Steering Electron–Hole Migration Pathways Using Oxygen Vacancies in Tungsten Oxides to Enhance Their Photocatalytic Oxygen Evolution Performance

Zhen Wei, Wenchao Wang, Wenlu Li, Xueqin Bai, Jianfeng Zhao, Edmund C. M. Tse, David Lee Phillips,* and Yongfa Zhu*

Abstract: The overall water splitting efficiency is mainly restricted by the slow kinetics of oxygen evolution. Therefore, it is essential to develop active oxygen evolution catalysts. In this context, we designed and synthesized a tungsten oxide catalyst with oxygen vacancies for photocatalytic oxygen evolution, which exhibited a higher oxygen evolution rate of 683 μmol h⁻¹ g⁻¹ than that of pure WO₃ (159 μmol h⁻¹ g⁻¹). Subsequent studies through transient absorption spectroscopy found that the oxygen vacancies can produce electron trapping states to inhibit the direct recombination of photogenerated carriers. Additionally, a Pt cocatalyst can promote electron trap states to participate in the reaction to improve the photocatalytic performance further. This work uses femtosecond transient absorption spectroscopy to explain the photocatalytic oxygen evolution mechanism of inorganic materials and provides new insights into the design of high-efficiency water-splitting catalysts.

Introduction

Efficient solar-to-chemical conversion is envisioned to help solve the impending energy crisis.¹ In particular, hydrogen production through water splitting using renewable energy has attracted much attention in recent decades.² However, large-scale hydrogen production by splitting water is mainly restricted by water oxidation reactions due to the complex multi-electron oxidation process (slow kinetics) and high activation energy barrier for O–O bond formation (uphill reaction thermodynamics).³ Therefore, overall water splitting efficiency is limited by the primary and pivotal water oxidation reaction. Ru- and Ir-based oxides are effective water oxidation catalysts (WOCs), but their low availability and robustness, and high cost severely handicap their application in practical scenarios.⁴ Alternatively, heterogeneous semiconductors demonstrate their superiority both in chemical stability and catalytic durability relative to noble metal catalysts.⁵ Tungsten oxide, as a typical semiconductor catalyst, has been deeply researched as one of the most prospective energy materials due to its high stability, low cost, and low toxicity,⁶ although a variety of new materials for water splitting have been reported recently.⁷ Most notably, surface oxygen vacancies can promote charge transfer to maximize water oxidation activity.⁸ Selective deposition of noble metal cocatalysts on special sites of semiconductors can further promote the photogenerated electron-hole separation efficiency of the overall photosystems.⁹

The mechanism of photocatalytic water oxidation has been unveiled to a certain extent through developed physical and chemical methods in recent years.¹⁰ A significant portion of the reported results attributed the increase in photocatalytic activity to the enhanced separation of electrons and holes¹¹ but few publications provided an in-depth investigation and detailed explanation on the electron and hole transfer processes because the time scale of charge migration processes generally ranges from femtoseconds to picoseconds.¹² Recently, ultrafast spectroscopy is presented as a powerful approach to probe electron transfer kinetics primarily. Specifically, ultrafast spectroscopy is well suited to probe the collective electronic behaviors in metals, inter-/intra-band transitions, and energy-level distributions in semiconductors, nonlinear optical in ferromagnetic alloys, as well as spintronic performance in metal oxides.¹³ Ultrafast spectroscopy has become a standard method to explore organic molecular systems and inorganic semiconductors with extended lattice structures. The extended lattice structures of inorganic semiconductors provide numerous attenuation channels, thereby facilitating the quick decay of single and collective element excitations in the excited state to the ground state and subsequently rendering this ultrafast physical decay process to be difficult to observe. Fortunately, femtosecond transient absorption can reach a higher time-
Results and Discussion

