

Communication

Visible-Light Photochromic Properties of an Inorganic–Organic Phosphomolybdic Acid/Polythiophene Hybrid Thin Film

Wanqing Zhao ¹, Hongmei Zhao ¹, Wei Feng ²  and Honggang Zhao ^{1,*}

¹ School of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi 830054, China

² Key Lab of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130021, China

* Correspondence: xjnu1609@xjnu.edu.cn

Abstract: A visible-light photochromic hybrid film was synthesized based on combining phosphomolybdic acid (PMoA) with the polythiophene (PTh) matrix. The microstructure and photochromic properties of the materials were analyzed through atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible spectra (UV-vis). According to FTIR spectra, the geometries of PMoA and PTh were well preserved in hybrid film and there exists a strong interaction at the interface of PMoA and PTh. The XPS spectra revealed the change in the chemical microenvironment and the reduction of Mo⁶⁺ atoms in the photoreduction reaction. Under visible light irradiation, the composite film changed from transparent to blue and deepened gradually, generating heteropoly blue. The hybrid film also shows reversibility in the presence of oxygen. The results indicated that the photochromic reaction was inconsistent with photoinduced electron transfer mechanism.

Keywords: phosphomolybdic acid; polythiophene; photochromism; hybrid film



Citation: Zhao, W.; Zhao, H.; Feng, W.; Zhao, H. Visible-Light Photochromic Properties of an Inorganic–Organic Phosphomolybdic Acid/Polythiophene Hybrid Thin Film. *Chemistry* **2024**, *6*, 469–475. <https://doi.org/10.3390/chemistry6030026>

Academic Editor: Matthias Lehmann

Received: 25 April 2024

Revised: 1 June 2024

Accepted: 5 June 2024

Published: 7 June 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Photochromic materials were considered as a promising research focus in functional materials and applied in the fields of optical information storage materials, photoelectric device, optical switching and biomedical research [1–4]. In recent years, the development of inorganic/organic composite materials and the introduction of self-assembly technology, template chemistry and other methods into the preparation greatly improved the photochromic properties of the materials, providing a broader application direction [5,6].

Heteropolyoxometalates are one of the most popular photochromic materials due to their high oxidation reducibility, high proton conductivity and excellent solubility [7,8]. In order to increase the application potential of heteropolyoxometalates, efforts have been made to introduce them into polymeric networks to improve the physical properties of the photochromic materials such as mechanical strength, optical transparency and machinability [9–11]. Heteropolyoxometalates, as an anionic charge carrier, were used in disordered films such as sol-gel films by bonding with cationic groups on organic polymer chains through weak interactions such as hydrogen bonding, electrostatic force and van der Waals force. Sun and coworkers [12] synthesized a PMoA/polyvinyl pyrrolidone (PVP) hybrid film and discovered that the main cause of the photochemical reaction was the proton transfer between PMoA and PVPd matrix. The interaction of polyoxometalates and polymer through non-covalent linkages offered a useful approach to improving physical and chemical properties of the inorganic/organic photochromic materials.

Polythiophene (PTh) has good photoelectric stability, good film forming properties, high conductivity and a low band gap width of 2.02 eV, which has great application potential in photoelectric chemistry. PTh has a large π -conjugated electron system, and its electron-giving ability is better than polypyrrole and polyaniline. PTh can form a

charge transfer bridge with heteropolyoxometalates, and heteropolyoxometalates and PTh polymer substrates can be connected by hydrogen bonds. Given these properties of PTh, a visible-light photochromic composite material was synthesized based on combining posphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, as called PMoA) with PTh matrix in this work. The microstructure and photochromic properties of the materials were analyzed through atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible (UV-vis) spectra. Based on these characterizations, the photochromic response principle of the multilayer and the charge transfer mechanism between PMoA and PTh polymer matrix were investigated.

2. Materials and Methods

2.1. Preparation

Posphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, PMoA) was reused after secondary recrystallization, and the other chemicals were used as received without further purification. The substrates were firstly immersed into Piranha solution (sulfuric acid:hydrogen peroxide = 7:3 volumetric ratio) for 1440 min at 353 K and then washed sequentially with deionized water and ethyl alcohol several times. After being rinsed with ethyl alcohol, the substrates were preserved in acetone for further use.

