Concave Bi₂WO₆ nanoplates with oxygen vacancies achieving enhanced electrocatalytic oxygen evolution in near-neutral water

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Experimental section

Synthesis of rod-like Bi₂O₃. Rod-like Bi₂O₃ was synthesized according to previous report. In a typical experimental procedure, 4 mmol of Bi(NO₃)₃·5H₂O was dissolved in 25 mL of dilute HNO₃ solution (containing 10 mL of 70% HNO₃) with addition of 2 mL of aqueous polyvinyl alcohol solution (PVA 17–88, 2.5 wt%). The obtained mixtures were stirred until they became a transparent solution. Then, 15 mL of 0.1 g mL⁻¹ NaOH solution was added into this solution drop by drop over 30 min under an ice water bath and intensively stirring condition. The white precipitates formed gradually. The whole mixture was then stirred for another 30 min, and then, the white suspension was heated at room for 2 h without stirring. The final yellow products were collected and washed with hot distilled water and absolute ethanol for several times and then dried at 60 °C under vacuum.

Synthesis of W₁₈O₄₉ nanowires. The synthesis of W₁₈O₄₉ nanowires followed previous report. In a typical procedure, 0.5 g of WCl₆ was put in 100 mL of absolute ethanol, and a transparent yellow solution was formed. The obtained transparent yellow solution was then transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. The final blue flocculent
precipitate was collected, washed with distilled water and absolute ethanol in turn, and dried in vacuum at 60 °C.

**Synthesis of Bi$_2$WO$_6$ nanoplates.** The synthesis of Bi$_2$WO$_6$ nanoplates is in line with the reference.$^3$ In a typical procedure, 1 mmol of Bi(NO$_3$)$_3$·5H$_2$O was added to 1 M HNO$_3$ to form a clear solution under stirring for 30 min at room temperature. Afterward, 25 mL of solution contained 0.5 mmol of Na$_2$WO$_4$·2H$_2$O and 1 mL of oleylamine was added into the above solution. The pH value of the suspension was adjusted to ca. 7 with NH$_3$·H$_2$O. The mixture was finally transferred into a 50 mL Teflon-lined autoclave and maintained at 200 °C for 20 h. The reactor was cooled to room temperature naturally. The resultant products were collected and washed several times with acetone and deionized water and dried at 60 °C in air.

**Calculations of adsorption energy.** The Bi$_2$WO$_6$ (010) surface was cleaved from Russellite crystal with space group $B2cb$.$^1$ The slab thickness was approximately 8.0 Å. The vacuum layer with the thickness of 10 Å was inserted to avoid interactions between two slabs. The supercell contained eight crystal units and eight atom layers with 16 Bi atoms, 8 W atoms, and 48 O atoms. To simulate the actual surface of the Bi$_2$WO$_6$ bulk, the top four layers of W and O atoms were relaxed and the bottom four layers of Bi and O atoms were fixed in all geometry optimization. All calculations were performed using Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) in Dmol$^3$ program embedded in Materials Studio 7.0 software.$^{2,5}$ Because H$_2$O adsorption on the surface involves noncovalent forces, such as hydrogen bonding and van der Waals interactions, dispersion correction for density functional theory (DFT) was performed using Ortmann-Bechstedt-Schmidt (OBS) method.$^6$ Due to the relativistic effects of Bi and W elements, all electron relativistic method was adopted to treat core electrons.$^7,8$ The basis set version 4.4 and the double-numeric basis plus polarization function (DNP) were used. The global real space orbital cutoff of atomic basis set was set to be 4.0 Å. The convergence criteria for geometry optimization and energy calculation were $2 \times 10^{-5}$ Hartree for energy, $4 \times 10^{-3}$ Hartree/Å for maximum force, $5 \times 10^{-3}$ Å for maximum displacement, and $1.0 \times 10^{-5}$ Hartree for the self-consistent field.$^9$

In Bi$_2$WO$_6$ crystal, W central atom is coordinated with six ligands of O atoms, which present a tetragonal bipyramidal structure. Similarly, the perfect Bi$_2$WO$_6$ surface also has similar octahedral structure, shown in Fig. S1. As an adsorbate, H$_2$O can be easily adsorbed on Bi$_2$WO$_6$ surface
through hydrogen bonding interaction between O atom on the top site and H atom of \( \text{H}_2\text{O} \). The adsorption energy \( (E_{\text{ad}}) \) can be defined as

\[
E_{\text{ad}} = E_{\text{water}} + E_{\text{surface}} - E_{\text{complex}}
\]

