

Article

Mild and Effective Decatungstate-Catalyzed Degradation of Methyl Orange Under Visible Light

Wenfeng Wu ^{1,†}, Lin Yu ^{1,†}, Lei Zha ¹, Feifei He ¹, Jiajia Ma ¹, Ouyang Wu ¹, Huanhuan Zhang ¹, Xinlan Chen ¹, Shuyin Yu ¹, Mengjing Lei ¹, Lin-Lin Yang ^{1,*}, Jiangang Chen ^{3,*} and Xiai Luo ^{2,*}

¹ College of Materials Science and Engineering, Guiyang University, Guiyang 550003, China; wff262224@163.com (W.W.); yulin15721747396@163.com (L.Y.); zhalei_gyu@126.com (L.Z.); 19185663855@163.com (F.H.); 2439494mj@sina.com (J.M.); wff262224@163.com (O.W.); 15508561586@163.com (H.Z.); 18096143374@139.com (X.C.); ysyjoker@163.com (S.Y.); 18685164152@139.com (M.L.)

² School of Pharmaceutical Sciences, Hunan University of Medicine, Huaihua 418000, China

³ School of Pharmacy, Xi'an Jiaotong University, Xi'an 710049, China

* Correspondence: yangll0325@126.com (L.-L.Y.); jiangang@stu.xjtu.edu.cn (J.C.); luoxiai@hnmu.edu.cn (X.L.)

[†] These authors contributed equally to this work.

Abstract: Decatungstate (DT) is a highly promising photocatalyst for dioxygen (O₂)-based reactions but has hardly been applied in the photocatalytic degradation technology of dye. Here, we synthesized hydrophilic DT-SO₃H salts by incorporating tetra-alkyl cations with sulfonic acid groups, aiming to enhance both the water solubility and catalytic efficiency of DT under visible light. Comprehensive characterization of DT-SO₃H using ultraviolet-visible spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Photocurrent (PTC), and Electrochemical Impedance Spectroscopy (EIS) confirmed its improved properties. DT-SO₃H demonstrated outstanding photocatalytic performance, achieving 90% degradation of methyl orange within 25 min under continuous visible light irradiation. This study presents a cost-effective and efficient method for degrading methyl orange, representing a significant advancement in the development of high-performance photocatalysts and opening new avenues for the study and application of photocatalytic dye degradation technologies.

Keywords: decatungstate photocatalysis; visible light; methyl orange degradation



Academic Editor: Christos Kordulis

Received: 7 April 2025

Revised: 29 April 2025

Accepted: 9 May 2025

Published: 20 May 2025

Citation: Wu, W.; Yu, L.; Zha, L.; He, F.; Ma, J.; Wu, O.; Zhang, H.; Chen, X.; Yu, S.; Lei, M.; et al. Mild and Effective Decatungstate-Catalyzed Degradation of Methyl Orange Under Visible Light. *Catalysts* **2025**, *15*, 494. <https://doi.org/10.3390/catal15050494>

Copyright: © 2025 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

The utilization of molecular oxygen (O₂) in photocatalytic oxidation systems has increasingly fascinated researchers due to its exceptional characteristics, such as cleanliness, minimal energy consumption, high efficiency, and absence of secondary pollution [1]. Among them, decatungstate (DT), distinguished by its unique photophysical and chemical properties [2–5], has significantly advanced the field of photocatalysis in recent years. Notably, DT has demonstrated remarkable efficacy in facilitating the synthesis of diverse organic compounds under mild photocatalytic conditions, including the photocatalyzed oxidation of aliphatic and aromatic alcohols [6–10], alkanes [11–16], and alkenes [17–20]. Despite its promising properties, the application of DT in organic synthesis is hindered by inherent limitations such as structural instability, low excitation efficiency, and limited visible light absorption. In response to these problems, various strategies have been devised to enhance DT-based photocatalytic systems. These include impregnating DT onto solid matrices [17,18], incorporating DT into sol-gel networks [21,22], binding DT onto silica surfaces [23,24], attaching DT to ion-exchange resins [25], encapsulating DT within polymer

membranes [26–28], etc. Collectively, continued research into optimizing DT-based systems will contribute to more sophisticated and versatile applications in organic synthesis.

Methyl orange (MO) is a commonly utilized azo dye in the textile industry, known for its intense coloration, resistance to photolysis, and chemical stability [29]. While these properties enhance its utility as a dye, they also pose significant challenges for wastewater treatment, as it is difficult to decompose once it enters the environment [30]. Traditional methods, such as physical precipitation, filtration, chemical precipitation, chemical oxidation, and biological processes, often prove inadequate for the efficient and economical degradation of MO [31]. Thus, finding efficient and cost-effective ways to degrade MO in wastewater has become a pressing issue for the textile industry. For instance, Zhu et al. utilized sodium DT as a catalyst for the UV-induced degradation of MO, achieving notable efficiency (30 min, pH = 2, 100%) in breaking down the dye (20 mg/L) [32]. Niu et al. developed titanium dioxide–DT nanocomposite films in the presence of H₂O₂, which demonstrated high degradation rates (90 min, 88.8%) of MO (20 mg/L) under UV light [33]. Nevertheless, the dependence on UV light in these systems presents a significant constraint and poses practical challenges for large-scale industrial applications. Consequently, developing more effective and scalable solutions for MO degradation that can operate under visible light conditions would reduce energy consumption and enhance feasibility for industrial use.