0.02 g PTh mixed with 20 mL *N,N*-dimethylformamide (DMF) to form solution No. 1 with a concentration of 0.1 mg/mL. 0.004 g PMoA mixed with 20 mL ethanol to form solution No. 2 with a concentration of 0.2 mg/mL. The above solutions were mixed with stirring to form solution No. 3. A pipetting gun was used to drop this mixed solution onto a quartz substrate to form a PMoA/PPy hybrid thin film with an amount of 100 μL , as shown in Figure 1. The thickness of the formed PMoA/PTh thin film was approximately 2.0 μm . The ultraviolet-visible spectrum of the sample was tested on a quartz sheet, the atomic force microscope (AFM) test of the sample was performed on a silicon sheet and the rest of the test was performed on a glass sheet.

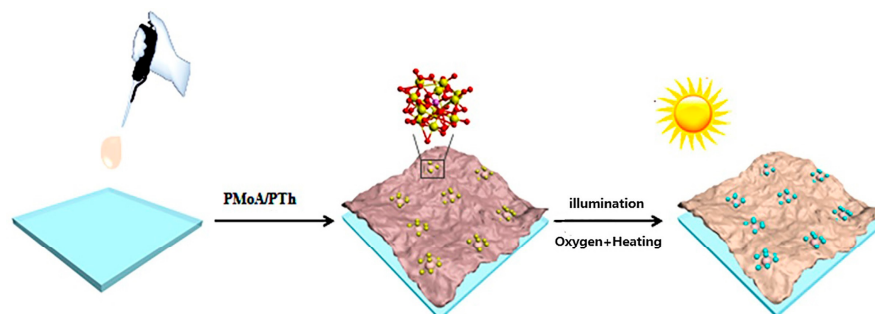


Figure 1. Process of synthesis and photochromic reaction.

2.2. Characterization

AFM images of samples were obtained on a 300 HV atomic force microscope (Seiko, Tokyo, Japan). FTIR spectra was determined with a Nicolet 550 Fourier transform infrared spectrometer (Nicolet, Madison, WI, USA) in the wavenumber range of 500–4000 cm^{-1} . XPS measurements were performed on an ESCALAB 250 photoelectron spectrometer (Thermo, Waltham, MA, USA) to obtain the information about chemical binding energy of samples. Absorbance curves were measured on a UV-Vis spectrophotometer (JASCO, Tokyo, Japan) with an optical resolution of 1 nm in the range of 400–900 nm.

2.3. Experiments

Photochromic experiments were carried out using a 300 W Xe lamp (PLS-SXE, Beijing Perfectlight Technology Co., Ltd., Beijing, China) with a UV filter (pass above 400 nm wavelength) as a visible light source without any other light sources. The distance between the lamp and the film was adjusted to 150 mm. Visible light irradiation experiments were performed in the air to obtain a series of absorbance curves under different irradiation

times. Then the composite film was kept in the dark to observe the bleaching process, and the corresponding absorbance was measured. All experiments were performed at room temperature.

3. Results

The FTIR spectra of pure PMoA, PTh and PMoA/PTh hybrid film in the range of 400–4000 cm^{-1} are shown in Figure 2. The absorption peaks at 1542 cm^{-1} and 1487 cm^{-1} are the characteristic absorption peaks of the thiophene ring, which are classified as asymmetric and symmetrical stretching vibrations of the polythiophene ring, respectively. The characteristic absorption peak at 1325 cm^{-1} was attributed to the C-S stretching vibration of the polythiophene ring, and the absorption peak at 1031 cm^{-1} and 1169 cm^{-1} is attributed to the in-plane bending vibration of the C-H bond on the polythiophene ring. The absorption peak at 783 cm^{-1} is attributed to the out-of-plane bending vibration of C-H bond, which was superimposed by the PMoA signals. These indicated that the structure of PTh is intact and not destroyed in the hybrid film, and the geometric structure of PTh was still retained in the composite film.