Tungsten oxide samples with oxygen vacancies were synthesized using dicyandiamide and a tungsten source via an annealing method. All samples synthesized as photocatalysts in this report were characterized using a suite of physical and chemical analytical methods. X-ray diffraction (XRD), Raman spectroscopy, and electron microscopy were used to study the structure of the as-prepared tungsten oxide samples. All the tungsten oxide samples were found to be monoclinic, which was consistent with PDF: 2343-1035. However, O₃-WO₃-550 exhibited a relatively lower crystallinity (Figure S1), indicating that the annealing temperature mainly affected the crystal structure. The diffraction peaks of O₃-WO₃-Pt and O₃-WO₃ were basically the same and no obvious diffraction peaks of a Pt species were observed in O₃-WO₃-Pt, because the size of photodeposited Pt was too small in size (2 nm, Figure S6C,D) and the content was low. WO₃ and O₃-WO₃ samples exhibited well-defined and intense Raman bands at 273, 327, 718, and 808 cm⁻¹ (Figure S2), which matched the four typical modes of monoclinic tungsten oxide (m-WO₃) observed in previous reports.[10] The bands at 273 and 327 cm⁻¹ correspond to the O-W bending modes of the bridging oxygen, and the bands at 718 and 808 cm⁻¹ are the corresponding stretching modes.[11] The bands intensity increased with the rising of the annealing temperature, consistent with the XRD results. According to the SEM images shown in Figure S4, the size of the O₃-WO₃ particles gradually changed from dozens of nanometers to microns when the annealing temperature rises from 550 to 650°C. As shown in Figure 1A, O₃-WO₃-600 prepared at 600°C contains nanoparticles of about 100 nm with a relatively uniform morphology. High resolution transmission electron microscopy (HRTEM) in Figure 1B and Figure S6 further revealed that O₃-WO₃-600 and O₃-WO₃-Pt had clear lattice fringes with a spacing of 0.384 nm, a feature corresponding to the (002) plane of tungsten oxide. Additionally, the irregular crystal lattices on the edge of nanoparticles can be attributed to the formation of oxygen vacancies, which has been validated to be a visualization method for detecting vacancy distribution in previous reports.[8b,16] The presence of oxygen vacancies is verified and discussed below through X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR). Furthermore, high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) mapping were conducted to verify the architecture of O₃-WO₃-Pt (Figure 1c), which demonstrated that Pt particles were distributed uniformly on O₃-WO₃-600 upon photodeposition.

The surface electronic structures of WO₃, O₃-WO₃-600, and O₃-WO₃-Pt were explored by using X-ray photoelectron spectroscopy (XPS). According to the XPS survey spectrum, only W, O, and C (adventitious carbon) elements were detected in O₃-WO₃-600 (Figure S7). The N element in the precursor has been removed in the calcination process. The W 4f spectra of O₃-WO₃-600 can be deconvoluted into four peaks (Figure 2B). The stronger peaks at 35.5 and 37.7 eV...
However, the W4f solution can only be deconvoluted into two peaks at 35.5 and 37.7 eV, both corresponding to WO6+. However, the W 4f spectrum of WO3 can only be deconvoluted into two peaks at 35.5 and 37.7 eV, both corresponding to WO6+. The existence of low-valent W indirectly indicated that oxygen vacancies were likely present on the surface of O3−-WO3-600. Moreover, in O 1s spectra of WO3 and O3−-WO3-600 (Figure 2C), the main peak at 530.2 eV can be assigned to the lattice oxygen of W−O bond in the crystalline WO3. The additional shoulder peak at 531.4 eV can be attributed to adsorbed oxygen ions or hydroxyl groups on the surface, especially around oxygen deficient regions. The ratio of adsorbed O increased to 16.7% in O3−-WO3-600 due to the surface oxygen vacancies, while it was 13.0% in WO3. This feature also serves as an indirect evidence for the presence of oxygen vacancies. Pt was also demonstrated to be photo-deposited onto O3−-WO3-600 through a survey spectrum (Figure S8), while the electronic structure of W and O were not changed in O3−-WO3-Pt. To confirm the presence of surface oxygen vacancies and investigate their properties further, in situ electron paramagnetic resonance (EPR) is a sensitive and direct method to monitor oxygen vacancies. O3−-WO3-600 exhibited relatively stronger EPR signal intensity at g ≈ 2.002 than that of WO3 under the same conditions, as shown in Figure 2D (g = hm/nBHr). As reported previously, g = 2.003 ± 0.001 can be attributed to oxygen vacancies on tungsten oxide surfaces, indicating the existence of surface oxygen vacancies on O3−-WO3-600.

