Efficient WO$_{3-x}$ nanoplates photoanode based on bidentate hydrogen bonds and thermal reduction of ethylene glycol

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ABSTRACT

In this study, an efficient WO$_{3-x}$ nanoplates photoanode was generated based on bidentate hydrogen bonds and subsequent thermal reduction of ethylene glycol (EG). An appropriate number of controllable oxygen vacancies (O$_v$) was generated in-situ on the surface of the WO$_3$ nanoplates without deep defects by bidentate hydrogen bonds. Density functional theory (DFT) calculations indicate that the distance between two alcoholic hydrogens (5.124 Å) in EG matches that of the diagonal oxygens (5.483 Å) in the WO$_3$ (002) surface, which allows EG to combine through the most stable bidentate hydrogen bonds with O–H intervals of approximately 2.5 Å. Diagonal oxygens are captured directly from the surface, leaving O$_v$ owing to the special hydrogen-bond structure and moderate reducibility of EG under appropriate thermal conditions. The photocurrent density of the WO$_{3-x}$ nanoplates improves considerably to 2.07 from the 0.91 mA cm$^{-2}$ of pristine WO$_3$ with the introduction of O$_v$, which demonstrates the superior surface reaction kinetics from the reduced holes-to-water resistance and increase in surface injection efficiency. DFT calculations of the oxygen evolution reaction reveal that surface O$_v$ could substantially decrease the reaction energy barrier for a lower overpotential of 0.494 V compared to that of WO$_3$ (1.037 V), which is consistent with the reduction in the Tafel slope from 412 to 243 mV dec$^{-1}$. Therefore, this study provides an innovative method to obtain an efficient WO$_3$ photoanode based on the treatment of EG.

1. Introduction

Photoelectrocatalytic (PEC) water splitting for H$_2$ generation is one of the most promising strategies for converting abundant solar power and realizing sustainable energy storage [1]. A considerable number of studies have been performed to develop various semiconductors (e.g., Fe$_2$O$_3$ [3,4], BiVO$_4$ [5,6], and ZnO [7,8]) for photoanodes, since solar water splitting was proposed in the 1970s [2]. WO$_3$ is recognized as a potential photoanode material among all transition metal oxides because of its suitable band gap and band edge, excellent electron transfer, long hole lifetimes, and chemical stability in acidic aqueous solutions [9–13]. Nevertheless, the PEC performance of WO$_3$ is substantially restricted by slow interface hole transfer, fast charge-carrier recombination, and sluggish kinetics [10,14,15].

Herein, WO$_{3-x}$ nanoplates with efficient interfacial charge transfer and superior surface reaction kinetics were obtained based on bidentate hydrogen bonds and the subsequent thermal reduction of ethylene glycol (EG). An appropriate number of controllable oxygen vacancies (O$_v$) was generated in-situ on WO$_{3-x}$ nanoplates. O$_v$ engineering has been effective at ameliorating the optical and electronic properties of semiconductor photoanodes to enhance water oxidation [16], which can promote solar light harvesting [17,18], increase the charge carrier densities by decreasing the of band gap [19,20], and dissociate water molecules as active sites [21,22].

However, the traditional methods for creating O$_v$ in WO$_3$, such as annealing in H$_2$, which is the most common method [23], can extend O$_v$ from the surface to the bulk region, introducing deep defects owing to its strong reducibility. The O$_v$ in bulk may act as recombination centers and...
decrease the electron mobility, which harms the PEC performance [24,25]. In contrast, the O decreases the electron mobility, which harms the PEC performance. Therefore, modulating O on the WO3 nanoplates can improve the PEC performance for rapid interfacial charge transfer.