Despite significant progress having been made in utilizing DT for the oxidation of organic compounds in organic media, the water solubility of DT is still far from satisfactory, and its application in aqueous photocatalytic systems has been rarely reported. Therefore, it is markedly challenging and of great importance to incorporate its excellent water solubility and strong catalytic performance into a DT-catalyzed photocatalytic system. In this work, we synthesized hydrophilic DT–SO₃H salts using tetra-alkyl cations with sulfonic acid groups. This novel approach aims to enhance both the water solubility and robust catalytic efficiency of DT in aqueous environments. The selection of Na₄DT as the benchmark material is based on its status as the prototypical decatungstate salt widely reported in photocatalytic studies [32]. As an unmodified tungsten–oxo cluster with aqueous solubility, Na₄DT provides a critical baseline for evaluating the efficacy of our sulfonic acid functionalization strategy. By systematically comparing DT–SO₃H with this conventional counterpart, we aim to establish structure–property relationships between cation modification and photocatalytic activity. This comparative framework ensures the meaningful evaluation of our functionalization approach. We characterized the photophysical properties of DT–SO₃H using UV–Vis, FT-IR, XPS, TPC, and EIS. Under continuous visible light irradiation, DT–SO₃H demonstrated remarkable catalytic efficiency, achieving 90% decolorization of methyl orange within 25 min. Our study presents an efficient and cost-effective method for the photocatalytic degradation of methyl orange under visible light. This innovative method, combining both inter- and intramolecular aggregation, represents a certain breakthrough in creating high-performance photocatalysts for environmental applications.

2. Results and Discussion

2.1. Photocatalytic Oxidation Degradation of Methyl Orange by O₂

Figure 1 illustrates the removal efficiency of methyl orange as a function of reaction time for experiments conducted with Na₄DT (details of the synthesis process are provided in Supplementary Materials) and DT–SO₃H under visible light irradiation. It was found that there is a negligible loss of methyl orange in the control experiment conducted without a catalyst. In contrast, the DT–SO₃H catalyst demonstrated a significantly higher degradation rate compared to Na₄DT; the removal efficiency of the DT–SO₃H catalyst reaches 90% after

25 min of reaction, while the same reaction degree requires a reaction time of more than 50 min for Na_4DT .

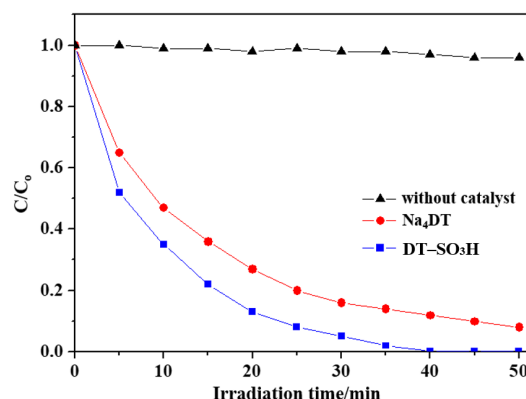


Figure 1. Degradation of methyl orange (20 mg/L) under visible light irradiation at room temperature, catalyst (8.5×10^{-4} M).

2.2. Characterization of Catalysts

FT-IR spectra: The FT-IR spectrum of $\text{DT-SO}_3\text{H}$ is shown in Figure 2A. The spectrum features three prominent peaks in the $800\text{--}1000\text{ cm}^{-1}$ range, specifically at 960 cm^{-1} , 860 cm^{-1} , and 804 cm^{-1} . These peaks belong to stretching vibrations of W=O_t (terminal oxygen), $\text{W-O}_b\text{-W}$ (O_b : bridged oxygen), and $\text{W-O}_c\text{-W}$ (O_c : central oxygen), respectively, reflecting the structural characteristics of the DT anion [34]. Notably, the second peak at 860 cm^{-1} appears at a lower wavelength compared to the standard decatungstate signatures reported in literature, suggesting that the presence of tetra-alkyl cations with sulfonic acid groups influences the DT anion structure due to their strong electron-withdrawing effect. Further, the spectrum exhibits four characteristic peaks of the $-\text{SO}_3\text{H}$ group at 1160 cm^{-1} , 1068 cm^{-1} , 620 cm^{-1} , and 535 cm^{-1} [35], indicating the successful synthesis of the novel hydrophilic $\text{DT-SO}_3\text{H}$ compound.

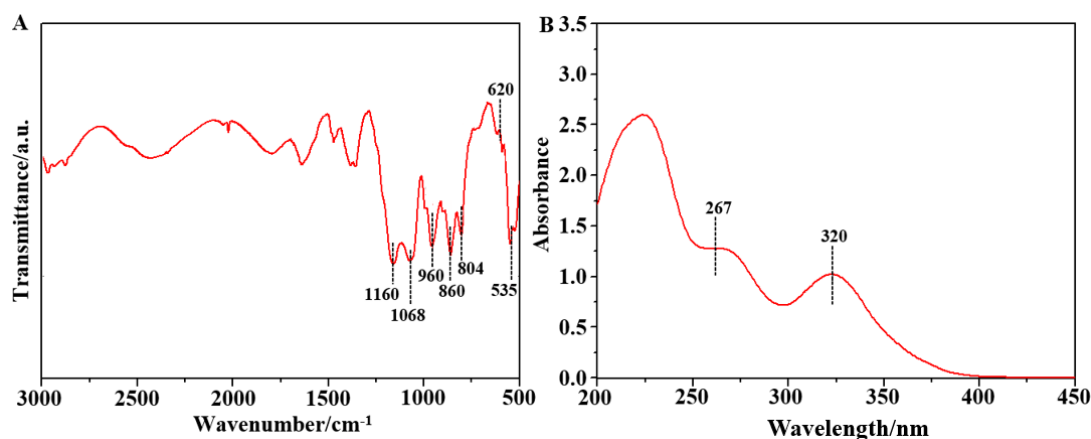


Figure 2. FT-IR (A) and UV-Vis (B) of $\text{DT-SO}_3\text{H}$ (9.6×10^{-6} M).

