Supporting Information for

End-on Bound Ir Dinuclear Heterogeneous Catalysts on WO₃ for Solar Water Oxidation

Yanyan Zhao,^{†,#} Xingxu Yan,^{‡,#} Ke R. Yang,^{§,#} Sufeng Cao,[#] Qi Dong,[†] James E. Thorne,[†] Kelly

L. Materna,[§] Shasha Zhu,[†] Xiaoqing Pan,^{‡,⊥} Maria Flytzani-Stephanopoulos,^{*//*} Gary W. Brudvig,[§]

Victor S. Batista, $^{\$}$ and Dunwei Wang *,†

Materials and Methods

Fabrication of WO₃ photoanodes

Ammonium metatungstate hydrate (Sigma-Aldrich, 99.99% trace metals basis) was dissolved in a 1:1 (volume ratio) mixture of diethylene glycol butyl ether (Sigma-Aldrich, purity \geq 99%) and ethanol (Sigma-Aldrich, anhydrous, purity \geq 99.5%) with a concentration of 0.2 mol L⁻¹. This solution was used as precursor for flame spray pyrolysis. This solution was fed at 5 ml min⁻¹ rate through a custom build nozzle, and atomized with an oxygen flow (O₂ = 5 L min⁻¹) at a set pressure drop ($\Delta P = 2$ bar). The resulting spray was ignited with a surrounding annular set of premixed methane/oxygen flame (CH₄ = 0.5 L min⁻¹, O₂ = 0.8 L min⁻¹). To prepare the photoelectrodes, the FTO coated glass substrates (TEC7, Dyesol) were cleaned by sonication for 10 min in acetone before deposition. The clean substrates were mounted at a height above burner of 6 cm on a copper substrate holder. The deposition time is 60 seconds. The prepared electrode was annealed at 500 °C in the air condition for 1 h.

Preparation of Ir DHC on WO3 and loading estimate

Step 1: A WO₃ substrate was soaked in the Ir dimer solution¹ for 16 h and then thoroughly rinsed with DI water to form the Ir heterogenized catalyst. The loading amount was estimated by comparing the change of the UV-Vis absorbance of the Ir molecular catalyst solution. We used the average absorbance decrease for a 26-time loading procedure. The Ir loading was calculated to be ca. 16 nmol/cm².

Step 2: The photochemical treatments were conducted using a UVO cleaner system (Jelight Company Inc.) equipped with a UV light. The process lasted 40 min to yield Ir DHCs.

Preparation of Ir SAC on WO₃

Similar to the preparation of Ir DHC, Ir SAC was obtained by placing the Ir heterogenized catalyst in the DRIFTS cell, which was heated to 105 °C under pure He for at 20 min to remove physically adsorbed H_2O and was then gradually cooled to room temperature. Afterwards, the cell was subjected to UV light irradiation under O_2 gas flow (10 ml/min) for up to 60 min.

STEM characterizations

All samples were scraped from the FTO electrode and collected by lacey carbon grids. All asprepared TEM grids were loaded into electron microscope without any further treatments.

High-resolution STEM-HAADF imaging was performed using a double aberration corrected JEOL Grand-ARM instrument operated at 300kV. The semi-angle of the probe-forming aperture was ca. 30 mrad. A 63 pm spatial resolution can be routinely achieved with a probe spherical-aberration corrector. The inner and outer semi-angles of the HAADF detector were ca. 70 and 200 mrad, respectively. A probe current of 10 pA and dwelling time of 16 µs per pixel were chosen for desirable signal-to-noise ratios. Energy dispersive X-ray spectroscopy (EDS) was performed by two JEOL Dry SD100GV silicon drift detectors. W M-edge, O K-edge and Ir M-edge were used for mapping the corresponding element distributions. Electron energy-loss spectrum (EELS) was collected by a Gatan 965 GIF Quantum ER spectrometer. A standard power-law background subtraction was utilized to remove the spectrum background, and the thickness was calculated from the low-loss EELS data in the commercial software package Digital Micrograph.