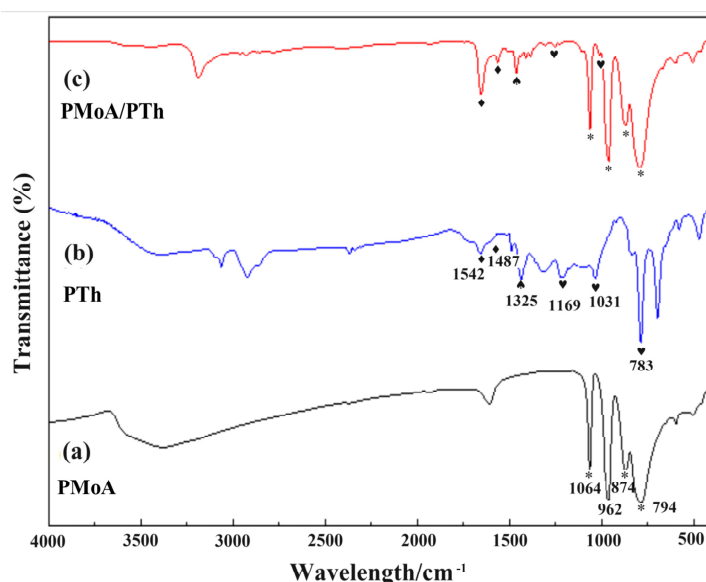


Figure 2. FTIR spectra of PMoA, PTh and PMoA/PTh hybrid film.

In the spectrum of PMoA/PTh, there are four typical bands at 1064, 962, 874 and 794 cm^{-1} corresponding to vibration bands of $\nu(\text{P-Oa})$, $\nu(\text{Mo-Od})$, $\nu(\text{Mo-Ob-Mo})$ and $\nu(\text{Mo-Oc-Mo})$, which are similar to those of pure PMoA and only have some shifts. It demonstrates that the Keggin geometry of PMoA is preserved in the composite film. The infrared wavelength of PMoA in the composite film is transformed due to the enhanced coulomb interaction between PMoA and polymer substrate, and the charge transfer occurs.

AFM images (Figure 3) depict the surface morphology of pure PTh and PMoA/PTh hybrid films before and after visible light irradiation. PTh film (Figure 3a) shows the peak-shaped structure of similar particle size and the root means square roughness (RMS) was 7 nm. As shown in Figure 3b,c, the morphology of the film changed obviously after the combination of PTh and PMoA; the RMS of PMoA/PTh hybrid films was 18 nm (compared with 7 nm for PTh). It can be inferred that the interaction of hydrogen bonds between PTh polymer chains is interfered with by the action of PMoA particles under the interaction force of hydrogen bonds between PMoA and PTh polymer chains. After optical-light illumination, the RMS of PMoA/PTh composite films increased from 18 to 31 nm, which indicated the formation of heteropoly blue in photoreduction reaction and proton transfer increased the spatial angle of the PTh polymer.

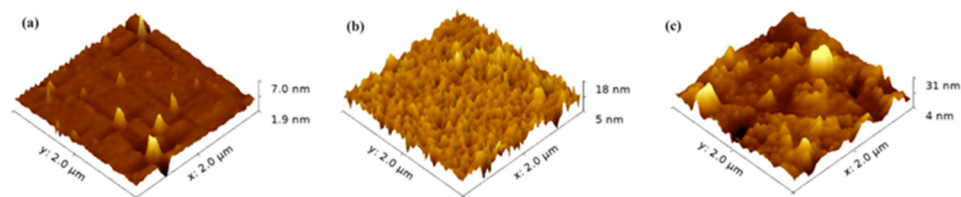


Figure 3. AFM images of (a) pure PTh and PMoA/PTh composite films (b) before and (c) after visible light irradiation.

The UV-Vis absorption spectra of PMoA/PTh with varied irradiation times in the coloration process were obtained in Figure 4a. Before irradiation, there was no obvious absorption peak within the visible light range. The absorption peak intensity increased with exposure time and reached the maximum value of 5.22 at 740 nm after being illuminated for 30 min. This characteristic absorption peak at 740 nm was attributed to metal-to-metal extra intervalence charge transfer (IVCT) ($\text{Mo}^{6+} \rightarrow \text{Mo}^{5+}$) [8]. As a result of the formation of heteropoly blue during the photochromic process, the hybrid film changed from transparent to blue and deepened gradually.