Where \( E_{\text{water}} \), \( E_{\text{surface}} \), and \( E_{\text{complex}} \) represent the energies of the water, surface, and adsorption complex between water and surface, respectively. As shown in Fig. S1c, one \( \text{H}_2\text{O} \) molecule can form two hydrogen bonds with two surrounding O atoms on the surface, in which the adsorption energy is 14.5 kcal/mol. When water exits on then \( \text{Bi}_2\text{WO}_6 \) surface with O vacancy (Fig. S1b), one \( \text{H}_2\text{O} \) molecule can occupy the O vacancy and be strongly adsorbed on the surface through coordination with surface W atom (Fig. S1d). The adsorption energy \( (E_{\text{ad}}) \) is up to 29.5 kcal/mol, which is larger than that on the perfect surface. Therefore, O vacancy can promote \( \text{H}_2\text{O} \) adsorption on the \( \text{Bi}_2\text{WO}_6 \) surface, which is beneficial for enhancing the OER activity of the catalysts.

**Fig. S1** (a) Perfect \( \text{Bi}_2\text{WO}_6 \) surface, (b) \( \text{Bi}_2\text{WO}_6 \) surface with one O vacancy, (c) \( \text{H}_2\text{O} \) adsorption on perfect \( \text{Bi}_2\text{WO}_6 \) surface, and (d) \( \text{H}_2\text{O} \) adsorption on \( \text{Bi}_2\text{WO}_6 \) surface with one O vacancy.
**Fig. S2** XRD pattern of the synthesized Bi$_2$WO$_6$ CNPs (a). Standard data obtained from JCPDS No. 73-1126 (b).

**Fig. S3** A typical TEM image of Bi$_2$WO$_6$ CNP.

By carefully measuring the TEM image (Fig. S3), the angles between the concave facets and the (100) facets are about 13.3°. To an orthorhombic system, the angle ($\theta$) between two different crystal planes can be calculated by the formula below:

$$\cos \theta = \frac{h_1 h_2}{a^2} + \frac{k_1 k_2}{b^2} + \frac{l_1 l_2}{c^2} \sqrt{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}\right)}$$

Where $\theta = 13.3^\circ$, $a = 5.457$, $b = 5.436$, $c = 16.427$, $h_1 = 1$, $k_1 = 0$, $l_1 = 0$
As a result, 

\[ 0.973 = \frac{h_2}{a^2} \sqrt{\frac{1}{a^2} \left( \frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2} \right)} \]

\[ h_2^2 = 19k_2^2 + 2l_2^2 \]

\[ Q \text{ are integers} \]

\[ Q I^2 = \frac{h_2^2 - 19k_2^2}{2} \geq 0 \]

*If* \( k_2 \neq 0 \), *then* \( h_2 \geq \sqrt{19k_2} \)

The least \( h_2 \) value is 5 in order to meet the above conditions.

*If* \( k_2 = 0 \), *then* \( h_2 = \sqrt{2l_2} \)

In order to reduce the error of the equation solution, the least \( h_2 \) and \( l_2 \) values are 3 and 2, respectively. In either case, \( h_2 \) is bigger than 3. Therefore the as-obtained Bi\(_2\)WO\(_6\) concave nanoplates contain high energy facets.

![EDX spectrum](https://via.placeholder.com/150)

**Fig. S4** EDX spectrum of the synthesized Bi\(_2\)WO\(_6\) CNPs.
Fig. S5 FE-SEM image of the sample synthesized without use of oleylamine.

Fig. S6 XRD patterns of the intermediates.
Fig. S7 FE-SEM images of the intermediates obtained at different reaction stages: 70 min (a), 100 min (b), 2 h (c), and 4 h (d).