Discussions of *in-situ* STEM observation (Figure S8)

Generally, the beam effects on an observed sample include one or a combination of two principal mechanisms: direct displacement of atoms (knock-on damage) by breaking the chemical bonds and heating effect caused by the phonons.² The heating effect may arise due to numerous factors, including the electron energy, thermal conductivity of the sample and/or sample thicknesses. Quantitatively, the maximal temperature enhancement (ΔT_{max}) on the Ir DHC on WO₃ can be estimated by the following equation.³

$$\Delta T_{\max} = \frac{I}{4\pi\kappa e} \left(\frac{\Delta E}{d}\right) (1 + 2\ln\frac{b}{r_0})$$

where *I* is the total electron dose current (10 pA), κ is the thermal conductivity of WO₃ (1.63 Wm⁻¹K⁻¹),⁴ ΔE is the total energy loss per electron in the sample of thickness *d*, and $\Delta E / d$ is linearly dependent on the atomic number and sample density, and close to 2.568 eV/nm for WO₃ at 300 kV, *b* is the radius of the heat sink, equal to the sample radius and approximately 50 nm~100 nm in our case, and r_0 can be treated as the size of the electron probe (0.05 nm). The *in-situ* observation was conducted at room temperature (25 °C). Based on all parameters as outlined above, ΔT_{max} was obtained as ca. 0.0186 K. Due to the lower probe current in STEM in comparison to traditional TEM observations, the heating effect is concluded to be negligible under our STEM conditions.

The knock-on damage may be quantitatively described by the maximum energy $E_{\rm m}$ transferred from incident electron with energy *E* to atomic nucleus as follows,⁵

$$E_{\rm m} = 2.1477 \times 10^{-9} \times E(E + 1.022 \times 10^6) / A$$
,

where *A* is the relative atomic mass, and the energies are in eV. Under our experimental conditions, the maximum transfer-energies are 4.43, 4.63 and 53.2 eV for Ir, W and O atoms, respectively. The transfer energies are rather large and are expected to break the Ir-O bonds, to yield displacement of Ir atoms on the surface of WO_3 .⁶

TEM specimen thickness measurement

For accurate interpretation of the STEM data, we need information on the specimen thickness. This was obtained by three independent methods: STEM images, low-loss EEL spectra and position averaged convergent beam electron diffraction (PACBED) patterns. The data are shown in Fig. S10 and S11 and S12.

(a) *Low-loss EEL spectra*. The thickness of the sample can be calculated by the ratio between the intensity of zero-loss peak (ZLP) and low-loss spectra. By measuring and analyzing the ZLP spectra, we obtained the local thickness (t) by the following equation:

$$t = \lambda \ln(\frac{I_t}{I_0}),$$

where λ is the inelastic mean free path (IMFP) for the material, I_0 is the area under ZLP and I_t is the total area under the whole spectrum (0-180 eV in our experiments). An absolute thickness measurement requires knowledge of the IMFP, which depends on the material, electron energy and collection semi-angle. $\lambda = 73.64$ nm was used for WO₃ under our experimental conditions.⁷ Fig. S10A and 10C show two mapping images of the measured thickness from the low-loss EELS at low and high magnifications, respectively. From Fig. S10B and 10D, we calculated the thickness of the region where Ir DHC STEM observations were made as 0.69-1.55 nm.

(b) *STEM images*. Because the HAADF-STEM intensity should be proportional to the thickness of the sample for uniform materials, it is possible to use the STEM intensity to estimate the sample thickness. As shown in Fig. S10F and 10H, we compared the STEM intensities at the center of the particle and the edge (where STEM observations of Ir DHCs were made) and obtained a thickness estimate of ca. 1 nm.

