Tungsten Blue Oxide as a Reusable Electrocatalyst for Acidic Water Oxidation by Plasma-Induced Vacancy Engineering

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In contrast to alkaline water electrolysis, acidic water electrolysis remains an elusive goal due to the lack of earth-abundant, efficient, and acid-stable water oxidation electrocatalysts. Here, we show that materials with intrinsically poor electrocatalytic activity can be turned into active electrocatalysts that drive the acidic oxygen evolution reaction (OER) effectively. This development is achieved through ultrafast plasma sputtering, which introduces abundant oxygen vacancies that reconstruct the surface electronic structures, and thus, regulated the surface interactions of electrocatalysts and the OER intermediates. Using tungsten oxide (WO₃) as an example, we present a broad spectrum of theoretical and experimental characterizations that show an improved energetics of OER originating from surface oxygen vacancies and resulting in a significantly boosted OER performance, compared with pristine WO₃. Our result suggests the efficacy of using defect chemistry to modify electronic properties and hence to improve the OER performance of known materials with poor activity, providing a new direction for the discovery of acid-stable OER catalysts.

Keywords: WO₃, vacancy engineering, plasma, acidic OER, reusable electrocatalyst

Water electrolysis is a process that can electrocatalytically dissociate water into molecular O₂ via oxygen evolution reaction (OER) and H₂ via hydrogen evolution reaction (HER), which promises an efficient way to produce hydrogen fuel.¹² Compared with alkaline conditions, the water electrolysis in acid is preferable because of the higher conductivity (>1.5 times) of protons than hydroxide ions and fewer side reactions.¹²
More importantly, the acidic water electrolyzers are readily compatible with commercially available proton-exchange membranes (PEM), and thus, possess many advantages, including fast system response, high voltage efficiency, high current density, and high gas purity. While inexpensive, robust, and efficient electrolysis catalysts are available for both the OER and HER in alkaline electrolytes, the only well-established catalysts that can stably drive the OER in acidic media are Ir- and Ru-based noble metal oxides. Ir and Ru are scarce, whereas conventional OER active earth-abundant materials, unfortunately, cannot survive in acidic media due to the anodic corrosion. Developing low-cost and acid-stable OER catalysts, therefore, is highly desirable for not only the widespread implementation of water electrolysis technology but also other half-reactions, including CO2 and N2 reduction that are involved in fuel productions.

According to the Pourbaix diagram, tungsten oxide (WO3) is stable in acidic conditions at OER potentials. WO3 is an n-type semiconductor with good carrier transport and has been widely used in photocatalysis and solar water splitting. It has recently demonstrated its efficacy for HER electrocatalysis. However, the use of WO3 for OER electrocatalysis in acidic conditions has not yet been explored. This is perhaps not surprising, as previous computational studies have already revealed that WO3 is likely inactive for OER due to its very weak binding to OH. Given that the activity is mostly determined by the OER energetics, which is influenced by the interactions of reaction intermediates (i.e., OOH, OH, and O) and catalyst surface active sites, it is possible to tune the activity through delicate modification of the interactions. The engineering of vacancies, therefore, offers a promising avenue to improve the activity of catalysts because it could modify the electronic structure and the local coordination chemistry, and consequently, the surface interactions. Furthermore, oxygen vacancies in oxides generally lead to an enhanced electrical conductivity, and therefore, it is expected that intrinsically catalytically inactive materials such as WO3 might become OER active through proper vacancy engineering. Hence, we started with density functional theory (DFT) studies aimed at identifying the impacts of oxygen vacancies on the electronic property and further OER energetics. The WO3 (001) facet was used for simulations, considering it is the most stable surface. To present a prototypical model by removing one surface oxygen atom from the WO3 model. As expected, such modification affected the electronic structure of the surface W, observable via an electron density difference (EDD) calculation. We attributed this improvement to the removal of the highly electro-negative terminal group from the stable surface that enhances the binding affinity with other negative groups such as OH.