In this paper, we reduced pristine WO3 by bidentate hydrogen bonds between EG and diagonal oxygens of WO3 to construct O on the surface rather than the bulk. The obtained WO3-x nanoplates photoanode had a significantly improved photocurrent density, increasing from 0.91 to 2.07 mA cm-2 at 1.23 V vs. reversible hydrogen electrode (RHE). Density functional theory (DFT) calculations indicate that the distance between two alcoholic hydrogens (5.124 Å) in EG matches that of the diagonal oxygens (5.483 Å) in WO3 (002) surface forming bidentate hydrogen bonds to capture surface oxygen atoms under thermal reduction. And DFT also revealed that surface O could lower the energy barrier of the oxygen evolution reaction (OER) with the overpotential decreasing from 1.037 to 0.494 V, which is consistent with the reduction in the Tafel slope from 412 to 243 mV dec-1. Therefore, thermal reduction by EG can introduce O on the WO3 nanoplates surface, while avoiding the creation of structural defects (bulk O3), and WO3-x can improve the PEC performance for rapid interfacial charge transfer.

2. Experimental

2.1. Synthesis of WO3 and WO3-x nanoplates

WO3 nanoplates were hydrothermally grown on fluorine-doped tin oxide (FTO) glass substrate [12]. Initially, 1.0 g of ammonium para-tungstate (NH4)2(H3W12O42) 4H2O was dissolved in 93 mL of deionized water and stirred for 1 h. Subsequently 2 mL of HCl (37%) and 4 mL of H2O2 (30%) were added and stirred for 1 h, respectively, to get transparent and clear solution. Afterwards the cleaned and faced down FTO was placed inside the Teflon-liner autoclave and reacted at 160 °C for 4 h. The hydrothermally synthesized films were annealed at 500 °C for 2 h to convert into crystalline WO3.

The WO3-x nanoplates photoanode was prepared via a facile and moderate thermal reduction by EG. The obtained WO3 substrate was immersed into pure EG (>99%) in a 30 mL reaction kettle, and reduced at 130 °C for 10 h to introduce controllable O by bidentate hydrogen bonds. The film was rinsed with deionized water repeatedly and dried in a vacuum oven at 50 °C for 1 h after the reactor cooled to room temperature. The resulting WO3-x electrode with the introduction of O on the surface catalysis was used for the following experiments.

2.2. Material characterization

The morphologies were investigated by field emission scanning electron microscopy (FE-SEM; Ultra Plus, Zeiss, Germany) with an accelerating voltage of 5 kV. The microstructure was determined by high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F30 S-TWIN, FEI, USA). X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (XRD; AXS-8 Advance, Bruker, Germany). Raman spectra were obtained using a LabRAM ARAMIS Raman system, exciting two wavelength lasers of 532 nm and 325 nm to characterize the position of O in the Raman spectrum (XPS; AXIS UltraDLD, Kratos, Japan) and XPS etching spectroscopy were performed using IR/Nicolet 6700 (Thermo Fisher, America). Electron paramagnetic resonance (EPR) signals were obtained on a Bruker E500 EPR spectrometer at room temperature. Ultraviolet-visible diffuse reflectance spectroscopy (UV–Vis DRS) were investigated by a UV–vis spectrophotometer (TU1900, Beijing Purkinje General Instrument Co. China).

2.3. PEC measurements

PEC measurements were obtained using a standard three-electrode cell, which included a Ag/AgCl electrode as the reference electrode, a Pt cathode as the counter electrode, and the as-prepared films as the working electrode. The electrolyte was a 0.2 M Na2SO4 aqueous solution, and the test was performed on an electrochemical workstation (CHI 660d, CH Instruments Inc., Shanghai). A 300 W Xenon lamp (PLS-SXE300) coupled with an AM 1.5G solar power system was used as an illumination source with a light instability of less than ±6% (10 h), and a centralized digital power management control mode based on a micro CPU. Photocurrent density–potential (J–V) curves were measured at a scan rate of 50 mV s-1 by linear sweep voltammery (LSV), and the chopped J-V curves were recorded by chopped light voltammery (CLV). The applied bias vs. RHE (E(RHE)) was calculated according to Eq. (1):

\[ E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + E(\text{Ag}/\text{AgCl}) \text{(reference)} + 0.0591 \times V \times \text{pH}. \]  

(1)

where EAg/AgCl is the applied bias vs. Ag/AgCl and EAg/AgCl (reference) is the standard electrode potential of the Ag/AgCl electrode (0.1976 V at 25 °C).