(c) Position averaged convergent beam electron diffraction (PACBED). The PACBED technique may be the most accurate to estimate the thickness. It has been demonstrated that visual comparison on the intensity distribution within the PACBED disks and the overlapping area can provide an estimate of the sample thickness at a precision of $<1 \text{ nm.}^{8,9}$ For this body of research, we compared experimental PACBED patterns to a series of simulated ones. Fig. S11A represents a PACBED pattern acquired at the region 1 nm away from the edge along the [002] direction. There are (200) and (002) discs in the PACBED pattern. The simulated PACBED pattern of a sample with a 0.77 nm thickness is shown in Fig. S11C. We see a close match of these two sets of data. To further confirm the thickness, line profiles of PACBED patterns along the [002] direction are plotted in Fig. S11B and compared to the simulated data of samples with thicknesses of 0.77, 1.55, 2.32 and 3.10 nm, respectively (Fig. S11D). The closest match was obtained for a sample thickness of 0.77 nm, consistent with our estimates made by analyzing EELS and STEM images as discussed above. Based on these set of experiments, we chose the WO₃ substrate with the thickness of 0.77 nm as the simulation model.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

In situ DRIFTS measurements were performed on a Nicolet iS50 FTIR spectrometer equipped with a DTGS KBr detector and a Harrick praying mantis HVC-DRP4 cell with KBr windows.¹⁰ The sample in cell was heated to 105 °C for 20 min to remove physically adsorbed moisture and was then cooled to room temperature with He purging to collect the background spectra. Afterwards, the gas flow was changed to 10% CO for 15 min before switching back to He to avoid possible interference of gaseous CO to the spectra. DRIFTS spectra were collected in the CO absorption region, 2200-1800 cm⁻¹ with varying He purging times. The spectral resolution was set at 4 cm⁻¹. 64 scans were recorded and averaged for each spectrum shown in this work to improve the signal-to-noise ratios.

Photoelectrochemical (PEC) characterization

PEC measurements were carried out by a potentiostat (Modulab XM equipped with Modulab XM ECS software). A solar simulator (100 mW/cm², Solarlight Model 16S-300-M Air Mass Solar Simulator, AM 1.5) was used as the light source. Ir DHC/WO₃, Ir SAC/WO₃, and WO₃ were used as the working electrodes, with an SCE electrode as the reference electrode, and a Pt wire was used as the counter electrode. The electrolyte was a 0.1 M K₂SO₄ solution with the pH adjusted

to 3.0 by H₂SO₄. The potential was corrected to the reversible hydrogen electrode (RHE) scale following the Nernst equation ($E_{RHE} = E_{SCE} + 0.059 \text{pH} + 0.241$). For the linear sweep voltammetry data, the scan rate was 20 mV/s.

Oxygen and peroxide species detection

Oxygen was quantified using a Clark-type BOD oxygen electrode (Thermo Scientific 9708 DOP). O_2 evolution experiments were carried out in a two-chamber cell, where the O_2 detector, the working electrode, and the reference electrode were in one chamber, and the Pt counter electrode was in the other chamber. N_2 gas was used to purge out dissolved O_2 and gaseous O_2 in the headspace for at least 1 h prior to the experiment. During the experiment, the oxygen sensor was allowed to stabilize to ca. 0 ppm for at least 30 min. The O_2 yield during photoelectrolysis was read directly by a pH meter connected to the oxygen sensor.

Non-oxygen byproducts from photoelectrolysis were measured by quantifying the amount of O_2^{2-} that was reduced by I^- reductant in solution (mainly H₂O₂) according to the following reactions.

$$H_{2}O_{2} + 2I^{-} + 2H^{+} \rightarrow I_{2} + 2H_{2}O \quad (1)$$
$$I_{2} + 2S_{2}O_{3}^{2^{-}} \rightarrow S_{4}O_{6}^{2^{-}} + 2I^{-} \quad (2)$$

Iodometry titration was carried out using ca. 6 mL electrolyte that was subjected to varying extent of photoelectrolysis. 1 M HCl was added to the electrolyte to adjust the pH to ca. 2.5. Afterwards, 2 mL of 2 wt. % KI solution and 50 μ L of a molybdate-based catalyst solution were added in to the solution above. The solution turned yellow after being placed in the dark condition for ca. 2 min, indicating the formation of I₂. The solution was then titrated by Na₂S₂O₃ to light yellow. 1 mL of 2 wt. % starch indicator was then added, and the solution was titrated until the blue indicator color disappeared. The quantity of O₂²⁻ was back calculated by the amount of Na₂S₂O₃ used.