The DFT calculations indicated that the vacancy engineering of the catalysts could improve the energetics for OER, suggesting a promising pathway to discover acid-stable OER catalysts. To test this hypothesis, we synthesized WO3 nanowires with rich oxygen vacancies (WO3−XO) and further investigated their OER performance in acidic media. A commonly used method of generating oxygen vacancies involves annealing of precursors at high temperature under reducing atmospheres, which is often accompanied by morphological deformation and particle aggregation, and therefore, could decrease the active surface area. Instead, plasma could induce rapid and efficient surface modification at relatively mild conditions due to its highly active ionic species. In this study, we employed Ar plasma to create oxygen vacancies at lower temperatures. For comparison, WO3 nanowires with limited oxygen vacancies were also synthesized by annealing the precursor at 300 °C in the air. It is commonly recognized that creation of vacancies could provide...
coordinatively unsaturated sites to allow molecular adsorption.37 Indeed, we observed an intense peak at 531.7 eV in the O 1s X-ray photoelectron spectroscopy (XPS) spectrum of WO3-Vo (Supporting Information Figure S3) arising from the oxygen species adsorbed at the vacancy sites, a typical feature of oxygen-deficient oxides.38 Accordingly, part of the W6+ in WO3-Vo was reduced to W4+/W5+. As determined by XPS, the ratio of surface W4+/W5+/W6+ is ∼0.03/0.37/0.6, corresponding to a chemical formula of WO2.79. Notably, the WO3-Vo was deep blue, whereas the WO3 was light green, suggesting that the vacancy generation affected the electronic property of the material and therefore its light adsorption (Supporting Information Figure S4). Despite the difference in vacancy concentration, both the WO3 and WO3-Vo possessed a hexagonal WO3 phase according to the X-ray diffraction (XRD) analysis (power diffraction file card #85-2460), and a nanowire morphology. The nanowires are grown along the [001] direction (c axis), as determined by the transmission electron microscopy (TEM) characterization (Figure 2a). The anisotropic structure was beneficial in exposing oxygen vacancies on the surface rather than embedding them in bulk. Careful observation revealed that a slight lattice disorder was apparent at the edges (as indicated by the arrows). The atomic image of WO3-Vo allowed the direct visualization of the O vacancies (Figure 2b). Numerous small pits were observed (as indicated by the arrows) which could offer more coordinately unsaturated sites for the OER electrocatalysis. The variation in atomic column intensity suggests a variation in the oxygen atomic occupation, indicating the presence of oxygen vacancies. The differences in intensity and contrast are further highlighted in the colored image and the line profile (Figure 2c). Besides, electron paramagnetic resonance (EPR) analysis showed that the WO3-Vo exhibited a much more intense EPR signal at ∼g = 2.002, compared with WO3 (Supporting Information Figure S5), further confirming the presence of a higher concentration of vacancies in WO3-Vo.43 The high-angle annular dark-field scanning TEM (HAADF-STEM) analysis revealed that both the W and O were evenly distributed over the nanowire, while the latter was more scattered (Figure 2d). These results, together with the XPS and EPR analyses, confirmed the generation of oxygen vacancies in WO3-Vo by plasma sputtering. In contrast, the crystal lattice of WO3 was highly ordered even at the edges, and the atomic column intensity was evenly distributed (Supporting Information Figure S6), demonstrating that the vacancy concentration was very low (the O/W ratio is 2.98 based on the XPS analysis, close to the stoichiometric ratio of WO3, see Supporting Information Figure S3).
Then we evaluated the OER performance of the WO$_3$-V$_o$ in 0.5 M H$_2$SO$_4$. The optimal OER activity was achieved on the WO$_3$-V$_o$ being treated by a 30 s plasma sputtering (Supporting Information Figures S7 and S8). A shorter or longer duration would lead to inferior performances of WO$_3$-V$_o$, though they were, in general, quite close (Supporting Information Figure S8).

