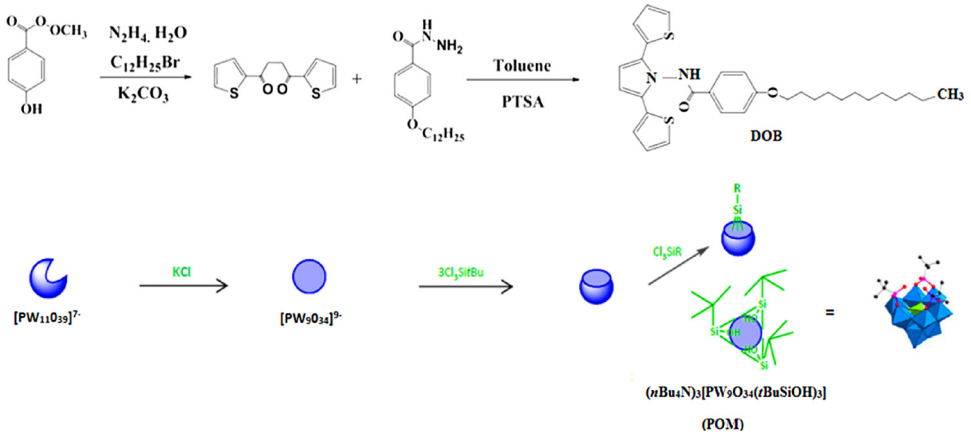
POM doped pDOB film was deposited potentiodynamically on ITO electrode from determined ratio of POM and DOB mixture. Cyclic voltammetry technique was carried out with cycle number of 5–10 at scan rates of 50–100 mV/s. The best result has been obtained at scan rate 100 mV/s and five cycles. Electronic structure of the composite film was investigated by switching between the oxidized (conductive) and the reduced (insulating) states. Oxidized composite film has a transparent sky blue color that turns dark green upon reduction. It is believed that the composite structure is formed by electrostatic interactions, due to the ionic interaction between the positively charged active centers of the oxidized pDOP and the negative charges of the anionic POM structure [44].

3.1. Characterization

The monomer, *N*-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)-4-(dodecyloxy) benzamide (DOB), has been synthesized via reaction of 1,4-di(2-thienyl)-1,4-butanedione and 4-(dodecyloxy)benzohydrazide. The structure of the monomer was confirmed by 1H-NMR and ^{13}C-NMR spectral analyses [42].

^{1}H NMR (400 MHz, CHCl$_3$) δ 8.6 (s; 1H^g), 6.5–7.8 (m; 12H^{d,e,f}), 4.0 (s; 2H^c), 1.2–1.9 (m; 20H^c), 0.7 (s; 3H^a).

^{13}C NMR (101 MHz, CHCl$_3$) δ166.72, 162.88, 132.60, 129.54,



Scheme 1. Synthesis routes of DOB and POM. Color codes: WO$_6$ octahedron, blue; PO$_4$ tetrahedron, green; organic silane, pink; C, black; O, red (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).