

Electrochromic behavior of drop-casted thin films combining a semi-conducting polymer mixed with a Keggin-type polyoxometalate

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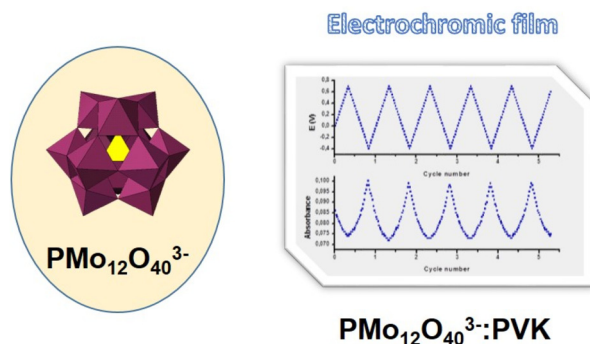
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HIGHLIGHTS

- A polyoxometalate has been incorporated into a polymer.
- An electrochromic behavior has been evidenced.
- An hybrid organic/inorganic film has been prepared with PVK.
- Electrochromism has been characterized by spectroelectrochemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

A drop-casted thin film consisting of a Keggin-type polyoxometalate cluster $K_3PMo_{12}O_{40}$ mixed with the semi-conducting poly(*N*-vinylcarbazole) (PVK) was deposited on top of ITO substrates. The resulting hybrid organic/inorganic film was characterized by electrochemistry, FT-IR spectroscopy, microscopies and spectroelectrochemistry. Interestingly, an electrochromic behavior could be evidenced from the resulting composite.

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1. Introduction

Hybrid organic–inorganic materials exhibit so adaptable properties that they can be considered as one of the most interesting classes of materials for the future development of both passive and active devices for photonic and electronic applications [1–4]. If the tunability of the optoelectronic properties is a highly desirable characteristic, the combination of fundamental properties such as

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switchability/reversibility/stability with the appealing features of being easy to handle and easy to fabricate remains a challenge. Among inorganic building blocks classically used for the design of hybrid organic-inorganic materials, polyoxometalates (POMs) are one of those [5–7]. Polyoxometalates constitute a large class of well-defined polynuclear oxo-bridged early transition metal compounds characterized by a vast diversity of structures. As specificity, POM clusters can undergo multiple reversible and stepwise electron-transfer reactions without significant modification of their structures, and the term of “electron reservoir” is often associated with these inorganic structures [8–16]. When metal-oxygen clusters based on vanadium, molybdenum and tungsten are reduced, generation of the reduced form leads to a drastic change in color of the solution that turns deep blue. It corresponds to the formation of the so called “heteropoly blue” anion [17–20] whose presence can be visually confirmed by the appearance of this typical color [21–23]. This unique property made V, Mo and W-based POMs attractive candidates for electrochromic applications [24–27]. Ability of POMs to change of color upon reduction is not limited to electrochromism and one of the most popular application of this for chemists is the detection of stains on thin layer chromatography (TLC). In this field, the most popular TLC revelation reagent is undoubtedly phosphomolybdic acid $H_3PMo_{12}O_{40}$ which is a cheap and commercially available material capable to stain most of the functional groups [28]. Upon reaction with the substances on TLC,

the initial Mo(VI) is reduced to Mo(V), giving rise to a color change of the stains from yellow-green to blue. While coming back to electrochromism of polyoxometalates, one major drawback of these inorganic compounds is clearly their lack of processability from the viewpoint of material science, drastically restricting the range of applications [29]. Typically, to be examined as electrochromic, polyoxometalates require to be assembled with a matrix to form a film of acceptable quality and polymers are candidates of choice for this purpose. Through of a proper selection of both the polyoxometalate and the polymer matrix, the resulting polyoxometalate/polymer hybrid material can uniquely exhibit the functionality of the selected polyoxometalate.