Figure 2e compares the $iR$-corrected linear sweep voltammetry (LSV) curves of WO$_3$-V$_o$ and WO$_3$ recorded at 0.5 mV s$^{-1}$. We observed several anodic peaks for the WO$_3$-V$_o$, arising from the oxidation of W$^{4+}$/W$^{5+}$ species and possibly the oxygen intercalation into the vacancies, whereas the WO$_3$ had negligible anodic peaks. This suggested that the vacancy engineering tuned the electronic properties, and hence, the oxidation behavior to intensify the electrocatalytic OER performance. Accordingly, the WO$_3$-V$_o$ exhibited a greatly enhanced activity with a current density of 21.3 mA cm$^{-2}$ at 1.90 V versus the reversible hydrogen electrode (RHE) (i.e., an overpotential of 670 mV), which is three times larger than that of WO$_3$ (5.1 mA cm$^{-2}$). No Ir or Ru was detectable after the OER operation of the catalysts (Supporting Information Figure S9). Furthermore, the carbon paper (CP) showed negligible oxidation current, indicating that the OER activity came from WO$_3$ itself. It should be noted that the presence of vacancies modified the electronic structure that not only altered the interactions of surface W and OER intermediates, as revealed by the DFT calculations but also improved the conductivity. As a result, the WO$_3$-V$_o$ exhibited a smaller charge-transfer resistance than that of WO$_3$ (Supporting Information Figure S10). Besides, the oxygen vacancies also provided more coordinately unsaturated sites that led to a larger electrochemically active surface area (ECSA) of the WO$_3$-V$_o$ (Supporting Information Figure S11). However, this difference (543 vs 314 cm$^2$) could not account fully for the dramatically enhanced performance of WO$_3$-V$_o$. Indeed, the WO$_3$-V$_o$ still showed much larger OER currents than WO$_3$ after being normalized by ECSA. For example, the current density of WO$_3$-V$_o$ at 1.90 V versus RHE was 2.4 times as large as that of WO$_3$ (0.038 vs 0.016 mA cm$^{-2}$ per ECSA, Supporting Information Figure S11). Similarly, the WO$_3$-V$_o$ also showed much larger Brunauer–Emmett–Teller (BET) surface area normalized OER currents than WO$_3$ (Supporting Information Figure S12), suggesting the enhancement of intrinsic
activity by vacancy engineering. This was supported further by the O₂ turnover frequency (TOF) calculation result. As shown in Figure 2f, the average TOF of the WO₃-Vo is four to eight times as large as that of WO₃ in the potential region of 1.8–2.0 V versus RHE. Furthermore, the WO₃-Vo also possessed a much smaller Tafel slope (183.3 mV dec⁻¹) than that of WO₃ (280.1 mV dec⁻¹; Supporting Information Figure S13). These observations confirmed the predictions from DFT results and suggested that the WO₃-Vo is an effective electrocatalyst for OER in acidic media, though the WO₃ had poor activity. The overpotentials of WO₃-Vo and WO₃ at 10 mA cm⁻² were 590 and 770 mV, respectively, close to the calculated result (500 and 750 mV). Although the overpotentials were 130–250 mV larger than the that of state-of-the-art OER catalysts (i.e., IrOₓ and RuOₓ), the WO₃-Vo had already outperformed many recently reported acidic OER catalysts, including some noble metal-based compounds such as Pt/C at a significantly reduced cost of WO₃-Vo being only ~1/250 and 1/1200 of IrOₓ or RuOₓ, respectively (Figure 2g and Supporting Information Table S1).