Photocatalytic oxygen evolution (POE) performance of O3−-WO3 series samples, O3−-WO3-Pt and WO3 was evaluated in the presence of sacrificial reagents (Na2S2O8 solution) with the irradiation of a Xenon lamp to investigate the role of oxygen vacancies and cocatalysts for POE performance of tungsten oxide. As the POE results shown in Figure 3A, O3−-WO3-600 prepared at 600°C exhibited superior POE performance compared with O3−-WO3-650 and O3−-WO3-550, likely due to the poor crystallinity of O3−-WO3-550 and the large particle size of O3−-WO3-650. The average O2 evolution rate of O3−-WO3-600 reaches 683 μmol h−1 g−1 with Na2S2O8 as a sacrificial agent under full-spectrum irradiation (Figure 3A), while WO3 only exhibited 159 μmol h−1 g−1 under the same condition. The POE performance of O3−-WO3-600 was 4.3 times higher than that of WO3 without oxygen vacancies, corroborating that surface oxygen vacancies played an important role in the POE process on tungsten oxide. To explore the effect of cocatalysts further, the POE performance of O3−-WO3-Pt was measured to contrast with O3−-WO3-600 in a Na2S2O8 solution. The oxygen evolution rate of O3−-WO3-Pt was 1037 μmol h−1 g−1, higher than that of O3−-WO3-600. A further test was carried out to interrogate the oxygen evolution performance of O3−-WO3-600 and O3−-WO3-Pt by changing different sacrificial agents (FeCl3 and KIO3) in Figure 3B and two trends were observed. First, when considering O3−-WO3-600 as the photocatalyst, the highest oxygen evolution rate was observed with Na2S2O8 as a sacrificial agent, followed by FeCl3 and KIO3, respectively. The same trend was observed when O3−-WO3-Pt was used as the catalyst as well. The influence of sacrificial agents was mainly caused by their redox potential and pH. Second, no matter which sacrificial agent was applied, the oxygen evolution rate of O3−-WO3-Pt was higher than that of O3−-WO3-600. Furthermore, pure WO3 exhibited the lowest POE performance.

To further monitor the photogenerated electron-hole separation and carrier dynamics of O3−-WO3 series materials, femtosecond transient absorption spectroscopy (fs-TA) measurements were systematically performed under 266 nm laser flash photolysis. As illustrated in Figure 4A, WO3 exhibited a distinct positive band at 450–500 nm, demonstrating the excited state absorption (ESA). For the absorption near 480 nm, the absorption intensity gradually increased in 3.95 ps. This feature corresponds to the ultrafast separation of charge carriers. When the electrons are excited from the valence band (VB) to the conduction band (CB) and form the photogenerated electrons and holes, part of the electrons and holes will recombine with some fluorescence emission. Meanwhile, some other photogenerated electrons survive through an electron-trapping process. Photoinduced absorption (PIA) or a decrease in the differential transmittance (i.e. −ΔT/T) can be captured when the photoexcited electrons at CB of materials are excited to higher energy levels by laser. Hence, the decay of the PIA transient or the recovery of the transient to the equilibrium reflects the depopulation of these photoexcited carriers (at the CB of the materials) to the intrinsic defects. Due to the abundant surface oxygen vacancies, the fs-TA spectra monitored at 480 nm of O3−-WO3-600 were quite different from the results of WO3. According to the decay traces for the absorption of the photoinduced electrons (Figure 4) and the corresponding kinetics fitting parameters (Table 1), two decay processes (15.3 and 441.7 ps) were observed in WO3, corresponding to the fast charge recombination and electron trapping, respectively. For O3−-WO3-600, the significantly shorter decay component of 27.1 ps can be attributed to the prolonged recombination lifetime of the photoinduced electron-hole pairs, and the longer component (749.1 ps) revealed the existence of the