The incident photon-to-current efficiency (IPCE) was measured using a system comprising a monochromator (Zolix, China), a 500 W xenon arc lamp, a calibrated silicon photodetector and power meter with monochromatic light irradiation. The IPCE was calculated using Eq. (2):

\[ \text{IPCE}(\%) = \left( \frac{1240 \times J_{\text{mono}} \times h}{P_{\text{mono}} \times \lambda} \right) \times 100\%. \]  

(2)

where Jmono is the measured photocurrent density at a specific wavelength, Pmono is the measure irradiance at a specific wavelength, and \( \lambda \) is the wavelength of the incident light.

The applied bias photon-to-current conversion efficiency (ABPE) of the films was computed using Eq. (3):

\[ \text{ABPE}(\%) = \left( J \times (1.23 - V_{\text{b}})/P_{\text{tot}} \right) \times 100\%. \]  

(3)

where J is the photocurrent density at the applied bias (mA cm-2), Vb is the applied bias (V vs. RHE), and Ptot is the power density of the incident light (mW cm-2).

Electrochemical impedance spectroscopy (EIS) was measured with AC frequencies from 100 kHz to 0.1 Hz, under irradiation at 1.23 V vs. RHE. Mott-Schottky (MS) plots were measured at a frequency of 1 kHz, with DC voltages from 0.2 to 1.4 V.

The charge carrier density (Nd) was obtained using Eq. (4) [27]:

\[ N_{\text{d}} = \left( \frac{2 e \epsilon_0 \varepsilon}{d} \right) \times \left( \frac{1}{\varepsilon} \right) \times \left( \frac{1}{d} \right) \times \left( \frac{1}{\varepsilon} \right) \times \text{cm}^{-2}. \]  

(4)

where C is the space charge capacitance in the semiconductor, e is the elementary charge value, \( \epsilon_0 \) is the permittivity of vacuum, and V is the relative permittivity of the semiconductor, and V is the applied potential.

2.4. Computational methods

Computational results were calculated using the Vienna Ab Initio Simulation Package (VASP), with the ion-electron interaction computed by the projector-augmented wave (PAW) method [28,29]. The exchange-correlation potential was simulated with the Perdew-Burke-Ernzerhof (PBE) function [30]. Additionally, the Hubbard model (DFT + U approach) was used for the correlation corrections, and the correlation energy was fixed at 6.2 eV for the 4f orbital of W [31]. The Kohn-Sham equations were self-consistent, solved by three-dimensional (3D) periodic boundary conditions with energy tolerance of 10-6 eV. Gamma-centered k-space grid 3 × 3 × 3 and 3 × 3 × 1 were used for the monoclinic phase and slab model, respectively, with 520 eV as the energy cutoff. The atom positions and vectors were optimized to achieve a calculated atomic force of < 0.01 eV Å-1 on each atom in the slabs.

Water oxidation involves four proton-coupled electron transfer steps with the OER on the anode as follows:
3. Results and discussions

3.1. Structural characterisation of the photoanodes

Fig. 1a illustrates the preparation of WO$_{3-x}$ nanoplates on FTO substrates, where orthorhombic WO$_3$·0.33H$_2$O precursors grew hydrothermally. WO$_3$·0.33H$_2$O samples were transformed into hexagonal WO$_3$ nanoplates in wax yellow by annealing at 500 °C for 2 h in air. Subsequently, the O$_v$ photoanode of WO$_3$ was obtained via a thermal reduction of EG at 130 °C for 10 h, which is the optimal reaction condition according to the photocurrent density in Table S1–S2. The light yellow WO$_3$ that formed at 130 °C introduced more controllable O$_v$ into the structure under moderate reaction conditions (Figure S1), compared to the olive-green sample that formed at 190 °C with a lower photocurrent density, owing to bulk O$_v$, which may promote visible light harvesting (Figure S2) but act as hole-and-electron recombination centers [24]. The long reduction time (15 h) may produce excess O$_v$ to decrease the photocurrent density for the lower slope in Figure S3 with higher carrier density [19,20]. The SEM images (Fig. 1b-c) of WO$_3$ display vertical rectangular (3D) nanoplates with a thickness of ~10 nm, and WO$_3$ nanoplates with the same morphology are shown in Figure S4. The XRD patterns (Figure S5) illustrate three sharp peaks located at 23.1°, 23.5°, and 24.3° for WO$_3$ and WO$_{3-x}$ at 130 and 190 °C.
monoclinic structure (PDF#43-1035) with negligible discrepancies in crystal phases. The total O 1 s XPS spectrum of WO$_3$ had an intensified signal at 531.5 eV corresponding to O$_{\text{surf}}$, which is confirmed by the deconvoluted O 1 s XPS spectra (Figure S6). A lattice-disordered layer of approximately 1 nm thickness can be seen in the HRTEM images of WO$_3$ (Fig. 1e-f), where oxygens may leave the surface to form O$_{\text{vac}}$ [33]. The interplanar distance of 0.383 nm corresponds to the exposed (0 0 2) surface.

