Synthetic Metals 244 (2018) 54–60

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

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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ARTICLE INFO

Keywords:
Polyoxometalates
Electrochemistry
Conducting polymer
Electrochromic
Spectroelectrochemistry

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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https://doi.org/10.1016/j.synthmet.2018.06.015
Received 18 April 2018; Received in revised form 25 June 2018; Accepted 27 June 2018