### Table 1: Exponential fitted parameters for the fs-TA spectra (pump: 266 nm) of WO3, O3−-WO3-600, and O3−-WO3-Pt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O3−-WO3-600</th>
<th>O3−-WO3-Pt</th>
<th>WO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ1 [ps]</td>
<td>27.1</td>
<td>2.4</td>
<td>15.3</td>
</tr>
<tr>
<td>τ2 [ps]</td>
<td>749.1</td>
<td>163.6</td>
<td>441.7</td>
</tr>
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Figure 3. A) Time course of photocatalytic OER for a series of O3−-WO3 samples and WO3 under full spectrum irradiation in an aqueous solution (50 mg, 0.1 M Na2S2O8, pH 10.5 adjusted by NaOH). B) O2 evolution rates of O3−-WO3-600, O3−-WO3-Pt, and WO3 in the presence of different sacrificial agents under full spectrum irradiation.
electron-trapping process, which was caused by defect states. We found that the high density of oxygen deficiency (trap states) in $\text{O}_x\text{WO}_3$ greatly improves the overall performance and charge separation process, because the density of the existing electron trap extends towards the conduction band edge.\cite{26} Compared with pure $\text{WO}_3$, the longer lifetime of the excited states of $\text{O}_x\text{WO}_3$, which was caused by electron trap states, was in favor of electron-hole separation.\cite{27} As a result, the long-lived trap states of $\text{O}_x\text{WO}_3$ promoted higher performance for the photocatalytic $\text{O}_2$ evolution reaction.

The kinetics and the fitted constants for $\text{O}_x\text{WO}_3$ and $\text{O}_x\text{WO}_3$-Pt are summarized in Figure 4F and Figure 4I. As expected, an extremely short component ($t_1 = 2.4$ ps) was obtained in $\text{O}_x\text{WO}_3$-Pt, which can be attributed to the quick recombination of the charge carriers. In contrast, the longer component ($t_2 = 163.6$ ps) was attributed to oxygen-vacancies induced charge trapping. This fast charge injection was caused by the intimate interaction and interfacial junction between $\text{O}_x\text{WO}_3$ and Pt. As a result, due to the heterojunction between the noble Pt and $\text{O}_x\text{WO}_3$, the resultant nano-material effectively suppresses electron-hole pairs recombination with ultrafast active electron injection from trap states to a metal center. Nanosecond transient absorption spectroscopy (ns-TA) measurements were used to monitor long-lived excited states and intermediate species, as shown in Figure S13 and S14. Similarly, both $\text{O}_x\text{WO}_3$ and $\text{O}_x\text{WO}_3$-Pt displayed a gradual decline of the broad absorption in the visible region ($400$–$700$ nm) on the $150$ ns timescale, respectively. This further assignment to the photogenerated electrons in $\text{W}^{5+}$ (oxygen vacancies) and thereby demonstrates their trapped nature.\cite{27}

Transient photovoltage (TPV) spectra (Figure 5A) of the samples were also measured to help understand the transfer and separation processes of the photogenerated charges. The first peak is at approximately $10^{-6}$–$10^{-7}$ s, which attributes to the surface photovoltage generated by photogenerated electrons in $\text{W}^{5+}$ (oxygen vacancies) and thereby demonstrates their trapped nature.\cite{27}