Liquid UV-Vis spectra: Figure 2B displays the UV-Vis spectrum of $\text{DT-SO}_3\text{H}$ in MeCN. In that, the curve exhibited two characteristic bands at 320 nm and 267 nm. The band at 320 nm is assigned to the charge transitions (CT) of O to W of four linear W-O-W bridge bonds in the photo-active species $[\text{W}_{10}\text{O}_{32}]^{4-}$ [24]. Meanwhile, the band at 267 nm is attributed to the CT process from oxygen to tungsten in the unstable structural subunit $[\text{W}_5\text{O}_{16}]^{2-}$ [25]. The spectral features observed in UV-Vis analyses suggest the successful synthesis of the $\text{DT-SO}_3\text{H}$ photocatalyst, consistent with the above FT-IR spectrum result.

XPS spectra: To investigate the influence of cations on the DT anion, the XPS spectra for the surface W and O elements of the Na₄DT and DT-SO₃H catalysts are shown in Figure 3. In Na₄DT, the O1s peaks deconvolute into two distinct energy levels at 531.8 eV and 530.5 eV, which are assigned to the W–O–W and W=O groups [36,37], respectively. In contrast, the O1s peaks in the DT-SO₃H are shifted to slightly higher binding energies, appearing at 532.1 eV and 530.9 eV (see curve 2 in Figure 3A). Figure 3B displays the W4f spectrum for DT-SO₃H, showing peaks at 35.8 eV (W4f_{7/2}), 37.9 eV (W4f_{5/2}), and 41.4 eV (W4f loss feature). These peaks are also shifted to higher energies compared to the corresponding peaks in Na₄DT, which appear at 35.6 eV, 37.7 eV, and 41.2 eV, respectively. This upward shift in binding energy for both the W and O elements in DT-SO₃H can be attributed to the electrophilic effect of the tetra-alkyl cation with the -SO₃H group. The increased binding energy suggests a reduction in electron density and a weakened electron screening effect [38–40].

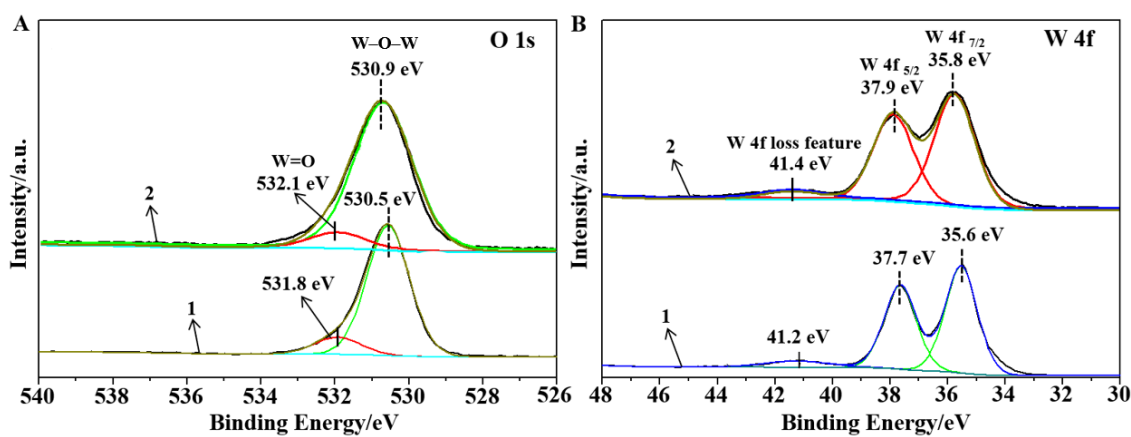


Figure 3. High-resolution (HR) XPS spectrum of Na₄DT (A) and DT-SO₃H (B).

Photocurrent and electrochemical impedance: Photocurrent (PTC) and electrochemical impedance (EIS) measurements of Na₄DT and DT-SO₃H were tested, and the obtained curves are displayed in Figure 4. Obviously, Na₄DT exhibits a low PTC response (curve 1, Figure 4A), attributed to the rapid recombination of photo-generated electron–hole pairs [41]. In contrast, DT-SO₃H demonstrates a significantly higher PTC response, attributed to the enhanced effect of the tetra-alkyl cation with -SO₃H on the separation and migration efficiency of photo-generated charge pairs, acting as excellent electron acceptors. Additionally, EIS measurements were employed to further elucidate the charge transfer kinetics for them. The impedance radius of DT-SO₃H is smaller than that of Na₄DT to some extent (Figure 4B), suggesting a reduction in interface resistance between the working electrode and the catalyst film for the DT anion [42]. This reduction in the impedance radius correlates with lower resistance in the charge transfer process, indicating the beneficial influence of the tetra-alkyl cation with -SO₃H [43].