The W 4f XPS spectra of WO$_3$ and WO$_{3-x}$ samples are shown in Fig. 1g. The characteristic peaks for WO$_{3-x}$ shifted to lower binding energies as the temperature increased (from 35.75 eV for WO$_3$ to 35.40 eV for WO$_{3-x}$/130 °C), suggesting a gradual increase in the presence of W$^{5-}$ with an increase in the O$_x$ amount [34,35]. Fig. 1h shows the O 1 s XPS spectra at a depth of approximately 50 nm, which could reflect the bulk oxygen species in the photoanodes [36]. The binding energy shifted to higher values with increasing temperature, which is attributed to an increasing amount of bulk O$_x$ [37], and the peak position of WO$_{3-x}$/130 °C was close to that of WO$_3$ for a similar amount of bulk O$_x$. Fig. 1i illustrates the Raman spectra under 532 nm excitation, which have three characteristic peaks: 274, 718, and 808 cm$^{-1}$; they are attributed to the bending vibration of δ(W-O-W) and stretching vibration of ν(W-O-W), which are in agreement with that of monoclinic WO$_3$ [38]. The Raman intensities gradually decreased as the temperature increased, indicating that the W coordination environment changed and the amount of O$_x$ was increased, as shown in Fig. 1j. The full width half maximum (FWHM) of the 332 nm Raman band around 808 cm$^{-1}$ shown in Table 1, reflects the amount of bulk O$_x$ [24,39] and the similar FWHMs of WO$_3$ and WO$_{3-x}$/190 °C indicates that few bulk O$_x$ were introduced by EG at 130 °C. Figure S7 illustrates the UV Raman spectra (325 nm excitation) to characterize the surface information of the samples [40]; the results indicate that WO$_3$ is 130 °C generated more surface O$_x$ than WO$_3$ because of its larger FWHM. The EPR signal of WO$_{3-x}$/190 °C was much stronger than those of WO$_3$ and WO$_{3-x}$/130 °C around 2.005 (g factor) as shown in Fig. 1j, indicating that more unpaired electrons were captured by O$_x$ with temperature increasing [41,42]. The overall characteristics indicate that thermal reduction by EG has controllably introduced an appropriate amount of O$_x$ onto the WO$_3$ surface, avoiding the deep defects of bulk O$_x$ in the structure.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM around 808 cm$^{-1}$</th>
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<tbody>
<tr>
<td>WO$_3$</td>
<td>16.54 cm$^{-1}$</td>
</tr>
<tr>
<td>WO$_{3/130}$</td>
<td>16.90 cm$^{-1}$</td>
</tr>
<tr>
<td>WO$_{3/160}$</td>
<td>18.66 cm$^{-1}$</td>
</tr>
<tr>
<td>WO$_{3/190}$</td>
<td>20.34 cm$^{-1}$</td>
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FWHM of primary Raman shifts under 532 nm excitation.