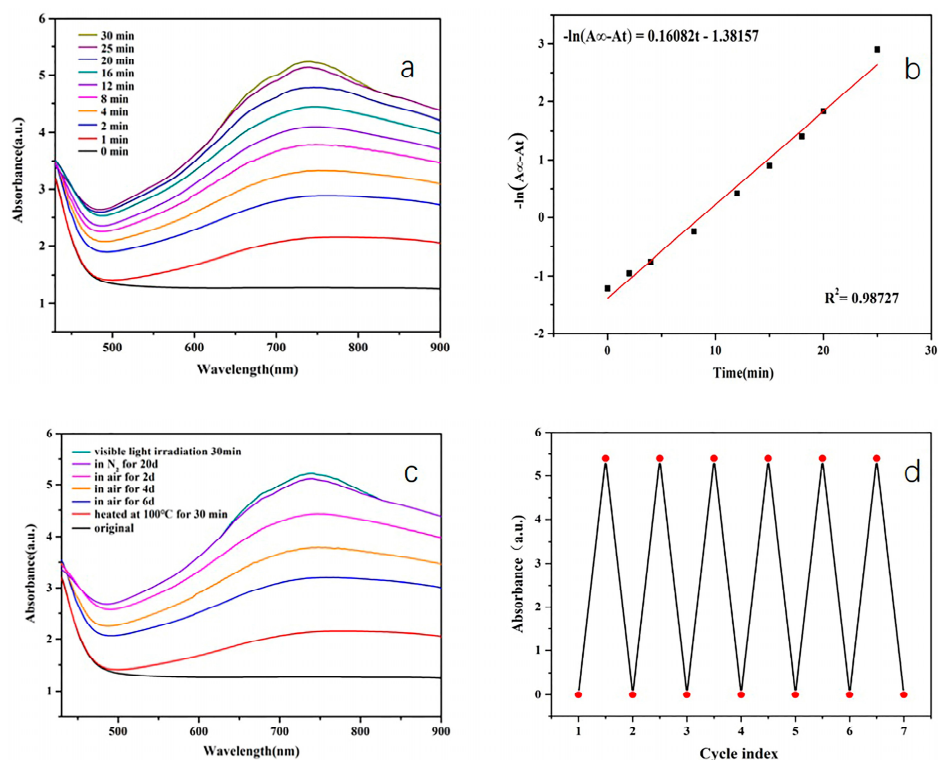


Figure 4. (a) UV-Vis absorption spectra of PMoA/PTh with varied irradiation time in the coloration process, (b) Kinetic plot of the first-order photochromic process of PMoA/PTh film, (c) UV-Vis absorption spectra of PMoA/PTh under different conditions in the decoloration process, (d) The reversibility of the coloration cycle of the PMoA/PTh film.

The kinetic process of coloration of PMoA/PTh at 740 nm was further analyzed (Figure 4b). It is revealed that the photochromic process satisfies the following first-order kinetic equation:

$$-\ln(A_{\infty} - At) = kt + b$$

where A_{∞} is the absorbance value at saturation; At is the absorbance value upon different irradiation times through the coloration process; k is the rate constant. The rate constant k of the coloration process is 0.16 min^{-1} , indicating the advantages of composite film in the photochromic response.

In Figure 4c, it was shown the fading process of the PMoA/PTh hybrid film. When the PMoA/PTh hybrid film was placed in the air, the color would gradually fade, but if the hybrid film was placed in N₂ atmosphere for 20 days, the color of the composite film would not fade. This phenomenon indicated that oxygen plays a key role in promoting the discoloration of the hybrid film. It was also found that heating can accelerate the fading process because the absorbance was reduced by 80% when the film was heated at 373 K for 30 min.

The coloration–discoloration cycle experiments were performed to determine the reversibility of the PMoA/PTh hybrid film. After visible light irradiation to reach the saturation absorbance, the film could be reused by heating treatment. As shown in Figure 4d, there was only a slight change in absorbance after recycling 7 times, demonstrating that PMoA/PTh hybrid film presented favorable photochromic properties, with high stability and good reversibility of the photochromic film [13].

As shown in Table 1, the PMoA/PTh hybrid film exhibited a high maximum absorbance compared with the other representative samples, which indicated that the protonation effect of PMoA toward PTh in the PMoA/PTh hybrid thin film could increase the maximum absorbance and greatly improved the photochromic properties of the PMoA/PTh hybrid film.