Furthermore, we examined the stability of WO₃-Vo by operating the OER at a constant current density of 10 mA cm⁻². As demonstrated in Figure 3a (and Supporting Information Figure S14), although the initial potential of RuO₂ is quite low, it rises quickly from ~1.45 to 2.0 V versus RHE in 30 min, essentially losing its activity. This result is in agreement with previous reports that the RuO₂ suffered from poor long-term stability, despite its high initial activity. The WO₃ was almost inactive for OER and required a high initial overpotential of 770 mV (vs 2.0 V RHE) at 10 mA cm⁻², and the potential sharply raised to higher than 2.5 V versus RHE after 3 h. In contrast, the WO₃-Vo was stable for at least 6 h, which was already 12 times as long as that of RuO₂. In fact, this number (operation time) is among the best-reported values of OER electrocatalysts achieved in acidic media (see the comparison in Supporting Information Table S1). Interestingly, we noted that during the OER catalysis, the surface color of WO₃-Vo changed gradually from deep blue to light green, maintaining the same color as WO₃. This observation indicated that the surface vacancies of WO₃-Vo had been filled though its bulk structure remained the same (Supporting Information Figure S15), which is likely responsible for the activity loss in WO₃.

Then we employed XPS to track the surface oxygen species and found that the original O 1s peak at 531.7 eV that is associated with oxygen vacancies disappeared.
after the electrocatalysis (Figure 3b). The surface $W^{5+}$ in WO$_3$-Vo had also been oxidized to $W^{6+}$ (Supporting Information Figure S15), further confirming the filling of oxygen vacancies upon the OER. This result revealed that the electronic property of WO$_3$-Vo after the OER was essentially similar to that of pristine WO$_3$. Furthermore, the nanowire morphology was observed to be retained mainly though a slight surface aggregation. This is different from that of WO$_3$, which underwent a more severe aggregation (Supporting Information Figure S16). As we demonstrated earlier, the vacancy engineering could effectively tune the electronic properties, and subsequently, boost the OER activity substantially. This finding provided us with an excellent opportunity to reactivate the WO$_3$-Vo-OER by regenerating the oxygen vacancies, especially given the highly reserved nanowire structures. Therefore, we conducted a second plasma treatment (30 s) on the catalyst and investigated further the OER performance of the plasma reactivated WO$_3$-Vo-OER (WO$_3$-Vo-PR; see the structural characterization in Supporting Information Figure S17). As shown in Figure 3c, the activity of WO$_3$-Vo gradually decays upon cycling. The overpotential at 10 mA cm$^{-2}$ increases from 590 to 675 mV after 500 continuous cyclic voltammetry (CV) cycles. While after plasma reactivation, the activity is recovered, and the overpotential drops back to 587 mV. A similar trend is again observed for the overpotential required at 20 mA cm$^{-2}$. Further confirming the efficacy of our strategy, we measured the same catalyst after 500 CV cycles, both WO$_3$-Vo and WO$_3$-Vo-PR possessed much stronger peak intensities, manifesting higher concentrations of vacancies. The simple and fast plasma reactivation prolonged the lifespan of the catalyst considerably without sacrificing the OER activity while avoiding the tedious and costly synthesis process, which significantly lowered the overall cost and greatly enhanced the catalyst utilization efficiency.