3.2. The model of bidentate hydrogen bonds

The generation of O$_x$ via thermal reduction by EG could be attributed to the moderate reducibility and chemisorption on the WO$_3$ surface, because of the hydrogen bonding based on DFT calculations. A (1 x 1) WO$_3$ slab was cleaved along the (0 0 2) plane, and a 15 Å vacuum layer was added to isolate periodic interactions (Figure S8). The stable surface of WO$_3$ was fully terminated with oxygens for annealing in air with a distance of 5.483 Å between diagonal oxygens, as shown in Fig. 2a. A reasonable EG molecule was obtained as shown in Fig. 2b with two alcoholic hydrogens 5.124 Å apart from each other. Therefore, EG hydroxyls could be adsorbed on the WO$_3$ surface through bidentate hydrogen bonds by the matched distances. The EG molecule was horizontally adsorbed on the WO$_3$ surface in the most stable pattern, as shown in the inset of Fig. 2c compared to the other modes (Table S3). The adsorption energy is calculated as $E_{\text{ad}} = E_{\text{total}} - E_{\text{surf}} - E_{\text{EG}}$, where $E_{\text{total}}$ is the total energy of binding EG and WO$_3$, $E_{\text{surf}}$ is the energy of the O-terminated surface and $E_{\text{EG}}$ is the energy of the EG molecule. The minimum adsorption energy of −0.728 eV at an O–H distance of 2.5 Å, signifies strong chemisorption [43]. Therefore, the alcoholic hydrogens in the EG connect with the diagonal oxygens on the WO$_3$ surface through two concomitant hydrogen bonds.

Fig. 2d illustrate the FT-IR spectra, which were used to detect the functional groups of EG (at 1042 and 1085 cm$^{-1}$ [44,45]) and WO$_3$ (at approximately 800 cm$^{-1}$ [35]). The WO$_{3-x}$ sample had three characteristic peaks of EG and WO$_3$, after the thermal reduction by EG, and another absorbance peak at approximately 1160 cm$^{-1}$ which corresponds to glyoxal [46]. It is assumed that, under appropriate thermal conditions, EG was adsorbed onto the surface of WO$_3$, through bidentate hydrogen bonds between two alcoholic hydrogens in EG and the lattice oxygen in WO$_3$, to generate H$_2$O, O$_x$ and glyoxal and leave uncoordinated W (Figure S9). Because of the mismatch with lattice oxygens in WO$_3$ next layer, the EG could controllably take the surface oxygens without forming deep defects, which were inevitably introduced in the oxygen-deficient atmosphere in previous works [20,23,34].

3.3. Photo-response performance

PEC water splitting measurements were performed using a three-electrode electrochemical system, with 0.2 M Na$_2$SO$_4$ as the electrolyte under 100 mW cm$^{-2}$ irradiation and with test bench in Figure S10. To exclude the possibility of EG being a sacrificial agent, LSV measurements of WO$_3$ were performed in different volumes of EG to compare with the photoanode immersed in EG (Figure S11); the results indicate that residual EG on WO$_3$ after reduction and drying does not

Fig. 2. (a) Top view of the O-terminated WO$_3$ surface; (b) structure of an EG molecule; (c) energy, top view, and side view of an EG molecule adsorbed by the WO$_3$ surface; and (d) FT-IR spectra of EG, WO$_3$, and WO$_{3-x}$ after thermal reduction.
Fig. 3. (a) J-V curves; (b) UV–vis absorption spectra; (c) IPCE curves at 1.23 V vs. RHE; and (d) ABPE curves of WO_3 and WO_{3-x}.