Table 1. Comparison of the maximum absorbance of photochromic materials.

Photochromic Material	The Thickness of Samples	The Maximum Absorbance	Reference
PMoA/PANI Hybridizing Thin Film	1.8 μm	3.46	[10]
ZnO/PMoA	-	0.21	[14]
WO ₃ -x QDs	-	2.75	[15]
PVP/HTA hybrids	-	0.78	[16]
CsPbBr ₃ Quantum Dot Films	-	0.78	[17]
PMoA/ZnO/PVP composite film	-	0.32	[18]
Aromatic Sulfonium Octamolybdates	solid-state	3.2	[19]
PMoA/PTh composite film	2.0 μm	5.27	This work

To further analyze the change of chemical microenvironment in the process of photochromism, XPS spectra of Mo 3d for the PMoA/PTh hybrid film without and with irradiation are exhibited in Figure 5 and Table 2. For the PMoA/PTh hybrid film, the peaks appeared at 232.9 eV and 236.0 eV assigned to 3d_{3/2} and 3d_{5/2} of Mo⁶⁺, respectively, and the peaks located at 235.5 eV and 231.8 eV were assigned to 3d_{3/2} and 3d_{5/2} of Mo⁵⁺, respectively. The appearance of the characteristic peaks of Mo⁵⁺ here can be inferred as X-ray excitation. After irradiation, the peaks of Mo⁶⁺ shift to 233.0 eV and 236.2 eV, and the peaks of Mo⁵⁺ appear at 231.7 eV and 235.0 eV. Compared to the spectrum before irradiation, the binding energy of 3d of Mo⁶⁺ increases, and the proportion of Mo⁵⁺ also increases from 0.09 to 0.33, which is attributed to Mo⁶⁺ being converted to Mo⁵⁺. It can be concluded that the chemical microenvironment of Mo atoms has been changed due to the photoreduction reaction.

Table 2. Binding energies of Mo3d energy level and Mo⁵⁺/Mo ratios of PMoA/PTh hybrid film before and after illumination.

Sample	Mo ⁵⁺		Mo ⁶⁺		Mo ⁵⁺ /Mo Ratios
	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	
Before	231.8	235.5	232.9	236.0	0.09
After	231.7	235.0	233.0	236.2	0.33

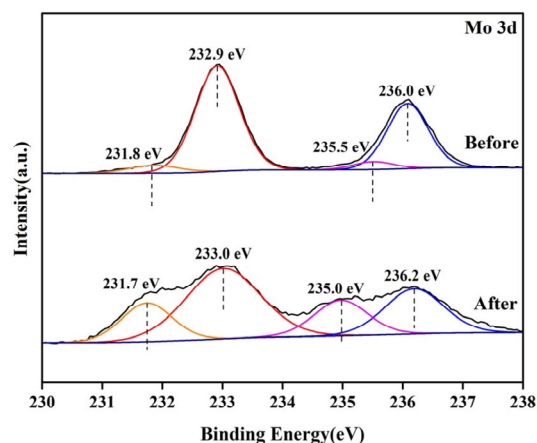


Figure 5. XPS spectra Mo 3d for PMoA/PTh hybrid film without and with irradiation.

To explain the above photochromic behavior, the mechanism of the hybrid film was investigated. The photochromic properties of the inorganic/organic hybrid films in this paper mainly depend on the interactions between inorganic and organic components. The metal ions in the oxidized polyoxometalates have d^0 electronic configurations; therefore, the low-energy electrons of oxygen 2p orbitals were excited to a high-energy state of metal d orbitals upon irradiation, which is the so-called oxygen-to-metal (O-M) ligand-to-metal charge transfer (LMCT). Thus, the electron and hole charges were separated, providing a condition for stable coloration of the composite film. The hole left at the oxygen atom interacted with non-bonding electrons on the sulfur atom of PTh. In this process, the Mo^{6+} atom was reduced to the Mo^{5+} atom, generating heteropoly blues. When the bleaching process occurred, an electron transferred from the Mo^{5+} atom to the oxygen molecule under aerobic conditions so that the polyoxometalates were oxidized.