Fig. S6 represents the XRD patterns of the samples synthesized for 70 min, 100 min, 2 h, and 4 h, respectively. As shown in Fig. S6, the crystal phase of Bi$_2$WO$_6$ has been produced within initial 70 min. With prolonged solvothermal treatment time, the crystallinity of Bi$_2$WO$_6$ products was further improved, judging from the increase of absolute intensities of all the diffraction peaks. SEM observations show that the intermediates were irregular nanoparticles (70 min), a small quantity of Bi$_2$WO$_6$ CNPs and irregular nanoparticles (100 min), small Bi$_2$WO$_6$ CNPs and big Bi$_2$WO$_6$ CNPs (2 h), and uniform Bi$_2$WO$_6$ CNPs (4 h), respectively. Therefore the formation of Bi$_2$WO$_6$ CNPs went through anisotropic growth of nanoparticles into concave nanoplates because of selective adsorption of oleylamine and Ostwald ripening process of concave nanoplates (large Bi$_2$WO$_6$ CNPs grow at the expense of small Bi$_2$WO$_6$ CNPs).
Fig. S8 Digital photo of the sample obtained through one-pot reaction.

Fig. S9 XRD pattern of rod-like Bi$_2$O$_3$. 
All diffraction peaks in Fig. S9 can be indexed to pure monoclinic-phase Bi$_2$O$_3$ (JCPDS No. 65-2366). As can be seen from Fig. S10, the products take on rod-like appearance.
All diffraction peaks in Fig. S11 can be indexed to pure monoclinic-phase $W_{18}O_{49}$ (JCPDS No. 71-2450). As can be seen from Fig. S12, the products are nanowires.

![FE-SEM image of the synthesized $W_{18}O_{49}$.](image)

**Fig. S12** FE-SEM image of the synthesized $W_{18}O_{49}$.

![LSV curves of Bi$_2$WO$_6$ CNPs and Bi$_2$WO$_6$ CNPs treated with potassium tartrate.](image)

**Fig. S13** LSV curves of Bi$_2$WO$_6$ CNPs and Bi$_2$WO$_6$ CNPs treated with potassium tartrate.
Fig. 14 CV curves of Bi$_2$WO$_6$ CNPs (a) and W$_{18}$O$_{49}$ nanowires (b). Charging current density differences plotted against scan rates for Bi$_2$WO$_6$ CNPs and W$_{18}$O$_{49}$ nanowires (c).

Fig. 14a and 14b represent CV curves of Bi$_2$WO$_6$ CNPs and W$_{18}$O$_{49}$ nanowires at different scan rates (from 20 to 100 mV s$^{-1}$ in 20 mV s$^{-1}$ increments) performed in a potential range in which no faradic processes were observed. The corresponding capacitive currents density at 0.025 V versus SCE are plotted as a function of scan rate, respectively. The results show that the current density has good linear relationship with the scan rate for the two materials, which is consistent with capacitive charging behavior. The linear slope obtained by fit is equivalent to twice of the double-layer specific capacitance. As a result, the specific capacitance of W$_{18}$O$_{49}$ nanowires (276 μF cm$^{-2}$) is about 2.6-times larger than that of Bi$_2$WO$_6$ CNPs (106 μF cm$^{-2}$).
Fig. S15 XRD pattern of the synthesized Bi₂WO₆ nanoplates.

Fig. S16 FE-SEM image of the synthesized Bi₂WO₆ nanoplates.
**Fig. 17** CV curves of Bi$_2$WO$_6$ flat nanoplates (a) and Bi$_2$WO$_6$ CNPs (b). Charging current density differences plotted against scan rates for Bi$_2$WO$_6$ CNPs and Bi$_2$WO$_6$ flat nanoplates (c).

**Fig. S18** UV-visible diffuse reflectance spectra of Bi$_2$WO$_6$ nanoplates and Bi$_2$WO$_6$ CNPs after treated with 40 mL of H$_2$O$_2$ (60 mg/mL).
### Table S1. OER activities of some typical inorganic electrocatalysts under neutral conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>Onset potential (V)</th>
<th>Current density (mA cm$^{-2}$) at $\eta = 0.54$ V</th>
<th>Reference</th>
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<tr>
<td>Co-Pi</td>
<td>0.28</td>
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<td>Co$_3$O$_4$/SWNTs</td>
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<td>$\delta$-MnO$_2$</td>
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<td>Co(PO$_3$)$_2$</td>
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<td>ZrS$_3$ nanosheets</td>
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<td>0.02</td>
<td>17</td>
</tr>
<tr>
<td>Mn$_3$(PO$_4$)$_2$·3$\text{H}_2\text{O}$</td>
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<td>0.03</td>
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<td>Mo$_5$O$_8$ nanoparticles</td>
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<tr>
<td>Co$_3$S$_4$ nanosheets</td>
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<td>10.00</td>
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**References**