Fig. 4. (a) J-V curves with/without 1 M Na_2SO_3; (b–c) charge injection and separation efficiencies (\(\eta_{\text{surface}}\) and \(\eta_{\text{bulk}}\)), respectively; (d) I-t curves collected at 1.23 V vs. RHE for 10000 s; (e) Nyquist and fitting plots of EIS; (f) MS plots for WO_3 and WO_{3-x}; (g–h) Tafel curves and LSV curves without irradiation, respectively, for WO_3 and WO_{3-x}; and (i) J-V and MS plots of WO_{3-x} after annealing in air for 1 h.
increase the photocurrent density significantly. The photocurrent density of 1.58 mA cm$^{-2}$ yielded a photocurrent density of 0.91 mA cm$^{-2}$ higher than the 0.91 mA cm$^{-2}$ of materials with O$_2$ introduced by other state-of-the-art methods (Table S4). To prove that the O$_2$ are responsible for the improved PEC performance rather than the EG, another method of producing O$_2$ in WO$_3$ used ascorbic acid [19] was performed for comparison which yielded a photocurrent density of 1.58 mA cm$^{-2}$ (Figure S13). The CLV curves for both photoanodes (Fig. 3a) had negligible transient spikes when the light switched on (positive spikes) or off (negative spikes). These photocurrent transients suggest that holes transferred to oxidize water at the semiconductor/electrolyte interface, rather than accumulate on the trap states, which may promote recombination [47,48]. The wavelength-dependent IPCEs of WO$_3$-x are shown in (Figure S15) which could indicate that the structure of O$_2$ has decreased from the surface terminated with oxygens. The Tafel slope of WO$_3$-x had better photoactivity, with a higher photocurrent density retention (38.6%) higher than that of WO$_3$ (20.6%) after 10000 s as shown in Fig. 4d [23]. After 10000 s test, the XPS and EPR observation (Figure S15) could indicate that the structure of O$_2$ was stable. EIS measurements were implemented to explore the effect of controllable O$_2$ on carrier transfer kinetics. The Nyquist plots for both photoanodes in Fig. 4e contain one semicircle relative to the interfacial charge transfer. The equivalent circuit model (inset of Fig. 4e) is fitted by ZSimWin, where $R_s$ is the systemic series resistance, $R_{ct}$ is the interfacial charge transfer resistance, and $C_d$ is the capacitance of the double layer. $R_{ct}$ of WO$_3$-x was fitted to (Table S5) a smaller value (158.1 $\Omega$) than that of WO$_3$ (257.2 $\Omega$), suggesting a lower holes-to-water resistance and better water oxidation kinetics [53,54]. The MS plots in Fig. 4f have positive slopes, indicating that WO$_3$ and WO$_3$-x were n-type semiconductors and the flat-band potential shifted slightly negative for O$_2$ introducing [19,20]. Using Eq. (4), the calculated carrier density is $\sim2.31 \times 10^{22}$ cm$^{-3}$ for WO$_3$-x 3.8 times over $\sim6.15 \times 10^{21}$ cm$^{-3}$ of WO$_3$. This suggests that more carriers transfer to the WO$_3$-x surface participating in the oxidation of water molecules compared to WO$_3$.

3.4. Photo- and electro-chemical analysis

To further investigate the improved PEC performance of WO$_3$-x, the photocurrent density ($J_{PEC}$) was calculated as Eq. (6) [49,50]

$$J_{PEC} = J_{abs} \times \eta_{bulk} \times \eta_{surface}$$

where $J_{PEC}$ is measured under 0.2 M Na$_2$SO$_4$, $J_{abs}$ is estimated with 100% conversion of absorbed photons to current density, $\eta_{bulk}$ is the bulk charge separation efficiency and $\eta_{surface}$ is the interface charge injection efficiency. Photogenerated holes arrive at the surface to oxidize water and suppress surface recombination ($\eta_{surface} \approx 100\%$) in the presence of hole scavenger (1 M Na$_2$SO$_4$). Therefore it can be expressed as $\eta_{surface} \approx J_{PEC}/J_{abs}$ and $\eta_{bulk} \approx J_{Na2SO4}/J_{abs}$ using the current curves in Fig. 4a [51]. $\eta_{surface}$ improved from 32.2% to 65.3% with the introduction of O$_2$ (Fig. 4b), whereas $\eta_{bulk}$ exhibited a slight increase from 51.4% to 57.7% (Fig. 4c). The doubling of $\eta_{surface}$ is attributed to the photogenerated holes that transferred to the semiconductor/electrolyte interface directly participating in water oxidation and overcoming the surface hole-and-electron recombination. Therefore, surface O$_2$ may act as reactive sites for water oxidation immediately after holes migrate to the surface. The increase in $\eta_{bulk}$ and the lower phase value in the Bode plots (Figure S14) at 1.23 V reflect the less-capacitive behavior of WO$_3$-x [52], indicating that separated charges were not accumulated in the bulk with no additional deep defects introduced for creating O$_2$.