The diagram of photochromic mechanism of the PMoA/PTh hybrid film is shown in Figure 6. Due to protonation, the electron density of PMoA decreased during the interaction with PTh, thus causing the spectral redshift, which verified the existence of interface interaction between PMoA and PTh. After light exposure, the heteropoly acid is reduced to heteropoly blue, and the protons are transferred to PMoA.

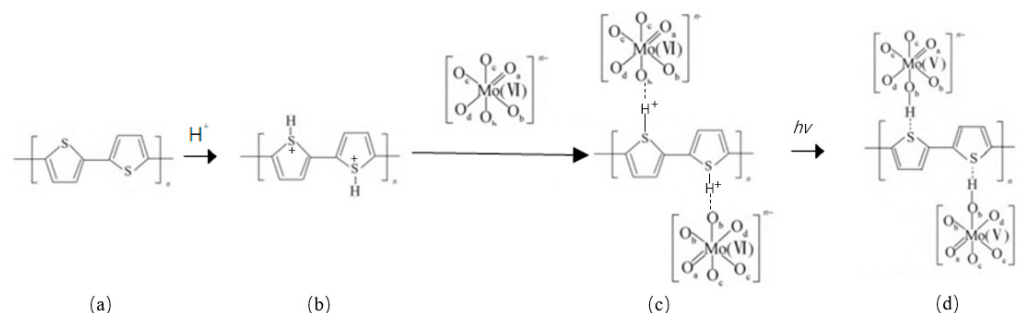


Figure 6. The diagram of the photochromic mechanism of PMoA/PTh hybrid film. (a) PTh, (b) PTh after protonation, PMoA/PTh composite film (c) before and (d) after visible light irradiation.

4. Conclusions

The PMoA/PTh photochromic materials were prepared by dropping the hybrid solution on the substrate to form a film. The geometries of PMoA and PTh were well preserved in hybrid film according to FTIR spectra. Upon irradiation, the protons in the organic polymer are excited and transferred to PMoA via a charge transfer bridge. Heteropoly blue was generated in a photoreduction reaction accompanied by the change of chemical microenvironment. The bleaching process occurred as Mo^{5+} atoms were oxidized to Mo^{6+} atoms in the presence of oxygen. Moreover, the hybrid film was of favorable

reversibility and stability. The protonation process between PMoA and the PTh matrix was considered the major cause of the photochemical reaction.