Computational details

We used the Vienna ab initio simulation package (VASP) for all periodic boundary calculations. ¹¹⁻¹⁵ Projector augmented wave (PAW) method^{16, 17} together with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional¹⁸ were employed to describe the electron-ion interactions. A cutoff of 500 eV was chosen for the plane wave basis set in all calculations. The Gaussian smear method was used to accelerate self-consistent field (SCF) convergence and the smearing parameter σ was chosen to be 0.1 eV. A 3 × 3 × 3 Monckhorst-Pack type k-point grid was chosen for the optimization of bulk WO₃. The energy convergence criterion was set to be 10^{-4} eV per unit cell and the geometry convergence criterion was set to be 10^{-3} eV per unit cell for energy difference between two consecutive ionic steps. The DFT optimized and experimental structural parameters are listed in Table S2.

Based on XRD and HAADF-STEM results (Figure S7), we focused on WO₃ (020) surfaces which have O termination as in the case of WO₃ (002) surfaces.¹⁹ We considered the adsorption of water molecules on O-terminated WO₃ (020) surface. Our results suggest water molecules are adsorbed molecularly on O terminated WO₃ (020), yielding O+OH₂ terminated WO₃ (020) surface as the most stable WO₃ (020) in aqueous condition (Figure S6). Therefore, we used O+OH₂ terminated WO₃ (020) surfaces for the rest of our study. Ir DHC and SAC models were prepared by adsorbing Ir(OH)₄(OH₂)₂ units on O+OH₂ terminated WO₃ (020) surfaces (Figure S9). Slab models were chosen to have 4 unit cells in the (020) plane and full geometry relaxation was performed for the adsorbed Ir unit, the top and bottom layers, while atoms in the middle layer were frozen at their bulk positions. A vacuum layer of more than 20 Å was used to avoid the interactions between periodic images. The resulting supercell of our slab models of WO₃ (020) surfaces has the dimension of 14.95 Å \times 40.75 Å \times 15.69 Å. We used a 1 \times 1 \times 1 Monckhorst-Pack type k-point grid for slab calculations. Because of the strong d-electron correlation effects of Ir, the calculations were carried out with the DFT+U method, using the formalism suggested by Dudarev et al.²⁰ The U_{eff} parameter for Ir was set to 3 eV according to our recent study of Ir DHC on hematite. The energy convergence criterion was set to be 10^{-4} eV per super cell and a force convergence criterion of 0.03 eV Å⁻¹ was used in the structure optimization of all slab models.

The catalytic mechanisms of Ir SACs and DHCs were studied with our Ir SAC and DHC models. All intermediates were optimized with the same setting of the Ir SAC and DHC models with the exception that the atoms in the bottom layers were frozen at their positions in Ir SAC and DHC models to save computation time. A supercell of $15 \text{ Å} \times 15 \text{ Å} \times 15 \text{ Å}$ and $1 \times 1 \times 1$ Monckhorst-Pack type k-point grid were used for the calculations of isolated molecules. The Gaussian smear method was used for molecule calculations and the σ value was chosen to be 0.1 eV.

The change of reaction free energy was calculated according to $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the change of electronic energy, ΔZPE is the change of zero-point energy (ZPE), ΔS is the change of entropy, and *T* is the reaction temperate (298.15 K in our calculations). Partial frequency

analysis was performed all intermediates in the catalytic cycle of Ir DHC and used to obtain the zero-point energy contribution for the absorbed species (*OH₂, *OH, *O*OOH, *OO) and the hydrogen bonded water molecule (---H₂O). The entropies of H₂O(l), O₂(g), and H₂(g) were used to consider the entropic energy contributions.²¹ The entropic contributions from absorbed species on the surfaces are small, so we omitted them, which is a common practice in the literature.^{22, 23} The zero-point energy and entropic energy contribution are listed in Table S3.

