



Preparation, characterization and photochromic behavior of phosphotungstic acid-ormosil nanocomposites



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HIGHLIGHTS

- Entrapment of HPW in sol–gel derived ormosil matrices yield photochromic films.
- Deeper insight into the nanocomposites structure is provided by XRD, NMR and HRTEM.
- Organic functionalities and HPW influence the structure of the silicate network.
- Organic modifiers influence the photochromic behavior and composition of the films.
- Photochromic response of the films decreases upon water removal by drying at 373K.

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ABSTRACT

Reversible UV-dose-dependent photochromic materials consisting of ormosil hybrid networks doped with phosphotungstic acid (HPW) have been obtained by sol–gel method. Tetraethyl orthosilicate (TEOS) and (3-glycidyloxypropyl)trimethoxysilane (GLYMO) were used as matrix-forming precursors while aminopropyltriethoxysilane (APTS) and 4-(Triethoxysilyl) butyronitrile (BuTS) as matrix-modifiers. The samples were characterized by XRD, FTIR, TEM, solid-state NMR, Raman spectroscopy, X-ray fluorescence spectroscopy and UV–Vis spectroscopy. The organic functionalities of ormosils (aminopropyl and butyronitrile groups) influence both the structure and photochromic behavior of these hybrid ormosil materials. Due to alkylammonium-phosphotungstate ion-pair formation ($-\text{NH}_3^+\cdot\text{PW}_{12}\text{O}_{40}^{3-}$), APTS induces incorporation of higher amount of phosphotungstate in the dip-coated films leading to higher photochromic response of these films compared to the BuTS-bearing ones. On the contrary, in drop-casted films with the same phosphotungstate content, the photochromic response is the same for BuTS- and APTS-containing ormosil films. However, the bleaching time required for re-oxidation of the reduced phosphotungstate is longer in APTS-based ormosil films than BuTS-based ones. The photochromic response of both kind of films decreases upon dehydration of the films suggesting the importance of the presence of water in the photochromic behavior of these films. The UV sensitivity, bleaching time and dehydration sensitivity of the ormosils can be tuned varying the matrix modifier nitrogenated silanes.

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1. Introduction

Photochromic materials have been the focus of much attention because of their potential for technological applications such as optical lenses and smart windows [1], information displays, high-density memory devices [2,3] and UV dosimetry [4]. Among these applications, UV dosimetry is particularly important because of its

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role in monitoring health risks caused by exposure to UV radiation. UV dosimetry also find important application in industrial processes depending on UV irradiation, for example photodegradation of pollutants, photo-inhibition of proliferation of pathogenic microorganisms and photo-polymerization. Therefore, research on innovative photochromic formulations for use in inexpensive and simple UV tape dosimeters is of paramount relevance.

Polyoxometalates are good candidates for the preparation of such materials because they can accept electrons and/or protons to yield mixed valence colored species (heteropolyblues or heteropolybrowns). Moreover, polyoxometalates also show good photocatalytic activity [5–7]. However, to apply these photochromic dyes in useful devices, the challenge is to develop matrix materials with adequate optical, mechanical, and chemical properties. Hybrid materials are highly appropriate in this context because they are versatile and offer the possibility to exploit the advantages of both organic and ceramic materials [8,9]. Among hybrid materials, ormosils are the natural choice to develop devices based on polyoxometalates because they can be easily incorporated by bottom-up procedures and their properties can be tuned by exploiting polyoxometalates' intermolecular interactions with different organic functionalities [10,11].

The photochromic response of the polyoxometalate ions is based on their photoreduction and, therefore, depends on their redox potential, on the pH of the medium as well as on the organic proton and electron donors [6]. Yamase has presented an explanation for the photochromic behavior of alkylammonium polyoxometalates [7], claiming that a charge transfer state is formed by the photoexcited polyoxometalate and the alkylammonium groups. Based on AFM and TEM data, Lu et al. [12] have demonstrated that a reversible photochromic film based on phosphotungstic acid (HPW) in a poly(acrylamide) host suffers morphological changes with increasing irradiation time, which were ascribed to the agglomeration of HPW nanoparticles and concomitant polymer cross-linking. The latter occurs when poly(acrylamide) transfers a proton to the bridged oxygen in the excited HPW anion ($W-O_b-W$) [13] to form a radical that starts the chain propagation and cross-linking reactions. Similarly, Carls et al. [14] observed that combining poly(vinyl alcohol), PVA, with HPW resulted in a hybrid material with photoresist properties, although a photoredox mechanism was claimed for layer-by-layer films with PVA/Dawson-type phosphotungstates/poly(allylamine hydrochloride), PAH [15]. These reports indicate the importance of both the organic functionalities and the self-assembly process in determining the photochromic response of such versatile photoactive materials. Organic functionalities can act as electron and proton reservoirs in the photochemical process, thus allowing the tuning of the photochromic efficiency, response time and reversibility.