Fig. 5. OER and cumulative reaction energies on the WO$_3$ surface terminated with oxygens.
(Fig. 4i) lower than that of WO$_{3-x}$. This indicates that there were few bulk O$_x$ in the original WO$_{3-x}$ near to WO$_3$ consistent with the results of Raman spectra in Fig. 1i, and the enhanced PEC performance is attributed to the surface O$_x$.

3.5. DFT calculations of the OER

DFT + U simulations were applied to investigate the change in the reaction energy of the OER because of the surface O$_x$. The OER is a four-proton transfer process, and the free energy change of each step can be calculated by Eq. (5) with ZPE and entropy corrections, as explained in Section 2.4. The corrected free energies of the gaseous molecules are listed in Table S6. It is assumed that the initial WO$_3$ surface, fully terminated with oxygen, corresponds to the *O intermediate without exposed W reactive sites [56]. Therefore, water oxidation initiates from reaction C to form HOO$^*$ with the dissociation of H$_2$O and a proton transfer to the electrolyte, as shown in Fig. 5. Subsequently, molecular oxygen desorbs from the slab with a proton into the electrolyte, leaving an undercoordinated W atom. The undercoordinated W acts as a reactive site to dissociate water molecules forming HO$^*$. Finally, a proton separates from the surface turning into the starting *O in a continuous catalytic cycle. The cumulative reaction energies follow the reaction process C-D-A-B for WO$_3$ as shown in the center of Fig. 5, with the corrected free energies shown in Table S7. The dissociation of a proton from HO$^*$ (step B) owns the maximum free energy change of 2.267 eV under no applied external potential (U = 0 V). The overall reaction energy is 0 eV for an applied potential of 1.23 V, and the overpotential ($\eta$) of the OER is 1.037 V, corresponding to step B, following Eq. (7) [57]:

$$\eta = \frac{\max(\Delta G_A, \Delta G_B, \Delta G_C, \Delta G_D)}{e} - 1.23$$

where $\Delta G_A, \Delta G_B, \Delta G_C,$ and $\Delta G_D$ are the free energy changes for reactions A-D calculated from Eq. (5), respectively.

EG may remove all the diagonal oxygens from the outermost layer, yielding a stable slab terminated with W-O-W as shown in Figure S4. The OER of WO$_{3-x}$ proceeds with the reaction pathway A-B-C-D, as shown in Fig. 6, owing to the undercoordinated W active sites introduced with the O$_x$; it begins with water dissociation on (*O) with the corrected free energy (Table S8). A proton dissociating from HO$^*$ has the highest energy change without an applied bias, similar to WO$_3$, with a $\Delta G$ of 1.724 eV [58]. The overpotential is 0.494 V with the application of 1.23 V for the maximum change in step B from Eq. (5). In comparison, the $\eta$ of WO$_{3-x}$ is much lower than that of WO$_3$ (1.037 V), consistent with the Tafel curves (Fig. 4f), and suggests superior surface reaction kinetics from the increase in $\eta_{\text{surface}}$ with O$_x$ [57]. These DFT calculations provide a rational basis for the high performance of O$_x$ in experiments and why the O$_x$ have a dramatically positive effect on the activity of WO$_3$ for water splitting.

4. Conclusion

We have proposed a novel method of that uses thermal reduction by EG at 130 °C to controllably introduce an appropriate number of O$_x$ on the WO$_{3-x}$ surface. The in-situ surface O$_x$ are generated through bidentate hydrogen bonds, which are caused by the matched distances between alcoholic hydrogens of EG and the diagonal oxygens of the WO$_3$ surface without deep defects (bulk O$_x$). The synthesized WO$_{3-x}$ nanoplates photoanode had a superior photocurrent density from the reduced interfacial holes-to-water resistance and the twice increase of injection efficiency compared to that of WO$_3$. Therefore, according to calculations and experiments, modulated surface O$_x$ can enhance the surface kinetics by lowering the OER overpotential to improve the PEC performance.

Declaration of Competing 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.

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Appendix A. Supplementary data

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