For reaction steps involving the H⁺ and e⁻, the computational hydrogen electrode (CHE) technique developed by Nørskov *et al.* was used to take into account the dependence of relative energies on pH and applied bias potential.²⁴ The potential for oxidation of H₂O(1) \rightarrow O₂(g) + 4H⁺(aq) + 4e⁻ is calculated to 1.11 V, while the experimental value is 1.23 V. We used this potential as an internal reference to obtain more reliable potentials for each oxidation process.

The simulation of *in situ* DRIFTS were performed by replacing the H₂O molecules coordinated to Ir centers to CO molecules and performing frequency analysis for the probe CO molecules. Under the condition of *in situ* DRIFTS experiments, samples were heated to 105 °C under pure He flow for at 20 min to remove adsorbed H₂O. Therefore, we removed all molecularly adsorbed H₂O on WO₃ (020) surfaces and optimized the CO adsorbed Ir SAC and DHC model (see structures in Figure 2 and Figure S4) before frequency analysis. The calculated frequencies were scaled with a scaling factor of 0.988.

All calculations mentioned above were done in vacuum. We also investigated solvation effects on the evolution of Ir DHC to Ir SAC. Solvation effects were considered with an implicit solvation model implemented in VASPsol²⁵ and a value of 80.0 was used to account the dielectric constant of water. The results are shown in Figure S9.



Figure S1 Surface oxygen distribution on metal oxide surfaces. Binding site for each Ir has been marked by green frames.

Table S1 Suface O density of c	different metal oxide surfaces.
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Facet	WO ₃ (020)	CeO ₂ (110)	CeO ₂ (111)	TiO ₂ (101)	TiO ₂ (001)	Fe ₂ O ₃ (001)
Surface O densities (nm ⁻²)	3.6	9.7	15.8	10.4	14.1	13.5
Binding sites distance (Å)	4.1	3.8	3.8	3.8	3.8	3.0



Figure S2 XPS spectra of Ir DHCs on WO₃. (**A**) The binding energies at ~65 eV and ~62 eV correspond to Ir $4f_{5/2}$ and Ir $4f_{7/2}$, respectively. (**B**) High resolution spectrum of N confirms the absence of the organic ligands in Ir DHCs.



Figure S3 EELS spectra from the surface region of Ir DHCs. The obvious N signal before photochemical treatments and its absence afterwards support that N-containing ligands have been successfully removed.



Figure S4 Identification of the binding nature of Ir SACs on WO_3 by *in situ* CO DRIFTS and DRIFTS simulations. (**A**) The atomic model used for the simulation. Green ball: Ir, brown ball: C, red ball: O, white ball: H, and grey ball: W. (**B**) Experimental and simulated DRIFTS spectra.



Figure S5 In situ CO DRIFTS spectra of side-on bound Ir DHCs on Fe₂O₃

We see in this DRIFTS data that only one group of Ir peaks is present, indicating that the coordination environments of the two Ir atoms are similar in a side-on binding mode.¹

Properties	Calculated	Experimental ^a
<i>a</i> / Å	7.48	7.31
b / Å	7.69	7.54
<i>c</i> / Å	7.84	7.69
β / degree	90.5	90.9
dW-O1 / Å	1.78	1.73
dW-O2 / Å	1.80	1.74
dW-O3 / Å	1.90	1.86
dW-O4 / Å	1.93	1.95
dW-O5 / Å	2.10	2.12
dW-O6 / Å	2.17	2.17

Table S2 Calculated and experimental structural parameters of bulk WO₃.

^a Experimental cyrstal structure taken from Loopstra, B. O.; Rietveld, H. M. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1969, B25, 1420.



Figure S6 Optimized structures of WO₃ (020) surfaces with different terminations and calculated hydration energies per water molecule from O terminated WO₃ (020) surfaces to OH and $O+OH_2$ terminated WO₃ (020) surfaces.



Figure S7 (**A**) XRD patterns of as-prepared WO₃. (**B**) HAADF-STEM image of the (020) facets and (**C**) the fast Fourier Transform (FFT) pattern. Scale bar: 1.5 nm.