Frontier Orbital Energy Levels: To explore the effect of the tetra-alkyl cation on the frontier orbital energy levels of DT anions, Mott–Schottky and UV–Vis diffuse reflectance spectroscopy were conducted on two catalysts: Na₄DT and DT-SO₃H. The relationship between the absorption coefficient (A) and the incident photon energy ($h\nu$) is $Ah\nu = C_1(h\nu - E_g)$ [44,45], where C_1 is the light absorption constant and E_g is the band gap energy of the photocatalyst. By applying this formula to analyze the UV–Vis diffuse reflectance data, Tauc curves were obtained (Figure 5A). Subsequent tangent processing of these curves enabled the analysis of the energy bands for Na₄DT and DT-SO₃H; the gap energies E_g are 3.03 eV and 2.82 eV. The smaller band gap energy observed for DT-SO₃H compared to Na₄DT suggests that the tetra-alkyl cation with -SO₃H contributes to improved

utilization of visible light by DT. The flat band potential (E_{FB}) of photocatalysts is typically derived from the Mott–Schottky curve [46]. Figure 5B illustrates the Schottky curves for the aforementioned DTs. It is evident that all DT catalysts exhibit *n*-type semiconductor behavior [47]. The E_{FB} values for Na_4DT and $\text{DT-SO}_3\text{H}$ are determined to be -0.63 eV and -0.54 eV, respectively, while the E_{FB} of *n*-type semiconductors is equal to the Fermi level (E_F), and E_{CB} is approximately equal to E_F [48]. Thus, the ECB of the above several DTs is approximately equal to E_{FB} , and the calculated EVB of Na_4DT and $\text{DT-SO}_3\text{H}$ is 2.40 eV and 2.28 eV, respectively, combined with the value of E_g ($E_g = \text{EVB} - \text{ECB}$). This indicates that the tetra-alkyl cation can affect the frontier orbital energy levels of DT.

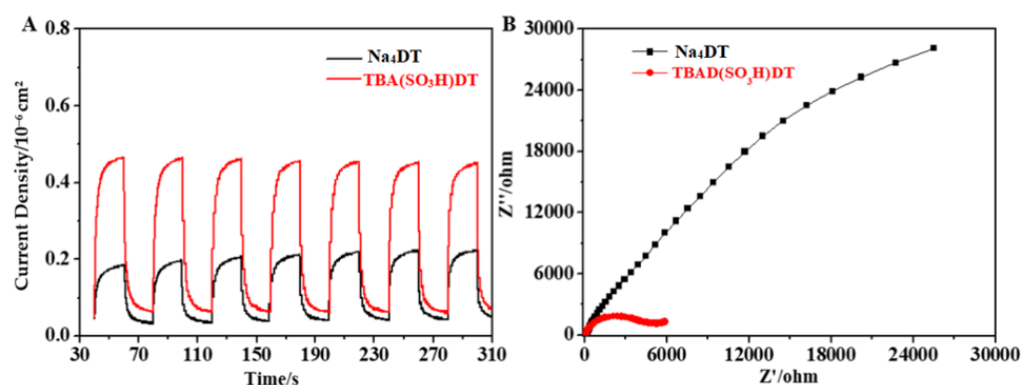


Figure 4. Photocurrent response (A) and electrochemical impedance spectroscopy (B) of Na_4DT (1.0×10^{-5} M) and $\text{DT-SO}_3\text{H}$ (1.0×10^{-5} M).

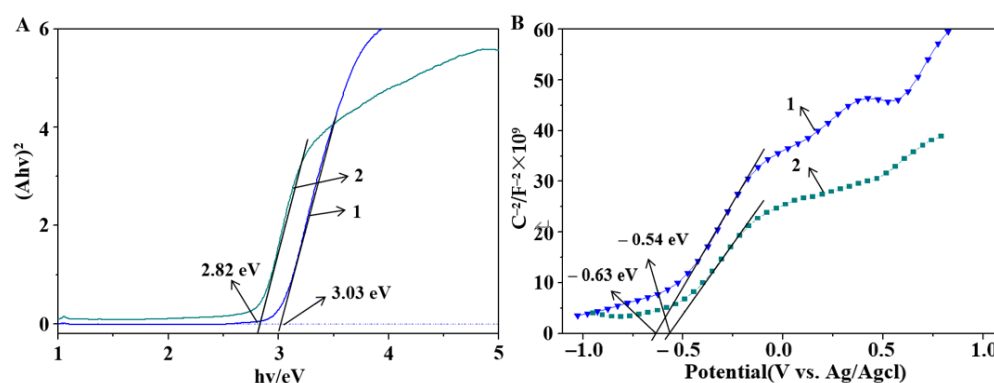


Figure 5. Tauc (A) curves obtained from the UV–Vis DRS spectra and Mott–Schottky curves (B) of samples. 1: Na_4DT (1.0×10^{-5} M); 2: $\text{DT-SO}_3\text{H}$ (1.0×10^{-5} M).

3. Experimental

3.1. Preparation of the Photocatalysts

All chemicals used were of analytical reagent (AR) grade and were utilized directly without any further treatment.