Figure 4. Fs-TA spectra of A,B) $\text{WO}_3$, D,E) $\text{O}_x\text{WO}_3$-600, and G,H) $\text{O}_x\text{WO}_3$-Pt dispersed in $\text{CH}_3\text{CN}$ and excited at $266$ nm; the decay kinetics monitored at $480$ nm of C) $\text{WO}_3$, F) $\text{O}_x\text{WO}_3$-600, and I) $\text{O}_x\text{WO}_3$-Pt.
charge separation under the electric field. The second peak at around $10^{-4}$ s corresponds to diffusion voltage. A higher photovoltage of the first peak means higher charge separation efficiency, and a longer time of the second peak means slower recombination of photogenerated charges.[30] O$_3$-WO$_3$-Pt and O$_3$-WO$_3$-600, exhibited higher photovoltaic of the first peak and longer time of the second peak. Therefore, O$_3$-WO$_3$-Pt presented the most efficient charge separation, followed by O$_3$-WO$_3$-600, and WO$_3$ was the lowest, which is consistent with the POE performance. Photoluminescence (PL) spectra (Figure 5B) were recorded to characterize the recombination of the photogenerated charges. When excited at 300 nm, O$_3$-WO$_3$-600, O$_3$-WO$_3$-Pt, and WO$_3$ exhibited a main emission peak at 525 nm. Weaker PL intensity of O$_3$-WO$_3$-600 indicated a lower recombination of the photogenerated charges, and Pt on the surface of O$_3$-WO$_3$-600 trapped the photogenerated electrons, resulting in further fluorescence quenching.[29] This observation is consistent with the photocatalytic performance of these samples.

The transient photocurrent response is also a facile technique for studying the generation, separation, and transfer processes of photogenerated electrons and holes in photocatalytic reactions.[30] As expected, O$_3$-WO$_3$-600 exhibited a higher photocurrent response than that of WO$_3$ obviously (insert in Figure 5C), where the transient photocurrent response was further enhanced with the photodeposition of Pt (Figure 5C). This phenomenon implied that the promoted separation of photogenerated electrons and holes via charge trapping was due to oxygen vacancies and a Schottky junction under irradiation. This observation can also be verified by electrochemical impedance spectroscopy (EIS) measurements (Figure S15), in which WO$_3$ showed the biggest Nyquist plot diameter no matter in the dark or upon illumination, indicating the highest charge-transfer resistance. O$_3$-WO$_3$-Pt exhibited much lower charge-transfer resistance than O$_3$-WO$_3$-600, which means that it was much more favorable for photogenerated charge carriers to transfer from O$_3$-WO$_3$-Pt to aqueous phase. These results indicated that surface oxygen vacancies and photodeposited Pt can lower the electronic impedance and improve charge mobility of these tungsten-based nanomaterials. This feature may be very beneficial for the photogenerated charge separation during photocatalytic process.

The aforementioned mechanism was mainly deduced from dynamics, while thermodynamic factors of O$_3$-WO$_3$ were explored further to unravel the POE mechanism. UV-visible diffuse reflectance spectrum (UV-vis DRS) can characterize the light absorption capability as well as confirm the position of an absorption band edge of semiconductor materials. As UV-vis DRS shown in Figure S16, WO$_3$ exhibited higher absorption at $< 500$ nm than the O$_3$-WO$_3$ samples, while it was opposite at $> 500$ nm because of the oxygen vacancies. The absorption band edges of O$_3$-WO$_3$-600 and WO$_3$ were measured to be 478 and 492 nm, corresponding to their band gaps of 2.59 eV and 2.52 eV, respectively. The absorption of the O$_3$-WO$_3$ samples showed slight enhancement and similar band gaps with increasing annealing temperature. However, the photodeposition of Pt significantly enhanced the absorption intensity of O$_3$-WO$_3$ from 400 to 650 nm. This result indicates that the O$_3$-WO$_3$ samples possess higher light efficiency for visible light.