Author Contributions: W.Z. contributed to overall organizing of all experiments, and writing-original draft preparation. H.Z. (Hongmei Zhao) contributed to photochromic properties experiments, data analysis and visualization. W.F. contributed to sample preparation and characterization. H.Z. (Honggang Zhao) contributed to providing ideas for all the experiments, methodology, and supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Qin, B.; Chen, H.Y.; Liang, H.; Fu, L.; Liu, X.; Qiu, X.; Liu, S.; Song, R.; Tang, Z. Reversible photoswitchable fluorescence in thin films of inorganic nanoparticle and polyoxometalate assemblies. *J. Am. Chem. Soc.* **2010**, *132*, 2886–2888. [[CrossRef](#)] [[PubMed](#)]
2. Gu, H.X.; Bi, L.H.; Fu, Y.; Wang, N.; Liu, S.; Tang, Z. Multistate electrically controlled photoluminescence switching. *Chem. Sci.* **2013**, *4*, 4371–4377. [[CrossRef](#)]
3. Lu, J.; Zhang, X.; Ma, P.; Singh, V.; Zhang, C.; Niu, J.; Wang, J. Photochromic behavior of a new polyoxomolybdate/alkylamine composite in solid state. *J. Mater. Sci.* **2018**, *53*, 3078–3086. [[CrossRef](#)]
4. Graca, V.C.; Sousa, C.M.; Coelho, P. Towards grey coloring photochromic materials using vinylidene-naphthofurans. *Dye. Pigment.* **2020**, *176*. [[CrossRef](#)]
5. Bao, H.F.; Wang, X.Y.; Yang, G.Q.; Li, H.; Zhang, F.; Feng, W. UV-light and visible-light photochromism of inorganic–organic multilayer films based on polyoxometalate and poly(acrylamide). *Colloid Polym. Sci.* **2014**, *292*, 2883–2889. [[CrossRef](#)]
6. Jing, X.F.; Zou, D.L.; Meng, Q.Q.; Zhang, W.; Zhang, F.; Feng, W.; Han, X. Fabrication and visible-light photochromism of novel hybrid inorganic–organic film based on polyoxometalates and ethyl cellulose. *Inorg. Chem. Commun.* **2014**, *46*, 149–154. [[CrossRef](#)]
7. Zhang, J.; Zou, Q.; Tian, H. Photochromic materials: More than meets the eye. *Adv. Mater.* **2013**, *25*, 378–399. [[CrossRef](#)] [[PubMed](#)]
8. Toshihiro, Y. Photo- and electrochromism of polyoxometalates and related materials. *Chem. Rev.* **1998**, *98*, 307–326.
9. Chen, J.; MeiAi, L.; Feng, W.; Xiong, D.Q.; Liu, Y.; Cai, W.M. Preparation and photochromism of nanocomposite thin film based on polyoxometalate and polyethyleneglycol. *Mater. Lett.* **2007**, *61*, 5247–5249. [[CrossRef](#)]
10. Zeng, O.R.; Guo, S.Y.; Sun, Y.B.; Li, Z.; Feng, W. Protonation Induced Enhanced Optical-Light Photochromic Properties of an Inorganic–Organic Phosphomolybdic Acid/Polyaniline Hybrid Thin Film. *Nanomaterials* **2020**, *10*, 1839. [[CrossRef](#)] [[PubMed](#)]
11. Lu, C.; Sun, Y.; Liu, J.L.; Wang, X.; Liu, S.L.; Feng, W. Enhanced photochromism of heteropolyacid/polyvinylpyrrolidone composite film by TiO₂ doping. *J. Appl. Polym. Sci.* **2015**, *132*, 41583. [[CrossRef](#)]
12. Sun, Y.; Wang, X.; Lu, Y.; Xuan, L.; Xia, S.; Feng, W.; Han, X. Preparation and visible-light photochromism of phosphomolybdic acid/polyvinylpyrrolidone hybrid film. *Chem. Res. Chin. Univ.* **2014**, *30*, 703–708. [[CrossRef](#)]
13. Wei, Y.; Han, B.; Dong, Z.; Feng, W. Phosphomolybdic acid-modified highly organized TiO₂ nanotube arrays with rapid photochromic performance. *J. Mater. Sci. Technol.* **2019**, *35*, 1951–1958. [[CrossRef](#)]
14. Yue, T.; Han, B.; Wang, X.; Bai, L.; Feng, W. Instantaneous visible-light photochromic performance of composite powders based on PMoA and ZnO nanotubes. *Chem. Lett.* **2019**, *48*, 851–854. [[CrossRef](#)]
15. Liu Qi Hu Ch Wang, X. Hydrothermal synthesis of oxygen-deficiency tungsten oxide quantum dots with excellent photochromic reversibility. *Appl. Surf. Sci.* **2019**, *480*, 404–409.
16. Li, D.; Wei, J.; Dong, S.; Li, H.; Xia, Y.; Jiao, X.; Wang, T.; Chen, D. Novel PVP/HTA hybrids for multifunctional rewritable paper. *ACS Appl. Mater. Interfaces* **2018**, *10*, 1701–1706. [[CrossRef](#)] [[PubMed](#)]
17. Qaid, S.M.; Alharbi, F.H.; Bedja, I.; Nazeeruddin, M.K.; Aldwayyan, A.S. Reducing Amplified Spontaneous Emission Threshold in CsPbBr₃ Quantum Dot Films by Controlling TiO₂ Compact Layer. *Nanomaterials* **2020**, *10*, 1605. [[CrossRef](#)] [[PubMed](#)]
18. Song, T.; Li, J.; Deng, Q.; Gao, Y. Preparation, characterization, photochromic properties, and mechanism of PMoA/ZnO/PVP composite film. *Molecules* **2023**, *28*, 7605. [[CrossRef](#)] [[PubMed](#)]
19. Kumar, A.; Gupta, A.K.; Devi, M.; Gonsalves, K.E.; Pradeep, C.P. Engineering Multifunctionality in Hybrid Polyoxometalates: Aromatic Sulfonium Octamolybdates as Excellent Photochromic Materials and Self-Separating Catalysts for Epoxidation. *Inorg. Chem.* **2017**, *56*, 10325–10336. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.