Synthesis of the novel decatungstate: According to the previously reported methods [49,50], the synthesis of DT salt is described as follows: 3.2 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved with 20 mL of water in a three-necked flask (100 mL), and the solution was heated at 85°C . Subsequently, a certain amount of 3 M HCl aqueous solution was added, reducing the pH to 2.1–2.3. After approximately 5 min, an aqueous solution of 4-(triethylammonio)butane-1-sulfonate bromide (2 M, 2 mL) was gradually added under continuous stirring and stable pH value. Then, the mixture was left to react at 90°C for 30 min. After, the mixture was concentrated and the white solids ($\text{DT-SO}_3\text{H}$) were dried at 85°C under vacuum.

3.2. Characterization

UV–Vis spectra of the samples were dissolved in MeCN and recorded from 200 to 800 nm on an UV-2450 spectrophotometer (Shimadzu, Tokyo, Japan). UV–Vis diffuse reflectance spectra (DRS) were obtained with a U-3310 spectrophotometer (HITACHI). Transmission FT-IR spectra of the samples were collected in the range of 400 to 4000 cm^{-1} on a Nicolet Nexus 510 P FT-IR spectroscope using a KBr disk (Madison, WI, USA). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Multi Lab 2000 system with a monochromatic Mg-K α source operated at 20 kV. The photoelectric current curve of the samples was measured in 0.5 M Na₂SO₄ solution with 0.3 V bias potential using a three-electrode system and CHI 660E workstation. Electrochemical impedance spectroscopy (EIS) was performed using the same photoelectrochemical test equipment, with the electrolyte replaced by a 0.1 M KCl solution containing 5 mM Fe(CN)₆^{3−/4−}. In this equipment, platinum wire was the counter electrode and Ag–AgCl was the reference electrode. The working electrode was prepared as follows: 20 mg of the catalyst was ultrasonically dispersed in 1 mL ethanol for 20 min, followed by the addition of 10 μL of Nafion to create a stable slurry. This slurry was then drop-cast onto ITO slices (0.4 mL per slice), forming a working electrode with an effective illumination area of 1 cm^2 after the ethanol had completely evaporated. A 300 W xenon lamp equipped with a 420 nm cutoff filter was used to provide visible light for photocurrent measurements.

3.3. Photocatalytic Evaluation Experiments

The photocatalytic oxidation experiments were performed using a custom-designed photoreactor equipped with an ethanol-cooled condenser and an oxygen storage vessel maintained at 1 atm pressure (see Figure S1 in Supporting Information (SI)). A 35 W tungsten–bromine lamp (with an UV light filter; light intensity, 535 mW/cm^2) was used as a light source. The whole lighting reaction was operated in the closed reactor under normal temperature and pressure. The detailed operating conditions and analytical method for the oxygenated products can be found in our recent publications [49].

4. Conclusions

To summarize, we obtained hydrophilic DT salts utilizing tetra-alkyl cations with a sulfonic acid group, which were developed for application in the degradation of methyl orange, which has the following merits: (i) photocatalysis is simple and effective; (ii) the DT-SO₃H sample possesses improved photophysical and chemical properties compared with Na₄DT; (iii) as a green photocatalyst in a homogeneous system, the novel catalyst has a very good degradation effect on simulated methyl orange, which provides a new way for the study of the photocatalytic degradation technology of dyes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15050494/s1>. Figure S1. The self-assembled photo-reactor used this work. Figure S2 is the structure of the DT-SO₃H. Figure S3 Left: (A) The light reaction device with built-in bromine-tungsten lamp. (B) The Electronic transformer (C). The lamp. (D) The lamp holder. Right: The emission spectra of 35 W bromine-tungsten lamp(400–1000 nm). Figure S4 is the UV–vis of Na₄DT (9.6×10^{-6} M). Figure S5 is the FT–IR spectrum of Na₄DT. Figure S6 is the UV–vis of Na₄DT (9.6×10^{-3} M) in a visible region.

Author Contributions: L.Y., X.L., F.H., J.M. and H.Z. carried out the experiments, design, and definition of intellectual content. L.Z. and O.W. conducted a literature search. W.W. and J.C. finished the data acquisition, data analysis, and manuscript preparation. X.C., S.Y. and M.L. provided assistance for data acquisition, data analysis, and statistical analysis. L.-L.Y. carried out a literature search, data acquisition, manuscript editing, and manuscript review. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation (22065004, 52463018), the Science and Technology Management Plan Foundation of Guizhou Province (ZK[2021]040), the Seventh Batch of Guizhou Province High-level Innovative Talent Training Program [2023], the Guizhou Provincial Department of Education Youth Science and Technology Talent Development Project (Qianjiaoj (2024)196), the scientific research funds of Guiyang University (GYU-KY-(2024)), the Youth Guidance Science and Technology Fund Project of Guizhou (2024), and the Youth Guidance Science and Technology Fund Project of Guizhou (Qiankehe (2024)084).