Figure S8 Ir DHCs on WO₃ by *in situ* STEM observations. (**A**) A series of STEM-HAADF images showing the change of Ir DHCs as a function of e-beam irradiation times (0 s to 99 s). Scale bars: 1 nm. (**B**) Comparison of line scan profiles of the same atomic chains from 0 s to 31 s and 99 s. The orange arrows mark the location of Ir. (**C**) Atomic model to show how Ir atoms move on the surface.

A. Gas phase condition





Figure S9 The energetic profiles of hydrolysis of Ir DHC on WO₃ (020) surfaces in the gas phase condition (**A**) and the quasi-aqueous condition (**B**).

To study how the end-on bound Ir DHCs evolve on the surface of WO₃, we considered the hydrolysis of the Ir_{top}-O bond in the Ir_{top}-O-Ir_{bottom} unit and Ir_{bottom}-O bond in the Ir_{bottom}-O-W unit in both pure gas phase and quasi-aqueous condition including the solvation effects. In gas phase computational condition which corresponds to the DRIFTS experimental condition with a limited amount of H₂O molecules, the hydrolysis of Ir_{top}-O bond requires 0.78 eV while the hydrolysis of Ir_{bottom}-O bond requires a higher energy, 0.98 eV. Therefore, the 0.2 eV energy difference makes it possible for the hydrolysis to stop at the Ir SAC stage, which is consistent with our experimental observation that under the DRIFTS experimental condition, we obtained Ir SACs evolved from Ir DHC. On the other hand, when the same process proceeds in quasi-aqueous condition including the solvation effects to mimic the UVO chamber with the relatively high humidity, the hydrolysis of Ir_{top}-O bond (0.73 eV). It is thus expected that the hydrolysis of Ir DHC in this case may not stop at the Ir SAC stage but could further aggregate to form Ir nanoparticles. In other words, H₂O promotes Ir atom diffusion on WO₃ surfaces.



Figure S10 (**A**) Absolute thickness mapping of the whole particle on which the high resolution STEM observations were made at a low magnification. The thickness was calculated using the low loss EELS data. (**B**) Line profile of the thickness mapping along the cyan arrow in (**A**). The maxim thickness was estimated as 91.2 nm. (**C**) Absolute thickness mapping of the same sample surface near the edge at a high magnification. (**D**) Corresponding line profile along the cyan arrow in (**C**). The thickness of the sample near the edge where the Ir DHCs were observed was estimated as 0.92 nm. (**E**) Low magnification STEM image of the same particle as shown in (**A**). (**F**) Line profile of the STEM intensity along the blue arrow as shown in (**E**). The maxim intensity was measured as ca. 1.18×10^6 counts in the thickest region. (**G**) High magnification STEM image of the same region as shown in (**C**). (**H**) Line profile of the STEM intensity along the blue arrow in (**G**). The red dashing line marks the region where the high resolution Ir DHCs STEM data were obtained.



Figure S11 Thickness measurement by the PACBED method. (**A**) Experimental PACBED pattern. The (200) and (002) disks are marked by yellow dashed circles. (**B**) Line profile along the [002] direction, as shown the red arrow in (**A**). The regions of (200), (400) and (600) disks are shown by blue dashed lines and arrows. (**C**) Simulated CBED patterns with a thickness of 7.7 Å. (**D**) Line profiles of CBED patterns of four samples with different thickness along the [002] direction, as shown the red dashed arrow in (**C**). The two black dashed arrows mark the overlapping region between (200) and (400), and that between (400) and (600), respectively. We see by comparing (**B**) and (**D**) that the sample thickness should be ca. 0.77 nm.



Figure S12 Comparison of line profiles from simulated HAADF images with different thickness through the [020] zone axis. The data used are from the same region as shown in Figure 3A and 3D in the main text. From top to bottom, the thicknesses are (1) 13.5 Å, (2) 7.7 Å as labeled on the right side. The Ir DHC positions are marked with two orange dashed lines. From this set of data, we concluded that Ir DHCs on WO₃ (020) surface would be indistinguishable by HAADF-STEM if the thickness of WO₃ through the [020] zone axis is > 1.35 nm.