Furthermore, we probed the evolution of oxygen vacancies during the OER catalysis by performing a synchrotron X-ray absorption fine structure (XAFS) analysis. Figure 4a displays the X-ray absorption near edge structure (XANES) spectra at the W L$_3$ edge of WO$_3$, WO$_3$-Vo, WO$_3$-Vo-OER, and WO$_3$-Vo-PR. The normalized spectra of all the four samples exhibit a broad white-line absorption because of the electronic dipole transitions from $W 2p_{3/2}$ to mainly 5$d$ orbitals. Though the spectral profiles are similar to each other, subtle differences among the samples are already visible in detailed comparisons of their white-line peaks (top-left inset of Figure 4a), revealing the difference in W local symmetry and electronic structure. The WO$_3$ exhibits the strongest intensity, suggesting the high symmetry of the local structure. The WO$_3$-Vo and WO$_3$-Vo-PR, in contrast, possess much weak intensities, which suggests the increased distortion of WO$_6$ octahedra because of the oxygen vacancies. The peak intensity of WO$_3$-Vo-OER is higher than WO$_3$-Vo, but it is still lower than that of WO$_3$, indicating that some of the oxygen vacancies survived even after the OER. This result is consistent with the EPR analysis, where the WO$_3$-Vo-OER still shows a weak signal, likely because the oxygen vacancies in the subsurface did not participate in the OER catalysis, given the reaction only occurred at/near the catalyst surface. The presence of vacancies led to a decrease in the W oxidation state, which was confirmed further by the $E_0$ value. The top-right inset of Figure 4a compares the $E_0$ value of the four samples, and the result reveals that the $E_0$ value of WO$_3$-Vo and WO$_3$-Vo-PR is smaller than that of WO$_3$ and WO$_3$-Vo-OER, indicating that the valence of W decreased as the vacancy concentration increased. The bottom panel of Figure 4a displays the second derivative curves of the XANES spectra, which provides further information on the W 5$d$ orbitals splitting. All the spectra exhibit lower and higher energy minima, corresponding to the splitting of the W 5$d$ into $t_{2g}$ and $e_g$ states. The splitting is $\sim$4.8 eV for WO$_3$, which decreases to 4.4 eV for WO$_3$-Vo-PR. This smaller splitting value is attributable to the disordered local structure, as well as the contribution of the uncoordinated W and O atoms.
results confirm the generation of oxygen vacancies by plasma and their loss after the OER. Figure 4b displays the Fourier transform (FT) of extended XAFS (EXAFS) spectra. The three intense peaks correspond to the single scattering (SS; at 0.7–1.8 Å), the multiple scattering (MS; at 2.2–3.1 Å) in the first shell, and the combined SS and MS signals in the second shell (at 3.1–3.9 Å), respectively.49,50 Notably, these peak positions are not necessarily the exact crystallographic values.51 Therefore, we further performed a curve fitting analysis to obtain the structural parameters. In the hexagonal WO3 structure, the corner-sharing WO6 octahedra build up three-dimensional (3D) frameworks with hexagonal channels.52 There are two W–O bonds with different lengths (1.80 and 2.05 Å) in an octahedron. The fitting result reveals that the W atoms in WO3-Vo-OER have a coordination number close to that of WO3 (i.e., 5.9 vs 6.0; see Supporting Information Table S2), suggesting the high symmetry of the WO6 in both samples. In contrast, the coordination numbers of W atoms in WO3-Vo and WO3-Vo-PR are much lower (5.4 and 5.3, respectively), which indicates a disordered local structure. Specifically, the W atoms in W–O bond with shorter length have a lower coordination number, identifying the main location of oxygen vacancies. This result agrees well with the XPS and EPR analyses, confirming the introduction of the oxygen vacancies by plasma and the loss of vacancies upon OER electrocatalysis. Together with the structural and electrochemical characterizations, the XAFS analysis strongly supports the critical role of oxygen vacancies in enhancing the OER activity of WO3-Vo.

In conclusion, we suggest a simple strategy that enables the turning of electrocatalytically inactive materials into efficient acidic OER catalysts through plasma-assisted vacancy engineering. We have shown that introducing oxygen vacancies regulates the surface interactions of electrocatalysts and the OER intermediates, hence greatly improving the OER energetics and consequently boosting the OER activity. As a result, we demonstrate both theoretically and experimentally that WO3, an acid-stable material with intrinsically poor OER catalytic activity, is able to stably drive an OER current of 10 mA cm$^{-2}$ at an overpotential of 590 mV for at least 6 h. Though the catalytic activity is still inferior to IrO2 and RuO2, W is much more abundant, and the cost is only ~1/1200 times that of Ir. Furthermore, we have shown for the first time that the WO3-Vo catalyst, after OER, could be reactivated by simple plasma retreatment. This prolongs the lifespan of the catalysts while avoiding the repetitive synthesis process, and hence, significantly reduces the overall cost, which is practically important for the water electrolysis industry. Our work points to a new direction of using defect chemistry to discover inexpensive, efficient, and acid-stable OER catalysts, which potentially could be used for large-scale water electrolysis and other OER involved applications.

Supporting Information
Supporting Information is available.

Conflict of Interest
There is no conflict of interest to report.

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