Data Availability Statement: The datasets used and/or analyzed during this current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Maldotti, A.; Molinari, A.; Amadelli, R. Photocatalysis with Organized Systems for the Oxofunctionalization of Hydrocarbons by O₂. *Chem. Rev.* **2002**, *102*, 3811–3836. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yue, B.; Tang, L.; Zhu, S.; Lin, X. Studies on White Powdery Tungstic Acid-Stability and Photochemistry of Decatungstic Acid in Aqueous Solution Containing Polyvinyl Alcohol. *Chem. J. Chin. Univ.* **1998**, *19*, 1453–1456.
- Duncan, D.C.; Netzel, T.L.; Hill, C.L. Early-Time Dynamics and Reactivity of Polyoxometalate Excited States. Identification of a Short-Lived LMCT Excited State and a Reactive Long-Lived Charge-Transfer Intermediate following Picosecond Flash Excitation of [W₁₀O₃₂]^{4−} in Acetonitrile. *Inorg. Chem.* **1995**, *34*, 4640–4646. [\[CrossRef\]](#)
- Texier, I.; Giannotti, C.; Malato, S.; Richter, C.; Delaire, J. Solar photodegradation of pesticides in water by sodium decatungstate. *Catal. Today* **1999**, *54*, 297–307. [\[CrossRef\]](#)
- Tanielian, C.; Duffy, K.; Jones, A. Kinetic and Mechanistic Aspects of Photocatalysis by Polyoxotungstates: A Laser Flash Photolysis, Pulse Radiolysis, and Continuous Photolysis Study. *J. Phys. Chem. B* **1997**, *101*, 4276–4282. [\[CrossRef\]](#)
- Nomiya, K.; Sugie, Y.; Miyazaki, T.; Miwa, M. Catalysis by heteropolyacids-ix. Photocatalytic oxidation of isopropyl alcohol to acetone under oxygen using tetrabutylammonium decatungstate. *Polyhedron* **1986**, *5*, 1267–1271. [\[CrossRef\]](#)
- Nomiya, K.; Sugie, Y.; Amimoto, K.; Miwa, M. Charge-transfer absorption spectra of some tungsten (VI) and molybdenum (VI) polyoxoanions. *Polyhedron* **1987**, *6*, 519–524. [\[CrossRef\]](#)
- Lykakis, I.N.; Tanielian, C.; Orfanopoulos, M. Decatungstate Photocatalyzed Oxidation of Aryl Alkanols. Electron Transfer or Hydrogen Abstraction Mechanism? *Org. Lett.* **2003**, *5*, 2875–2878. [\[CrossRef\]](#)
- Lykakis, I.N.; Tanielian, C.; Seghrouchni, M.; Orfanopoulos, M. Mechanism of decatungstate photocatalyzed oxygenation of aromatic alcohols: Part II. Kinetic isotope effects studies. *J. Mol. Catal. A Chem.* **2007**, *262*, 176–184. [\[CrossRef\]](#)
- Yang, B.; Hu, W.; Wan, F.; Zhang, C.; Liu, Y. Adjusting effect of additives on decatungstate-photocatalyzed HMF oxidation with molecular oxygen under visible light illumination. *Chem. Eng. J.* **2020**, *396*, 125345. [\[CrossRef\]](#)
- Su, A.; Chen, M.; Fu, Z.; Yang, B.; She, J.; Wan, F.; Zhang, C.; Liu, Y. Hybridizing Engineering Strategy of Decatungstate. 2. Regulated Effect of Doping Transition Metal Ions on Photocatalytic Oxidation Performance of (nBu₄N)₄W₁₀O₃₂. *Inorg. Chem.* **2020**, *59*, 7520–7530. [\[CrossRef\]](#)
- Yang, B.; Zhu, J.; Hu, S.; Deng, Y.; Luo, M.; She, J.; Liu, Y.; Zhang, C.; Tang, S.; Fu, Z. Hybridizing strategy of decatungstate by Au nanoparticles for enhanced photo-catalytic oxidation of hydrocarbons by dioxigens. *Appl. Catal. A Gen.* **2022**, *630*, 118473. [\[CrossRef\]](#)
- Yang, B.; Zhang, H.; Wan, F.; Deng, Y.; Jiang, D.; Zhang, Q.; Liu, Y.; Zhang, C.; Fu, Z. Molybdenum Isomorphously Substituted Decatungstates as Robust and Renewable Photocatalysts for Visible Light-Driven Oxidation of Hydrocarbons by Molecular Oxygen. *ChemCatChem* **2021**, *13*, 2253–2261. [\[CrossRef\]](#)
- Lykakis, I.N.; Orfanopoulos, M. Deuterium kinetic isotope effects in homogeneous decatungstate catalyzed photooxygenation of 1, 1-diphenylethane and 9-methyl-9H-fluorene: Evidence for a hydrogen abstraction mechanism. *Tetrahedron Lett.* **2005**, *46*, 7835–7839. [\[CrossRef\]](#)
- Lykakis, I.N.; Orfanopoulos, M. Photooxidation of aryl alkanes by a decatungstate/triethylsilane system in the presence of molecular oxygen. *Tetrahedron Lett.* **2004**, *45*, 7645–7649. [\[CrossRef\]](#)
- Lykakis, I.N.; Orfanopoulos, M. Decatungstate-Catalyzed Photooxygenation of S-2-Phenylbutane and Cumene via a Free Carbon-Radical Intermediate. *Curr. Org. Chem.* **2009**, *13*, 1737–1745. [\[CrossRef\]](#)
- Molinari, A.; Amadelli, R.; Mazzacani, A.; Sartori, G.; Maldotti, A. Tetraalkylammonium and Sodium Decatungstate Heterogenized on Silica: Effects of the Nature of Cations on the Photocatalytic Oxidation of Organic Substrates. *Langmuir* **2002**, *18*, 5400–5405. [\[CrossRef\]](#)