Figure S13 (**A**) HAADF-STEM image of Ir DHCs on WO₃. (**B-D**) EDS mapping of oxygen (green), tungsten (red) and iridium (blue), in the same region as (A). Scale bars: 20 nm. (**E**) EDS spectra of Ir DHCs on WO₃. This set of data clearly support that Ir atoms are evenly distributed on WO₃ without observable aggregations.



Figure S14 More HAADF-STEM images of Ir DHCs on WO₃. (A-C) STEM images acquired through the [020] zone axis. (**D**) STEM image acquired from the direction slightly tilted from the [020] zone axis. (**E**) STEM image by tilting to the direction close to $[0\overline{1}1]$. All possible Ir locations are marked by orange circles. Scale bars: 2 nm.



Figure S15 *J_{sc}*/*V_{oc}*/FF/data with error bars. The error bars represent the variations of measurements on 3 different batches of samples.



Figure S16 Chronoamperometry showing the stability of the samples over 2 h at 1.2 V vs. RHE. Electrolyte: 0.1 M K₂SO₄ (pH adjusted to 3.0 by H₂SO₄); lighting condition: AM 1.5 illumination at 100 mW cm⁻²; applied potential: 1.2 V vs. RHE.



Figure S17 Proposed catalytic cycle I for the Ir SAC with calculated reactions free energies at zero bias potential (U = 0 V) (inset). DFT optimized structures of intermediates (A-H).



Figure S18 Proposed catalytic cycle II for the Ir SAC with calculated reactions free energies at zero bias potential (U = 0 V) (inset). DFT optimized structures of intermediates (A'-H').

Discussion of two proposed cycles for the Ir SAC

We proposed two catalytic cycles for Ir SAC (Figure S17 and Figure S18). In both cycles, Ir SAC would undergo PCET processes twice in the beginning. The key difference between the two cycles lies in the third step. The proposed cycle II undergoes a third PCET (Steps **C'** to **D'** in Figure S18) before forming the O-O bond, similar to Ir DHC. However, the third PCET would require too high an energy (1.85 eV). Alternatively, the Ir SAC could bind to a H₂O substrate and form the O-O bond first (Steps **C** to **E** in Figure S17) before the third PCET in the proposed cycle I, which is more favorable.

	TS (eV)	ZPE (eV)
$H_2(g)$	0.40	0.27
O ₂ (g)	0.63	0.10
$H_2O(l)$	0.67	0.57
*OH ₂	0.00	0.71
*OH	0.00	0.39
*0	0.00	0.07
*OOH	0.00	0.47
*00	0.00	0.13
H ₂ O	0.00	0.71

Table S3 Entropic energy contributions (T = 298.15 K) and ZPE corrections for isolated molecules and adsorbed species on Ir SAC and DHC.



Figure S19 Comparison of catalytic cycles between the end-on bound Ir DHC (**A**) and side-on bound Ir DHC (**B**).¹ Key difference is found in the chemical steps (highlighted by light yellow shadows), which are usually regarded as the rate limiting steps.



Figure S20 TOF calculations of Ir-based catalysts with different binding modes for solar water oxidation reaction.

The turnover frequency (TOF) was estimated using the following equation. Here, we focused on four-electron process for water oxidation at 1.23 V vs. RHE:

$$TOF = \frac{I_{sample} * FE(sample) - I_{bare} FE(bare)}{4FN_{Ir}}$$

where I_{sample} is the current passed through the WO₃ electrode with catalyst (C/s·cm²), I_{bare} is the current passed through the bare WO₃ electrode (C/s·cm²), F is the Faraday constant (96485 C/mol), and N_{Ir} is the amount of iridium loading on the electrode surface (mol/cm²). Faradaic efficiency (*FE*) was determined by dividing the measured moles of O₂ by the theoretical yield.



Figure S21 STEM characterization of WO₃ substrate surface (**A** and **B**) and Ir element distribution (**C**) after chronoamperometry stability test.

We observed two features of the Ir DHC/WO₃ after reaction. First, the surface of WO₃ became rougher afterwards (**Figure S21A** and **21B**). Second, the EDS-STEM revealed no aggregation of Ir on the surface (**Figure S21C**).

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