Moving from organic matrices to the “inorganic” or ormosil materials, reports on nanocomposite films with reversible photochromism are less common; only few works based on phosphomolybdate [16], phosphotungstate [16–18], or silicotungstate [16] in ormosils bearing 3-aminopropyltriethoxysilane (APTS) and tetraethylorthosilicate (TEOS) have been reported. HPW was incorporated in ormosils prepared from tetraethylorthosilicate and tetraethyleneglycol [19]. Pan et al. [11] have claimed that silicotungstate, when entrapped in a hybrid material bearing metacrylamide and vinyl functionalities, results in a nanocomposite with HPW nanoparticles ranging from 40 to 90 nm in diameter. Their synthetic route involved polymerization of the silanol groups on silanes as well as radical polymerization of the vinyl groups. The film-cast and cured material showed reversible photochromism with a fast coloration process and a change of 0.15 units in absorbance and it is suggested that the organic groups grafted in the ormosil network play an important role in the coloration/

discoloration mechanism [11].

While all these above mentioned studies report interesting synthetic strategies for the preparation of photochromic ormosil-polyoxometalate nanocomposites, an understanding of how the interaction between the entrapped polyoxometalate species and organic modifiers (especially alkylamino and/or alkylammonium groups) influences the photoactive behavior and structural assembly of these nanocomposites is not clear and complete. To address some of these aspects, in a previous study [20] of HPW-doped organomodified silicate xerogels, we investigated the impact of number of amino groups in the nitrogenated organosilane on the photochromic behavior and structure of these hybrid xerogels. A combination of various solid state NMR techniques was used to probe the local structure of HPW polyoxoanions inside the hybrid network. Spin-echo double resonance (SEDOR) experiments indicated a state of restricted mobility of the HPW ions and the surrounding molecular groups in the N-(3-(trimethoxysilyl)propyl)-ethylenediamine (TSPEN) hybrid due to strong interaction between the polyoxoanions and the chelating diamino groups of TSPEN [20]. Also, the TSPEN based hybrid material showed higher photochromic response than the one modified with 3-aminopropyltrimethoxysilane (APTS), thus indicating a positive correlation between the number of amino groups and the observed photoresponse. However, while such TEOS-APTS and TEOS-TSPEN derived hybrid materials present good photochromic response, the obtained sols yield opaque and non-uniform films, which significantly limits their practical applicability.

More recently, we studied the surface structure and photocatalytic activity of ormosil-phosphotungstate films prepared by using tetraethylorthosilicate (TEOS) and 3-glycidyloxypropyl trimethoxysilane (GLYMO) as matrix-forming precursors and aminopropyltriethoxysilane (APTS) and 4-(Triethoxysilyl) butyronitrile (BuTs) as matrix-modifiers [21]. In this case, transparent, reproducible and uniform films were obtained. Interestingly, the photocatalytic efficiency of the films was influenced by the supramolecular interaction between the polyoxometalate species and the nitrogenated organic functionalities, which suggested a competition among reversible photochromism and photocatalytic pathways in these materials. In order to further understand the photoactive behavior and structure of these hybrid materials, in the present study, we systematically studied the role of the HPW and nitrogenated silanes in the supramolecular self-assembly and its impact on the photochromic response of the obtained nanocomposites. An extended structural picture of the bulk composition of the ormosils was assembled using results from a broad set of experimental techniques including transmission electron microscopy (TEM), x-ray diffraction (XRD), solid-state nuclear magnetic resonance (NMR), and optical spectroscopies. Furthermore, we also discuss certain important aspects of the preparation of photochromic ormosil-polyoxometalate nanocomposites such as the role of the organic modifiers in the incorporation of the polyoxometalates species in dip-coated films and the role of water in the photochromic mechanism. Such aspects have been overlooked by other previous studies.

2. Materials and methods

2.1. Chemicals

Phosphotungstic acid hydrate (HPW), tetraethylorthosilicate (TEOS, 98%), 3-Aminopropyltriethoxysilane (APTS, 98%), (3-glycidyloxypropyl)trimethoxysilane, (GLYMO, 98%), and 4-(Triethoxysilyl)butyronitrile (BuTs, 98%) were purchased from Sigma–Aldrich (MA, USA) and used without further purification. Acetone, 99.5%, was supplied by QHEMIS (SP, Brazil).

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