In this work, we propose hybrid films combining the well-known polyoxometalate cluster $PMo_{12}O_{40}^{3-}$ mixed with the semi-conducting polymer poly(*N*-vinyl-carbazole) (PVK). Precisely, $PMo_{12}O_{40}^{3-}$ was selected due to its commercial availability, redox properties and stability [24]. Parallel to this, PVK was chosen as host for $PMo_{12}O_{40}^{3-}$ due to its excellent film-forming properties, its high glass-transition temperature (200 °C), its good solubility in common organic solvents and its insolubility in water [30]. This polymer is also cheap, transparent and inert in the window of potential in which the electrochromic properties of the polyoxometalate cluster will be studied. Due to its high conductivity characteristics and insolubility in water, PVK is thus a good candidate to immobilize $PMo_{12}O_{40}^{3-}$ and examine uniquely the electrochromic

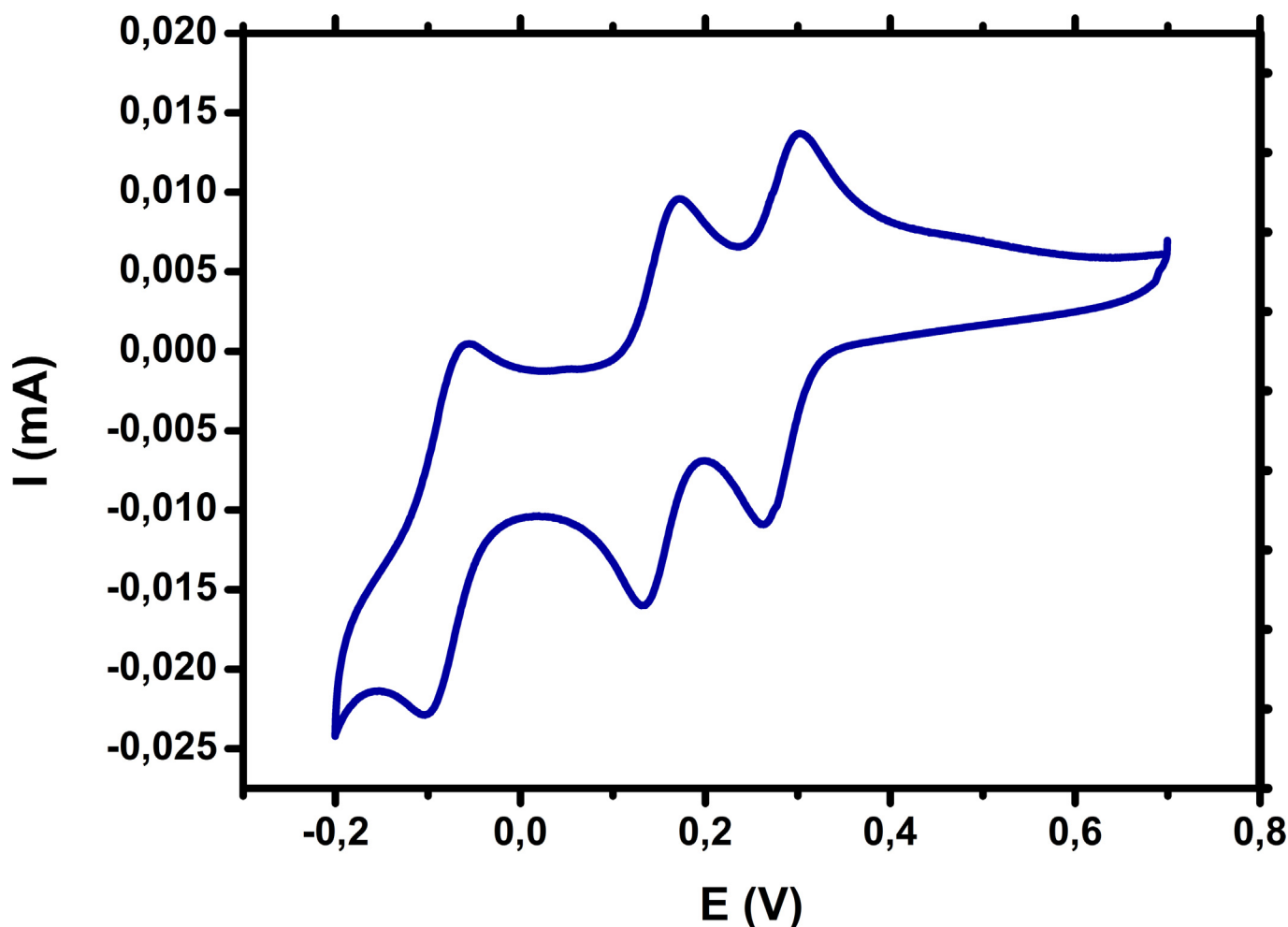


Fig. 1. Cyclic voltammogram (vs. Ag) of $H_3PMo_{12}O_{40}$ in solution (H_2SO_4 :dioxane, 1:1, v:v) pH = 1. Scan rate 50 mV/s.

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