The conduction band of n-type semiconductors can be estimated through flat band potential ($V_{fb}$) measurements by extrapolating the linear portion of a Mott-Schottky plot and obtaining the x-intercept.[31] According to the Mott-Schottky plots (Figures S17 and S18), $V_{fb}$ of WO$_3$ and O$_3$-WO$_3$-600 were determined to be $-0.24$ V and $0.10$ V (vs. Ag/AgCl), respectively. Assuming the gap between $V_{fb}$ and the conduction band minima (CBM) of the n-type semiconductor can be ignored, the $V_{fb}$ of the samples can be approximated as the potential of the CBM. Combining with the band gap, the CBM of WO$_3$ and O$_3$-WO$_3$-600 were calculated to be 0.37 and 0.71 eV, and their valence band maximum (VBM) were 2.89 and 3.3 eV, respectively. Evidently, O$_3$-WO$_3$-600 exhibited a deeper valence band potential, which is beneficial to a photocatalytic oxidation process, such as oxygen evolution. XPS valence band spectroscopy is a powerful tool to study the electronic structure of solid materials. The valence band absorption position of WO$_3$ was slightly lower than that of O$_3$-WO$_3$-600 in the valence band spectra (Figure S10), which is consistent with the results we calculated via the preceding electrochemical methods.

The ground-state electrocatalytic oxidation capability of our tungsten-based nanomaterials were characterized using linear sweep voltammetry (LSV). Figure 5D showed the LSV curves collected for WO$_3$, O$_3$-WO$_3$-600, and O$_3$-WO$_3$-Pt. The oxygen evolution onset potential of O$_3$-WO$_3$-Pt was more negative than that of O$_3$-WO$_3$-600, while WO$_3$ exhibited the most positive onset potential. This result suggests that O$_3$-WO$_3$-Pt is the most competent POE catalyst in the ground state among the three materials. This trend of oxygen evolution onset potential is also consistent with the photocatalytic oxygen evolution performance.

The mechanism of O$_3$-WO$_3$ POE system can be summarized into three key points (Scheme 1). First, the trap states can form more easily due to the presence of oxygen vacancies, which can trap a portion of excited electrons to partially inhibit direct recombination of the photogenerated carriers. This process can prolong the lifetime of active electrons to enhance their photocatalytic activity. Second, the photodeposited Pt can serve as an active site to capture the trapped state electrons to react with electron sacrificial agents, thereby accelerating the POE process further. Third, some thermodynamic factors like VBM, light absorption, and ground-state OER onset potential can act as POE perfor-
mance predictors of the O$_2$-WO$_3$ samples. In short, O$_2$-WO$_3$ exhibited higher POE performance than WO$_3$, while Pt can promote the POE activity even further.

**Conclusion**

We synthesized tungsten oxide with oxygen vacancies via a direct annealing method that is amenable to large-scale preparation. Through the use of femtosecond transient absorption spectroscopy, it is found that the defect structure of O$_2$-WO$_3$ can generate more electron trapping states during the photocatalytic process, inhibiting the direct recombination of photogenerated carriers and enhancing the photocatalytic oxygen evolution performance. Photocatalytic oxygen evolution rates of O$_2$-WO$_3$-600 can reach 683 μmol h$^{-1}$ g$^{-1}$ under the full spectrum, a promising activity that is 4.3 times higher than that of WO$_3$. A Pt cocatalyst can activate trapped state electrons to participate in the reaction to further improve the photocatalytic oxygen evolution performance of O$_2$-WO$_3$-600. This work provides a novel concept for the design of efficient oxygen evolution catalysts as well as offers an experimental framework for using ultrafast spectroscopy to examine photocatalytic reactions facilitated by inorganic materials.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** charge migration · femtosecond transient absorption spectroscopy · oxygen vacancies · photocatalytic oxygen evolution · tungsten oxide

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