18. Maldotti, A.; Molinari, A.; Varani, G.; Lenarda, M.; Storaro, L.; Bigi, F.; Maggi, R.; Mazzacani, A.; Sartori, G. Immobilization of $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ on Mesoporous MCM-41 and Amorphous Silicas for Photocatalytic Oxidation of Cycloalkanes with Molecular Oxygen. *J. Catal.* **2002**, *209*, 210–216. [\[CrossRef\]](#)
19. Lykakis, I.N.; Orfanopoulos, M. Lone Selectivity of the Decatungstate-Sensitized Photooxidation of 1-Substituted Cycloalkenes. *Synlett* **2004**, *12*, 2131–2134.
20. Lykakis, I.; Vougioukalakis, G.; Orfanopoulos, M. Homogeneous decatungstate-catalyzed photooxygenation of tetrasubstituted alkenes: A deuterium kinetic isotope effect study. *J. Org. Chem.* **2006**, *71*, 8740–8747. [\[CrossRef\]](#)
21. Guo, Y.; Hu, C.; Wang, X.; Wang, Y.; Wang, E.; Zou, Y.; Ding, H.; Feng, S. Microporous Decatungstates: Synthesis and Photochemical Behavior. *Chem. Mater.* **2001**, *13*, 4058–4064. [\[CrossRef\]](#)
22. Molinari, A.; Bratovic, A.; Magnacca, G.; Maldotti, A. Matrix effects on the photocatalytic oxidation of alcohols by $[\text{nBu}_4\text{N}]_4\text{W}_{10}\text{O}_{32}$ incorporated into sol-gel silica. *Dalton Trans.* **2010**, *39*, 7826–7833. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Maldotti, A.; Molinari, A.; Bigi, F. Selective photooxidation of diols with silica bound $\text{W}_{10}\text{O}_{32}^{4-}$. *J. Catal.* **2008**, *253*, 312–317. [\[CrossRef\]](#)
24. Ni, L.; Ni, J.; Lv, Y.; Yang, P.; Cao, Y. Photooxygenation of hydrocarbons over efficient and reusable decatungstate heterogenized on hydrophobically-modified mesoporous silica. *Chem. Commun.* **2009**, 2171–2173. [\[CrossRef\]](#)
25. Fornal, E.; Giannotti, C. Photocatalyzed oxidation of cyclohexane with heterogenized decatungstate. *J. Photochem. Photobiol. A Chem.* **2007**, *188*, 279–286. [\[CrossRef\]](#)
26. Moriguchi, I.; Orishikida, K.; Tokuyama, Y.; Watabe, H.; Kagawa, S.; Teraoka, Y. Photocatalytic Property of a Decatungstate-Containing Bilayer System for the Conversion of 2-Propanol to Acetone. *Chem. Mater.* **2001**, *13*, 2430–2435. [\[CrossRef\]](#)
27. Carraro, M.; Gardan, M.; Scorrano, G.; Drioli, E.; Fontananova, E.; Bonchio, M. Solvent-free, heterogeneous photooxygenation of hydrocarbons by Hyflon[®] membranes embedding a fluorine-tagged decatungstate. *Chem. Commun.* **2006**, 4533–4535. [\[CrossRef\]](#)
28. Su, A.; Chen, M.; Fu, Z.; Yang, B.; She, J.; Wan, F.; Zhang, C.; Liu, Y. Hybridizing engineering strategy of non-lacunary $(\text{nBu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ by carbon quantum dot with remarkably enhanced visible-light-catalytic oxidation performance. *Appl. Catal. A Gen.* **2019**, *587*, 117261. [\[CrossRef\]](#)
29. LXu, Y.; Tian, Q.P.; Xu, M.; Xie, S.; Huang, H. Preparation of small of small sand garins/ TiO_2 and its photocatalytic behaviors in degradation of methylene blue. *Ind. Catal.* **2022**, *30*, 45–47.
30. Tao, J.Q.; Wang, Y.Q.; Zhang, Z.M.; Lang, D. Study on the technology of electro Fenton reaction by using MoS_2 as co-catalyst. *Appl. Chem. Ind.* **2020**, *49*, 3361–3371.
31. Matilainen, A.; Vepsäläinen, M.; Sillanpää, M. Natural organic matter removal by coagulation during drinking water treatment: A review. *Adv. Colloid Interface Sci.* **2010**, *159*, 189–197. [\[CrossRef\]](#)
32. Zhuang, H.S.; He, N. Preparation of sodium decatungstate and photocatalytic degradation of methyl orange solution. *Ind. Water Treat.* **2006**, *26*, 53–56.
33. Niu, P.; Hao, J.C. Photocatalytic degradation of methyl orange by titanium dioxide-decatungstate nanocomposite films supported on glass slides. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, *431*, 127–132. [\[CrossRef\]](#)
34. Shi, D.; Zhao, J.-W.; Chen, L.; Ma, P.; Wang, J.; Niu, J. Four types of 1D or 2D organic-inorganic hybrids assembled by arsenotungstates and CuII-LnIII/IV heterometals. *CrytEngComm* **2012**, *14*, 3108–3119. [\[CrossRef\]](#)
35. Wilson, K.; Lee, A.F.; Macquarrie, D.J.; Clark, J.H. Structure and reactivity of sol-gel sulphonic acid silicas. *Appl. Catal. A Gen.* **2002**, *228*, 127–133. [\[CrossRef\]](#)
36. Ženíšek, J.; Ondračka, P.; Čechal, J.; Souček, P.; Holec, D.; Vašina, P. W 4f electron binding energies in amorphous W-B-C systems. *Appl. Surf. Sci.* **2022**, *586*, 152824. [\[CrossRef\]](#)
37. Chenakin, S.; Kruse, N. XPS characterization of transition metal oxalates. *Appl. Surf. Sci.* **2020**, *515*, 146041. [\[CrossRef\]](#)
38. Zhang, Z.; Huang, J.; Zhang, M.; Yuan, Q.; Dong, B. Ultrathin hexagonal SnS_2 nanosheets coupled with $\text{g-C}_3\text{N}_4$ nanosheets as 2D/2D heterojunction photocatalysts toward high photocatalytic activity. *Appl. Catal. B-Environ.* **2015**, *163*, 298–305. [\[CrossRef\]](#)
39. Deng, Y.; Tang, L.; Feng, C.; Zeng, G.; Chen, Z.; Wang, J.; Feng, H.; Peng, B.; Liu, Y.; Zhou, Y. Insight into the dual-channel charge-carrier transfer path for nonmetal plasmonic tungsten oxide based composites with boosted photocatalytic activity under full-spectrum light. *Appl. Catal. B Environ.* **2018**, *235*, 225–237. [\[CrossRef\]](#)
40. Lei, Z.N.; Wang, W.Q.; Sun, T.; Liu, E.Z.; Gao, T. Efficient photocatalytic H_2 evolution over SnS_2 /twinned $\text{Mn}_{0.5}\text{Cd}_{0.5}\text{S}$ hetero-homojunction with double S-scheme charge transfer routes. *J. Mater. Sci. Technol.* **2025**, *216*, 81–92. [\[CrossRef\]](#)
41. Ingrosso, C.; Corricelli, M.; Disha, A.; Fanizza, E.; Bianco, G.V.; Depalo, N.; Panniello, A.; Agostiano, A.; Striccoli, M.; Curri, M.L. Solvent dispersible nanocomposite based on Reduced Graphene Oxide and in-situ decorated gold nanoparticles. *Carbon* **2019**, *152*, 777–787. [\[CrossRef\]](#)
42. Shiraishi, Y.; Yasumoto, N.; Imai, J.; Sakamoto, H.; Tanaka, S.; Ichikawa, S.; Ohtani, B.; Hirai, T. Quantum tunneling injection of hot electrons in Au/TiO_2 plasmonic photocatalysts. *Nanoscale* **2017**, *9*, 8349–8361. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Zou, Y.; Shi, J.-W.; Ma, D.; Fan, Z.; Lu, L.; Niu, C. In situ synthesis of C-doped TiO_2 @ $\text{g-C}_3\text{N}_4$ core-shell hollow nanospheres with enhanced visible-light photocatalytic activity for H_2 evolution. *Chem. Eng. J.* **2017**, *322*, 435–444. [\[CrossRef\]](#)

44. Aragon-Martinez, O.H.; Isiordia-Espinoza, M.A.; Galicia, O.; Romo, S.A.; Gómez, A.G.; Romano-Moreno, S.; Martinez-Morales, F. Measurement of levofloxacin in human plasma samples for a reliable and accessible drug monitoring. *Clin. Biochem.* **2017**, *50*, 73–79. [[CrossRef](#)]
45. Zheng, J.; Chang, F.; Jiao, M.; Xu, Q.; Deng, B.; Hu, X. A visible-light-driven heterojuncted composite WO₃/Bi₁₂O₁₇Cl₂: Synthesis, characterization, and improved photocatalytic performance. *J. Colloid Interface Sci.* **2018**, *510*, 20–31. [[CrossRef](#)] [[PubMed](#)]
46. Lin, X.; Sun, M.; Gao, B.; Ding, W.; Zhang, Z.; Anandan, S.; Umar, A. Hydrothermally regulating phase composition of TiO₂ nanocrystals toward high photocatalytic activity. *J. Alloys Compd.* **2021**, *850*, 156653. [[CrossRef](#)]
47. Mao, C.; Zuo, F.; Hou, Y.; Bu, X.; Feng, P. In Situ Preparation of a Ti³⁺ Self-Doped TiO₂ Film with Enhanced Activity as Photoanode by N₂H₄ Reduction. *Angew. Chem. Int. Ed.* **2014**, *53*, 10485–10489. [[CrossRef](#)] [[PubMed](#)]
48. Liu, Z.; Wang, B.; Wu, J.; Dong, Q.; Zhang, X.; Xu, H. Effects of Hydroxylation on PbS Quantum Dot Sensitized TiO₂ Nanotube Array Photoelectrodes. *Electrochim. Acta* **2016**, *187*, 480–487. [[CrossRef](#)]
49. Wu, W.; Fu, Z.; Tang, S.; Zou, S.; Wen, X.; Meng, Y.; Sun, S.; Deng, J.; Liu, Y.; Yin, D. (nBu₄N)₄W₁₀O₃₂-catalyzed selective oxygenation of cyclohexane by molecular oxygen under visible light irradiation. *Appl. Catal. B-Environ.* **2015**, *164*, 113–119. [[CrossRef](#)]
50. Yang, B.; Fu, Z.; Su, A.; She, J.; Chen, M.; Tang, S.; Hu, W.; Zhang, C.; Liu, Y. Influence of tetraalkylammonium cations on quality of decatungstate and its photocatalytic property in visible light-triggered selective oxidation of organic compounds by dioxigens. *Appl. Catal. B Environ.* **2019**, *242*, 249–257. [[CrossRef](#)]

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.