Restructuring highly electron-deficient metal-metal oxides for boosting stability in acidic oxygen evolution reaction

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The poor catalyst stability in acidic oxidation evolution reaction (OER) has been a long-time issue. Herein, we introduce electron-deficient metal on semiconducting metal oxides consisting of Ir (Rh, Au, Ru)-MoO₃ embedded by graphitic carbon layers (IMO) using an electrospinning method. We systematically investigate IMO’s structure, electron transfer behaviors, and OER catalytic performance by combining experimental and theoretical studies. Remarkably, IMO with an electron-deficient metal surface (Irₓ⁺; x > 4) exhibit a low overpotential of only ~156 mV at 10 mA cm⁻² and excellent durability in acidic media due to the high oxidation state of metal on MoO₃. Furthermore, the proton dissociation pathway is suggested via surface oxygen serving as proton acceptors. This study suggests high stability with high catalytic performance in these materials by creating electron-deficient surfaces and provides a general, unique strategy for guiding the design of other metal-semiconductor nanocatalysts.
Hydrogen (H₂) fuel, as a clean energy carrier, is promising to provide an environmentally benign solution for global energy needs. Among different ways of producing H₂, electrochemical water splitting plays a vital role in utilizing renewable energy sources. Though the alkaline water electrolysis technology is dominating the large-scale production of H₂, proton exchange membrane (PEM) water electrolysis has clear advantages such as compact configuration, larger maximum current densities, higher energy efficiency, less H₂ impurity, and dynamic flexibility of operation. As a half-reaction of water splitting, oxygen evolution reaction (OER) is a major bottleneck due to its sluggish kinetics, while the current OER catalysts typically degrade rapidly under acidic conditions, are not stable in highly oxidative environments and are of high cost. Thus, developing low-cost and high-efficiency OER catalysts, especially those stable in acidic media, has been a pressing need but remains a grand challenge.

Significant progress has been achieved in developing active OER catalysts, though the stability under acidic conditions is still a big hurdle. Among others, the first-row (3d) transition-metal oxides showed good promise as OER catalysts. For instance, Smith and coworkers developed the amorphous metal oxide (MoO₃) and Ribeiro et al. investigated (Ni, Fe) oxyhydroxides layer structures. Xin Wang and coworkers proposed a lattice oxygen oxidation mechanism pathway using metal oxyhydroxides, when two adjacent oxidized oxygen atoms can bond to create an electron-deficient oxygen vacancy. Du and coworkers synthesized an Ag₁/IrOₓ single-atom catalyst, uncovering the high-valence Ir⁴⁺ (x > 4) is responsible for the high catalytic OER performance. Recently, Juan-Jesús Velasco-Vélez et al. probed clearly that the oxidation state of Ir is reduced to Ir⁻¹ in the rotating collector using PVP substrate. PVP, firstly proposed as "polyl reduction" for synthesizing metallic Co and Ni from the oxide valence state by Figlarz et al., has been assigned as a steric stabilizer or capping agent to synthesize various nanocrystals. To the best of our knowledge, PVP was first applied to fabricate the metal (Ir, Rh, Ru, and Au)-semiconductor (MoO₃) nanocomposites (Fig. S1). The different formation energies for these metal-oxides (~0.281 eV/atom for AuOₓ; ~0.862 eV/atom for IrO₂; ~0.917 eV/atom for RhO₃; ~1.202 eV/atom for RuO₂; ~1.929 eV/atom for MoO₃) can form the basis for a general and unique strategy for designing metal-semiconductor catalysts. Note that the thermal decomposition of PVP also acting as graphitic carbon layers in the semiconductor of MoO₃ resulted in high conductivity, facilitating electron transfer during the OER process with high stability. The nanorods of IMO, a representative metal-semiconductor, were successfully fabricated by means of a pot economy and one-pot synthesis, forming the three-dimensional (3D) network structures observed from the scanning electron microscope (SEM) and the annealing diagram (Fig. 1b). As expected, we got the nano-composed IMO in which IrO₂ is reduced to Ir, and MoO₃ is formed as the oxide state. The annealing procedure at 500 degrees in the air can induce the electron-deficient surface of metallic Ir due to the surface oxygen and heterointerface junction with the semiconductor of MoO₃.

More detailed evidence is given as follows.

**Results and discussion**

Principle and synthesis of metal-metal oxides—Ir (Rh, Au, Ru)-MoO₃—catalysts. To fabricate the IMO with electron-deficient surface, the electrosprinning synthetic scheme was designed for the IMO precursor (Fig. 1a). Consequently, the nanocomposite fiber of IMO precursor is formatted in the rotating collector using PVP substrate. PVP, firstly proposed as "polyl reduction" for synthesizing metallic Co and Ni from the oxide valence state by Figlarz et al., has been assigned as a steric stabilizer or capping agent to synthesize various nanocrystals. To the best of our knowledge, PVP was first applied to fabricate the metal (Ir, Rh, Ru, and Au)-semiconductor (MoO₃) nanocomposites (Fig. S1). The different formation energies for these metal-oxides (~0.281 eV/atom for AuOₓ; ~0.862 eV/atom for IrO₂; ~0.917 eV/atom for RhO₃; ~1.202 eV/atom for RuO₂; ~1.929 eV/atom for MoO₃) can form the basis for a general and unique strategy for designing metal-semiconductor catalysts. Note that the thermal decomposition of PVP also acting as graphitic carbon layers in the semiconductor of MoO₃ resulted in high conductivity, facilitating electron transfer during the OER process with high stability. The nanorods of IMO, a representative metal-semiconductor, were successfully fabricated by means of a pot economy and one-pot synthesis, forming the three-dimensional (3D) network structures observed from the scanning electron microscope (SEM) and the annealing diagram (Fig. 1b). As expected, we got the nano-composed IMO in which IrO₂ is reduced to Ir, and MoO₃ is formed as the oxide state. The annealing procedure at 500 degrees in the air can induce the electron-deficient surface of metallic Ir due to the surface oxygen and heterointerface junction with the semiconductor of MoO₃.

More detailed evidence is given as follows.

**Characterization of morphologies and structures.** X-ray diffraction (XRD) patterns of IMO (Fig. 2a) indicated that phase properties of iridium are metallic as assumed above. The XRD pattern of IrO₂-MoO₃ (IOMO) indicated that the bi-metallic oxidized was synthesized successfully by comparison with IMO catalyst (Fig. S2). The morphology and distribution of IMO are
further explored using transmission electron microscopy (TEM). The nanorod is connected to each other to form the 3D network heterostructure with the help of graphitic carbon layers (Fig. 2b), consistent with the SEM image (Fig. 1b). Further, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM; Fig. S3a) and annular bright-field scanning transmission electron microscopy (ABF-STEM; Fig. S3b) were performed at low-magnification and aided by energy-dispersive X-ray spectroscopy (EDS). The overview morphology and elemental distribution of Ir, Mo, O, and C indicate that the heterostructure of IMO was successfully fabricated. The different contrast TEM images (Fig. 2c, d) show the Mo and Ir distribution according to the atomic number dependence of Z contrast, as verified by the line energy-dispersive X-ray spectroscopy (EDS) elemental maps (Fig. S4). Furthermore, the EDS mapping image proves that the elements of Mo, Ir, and O are distributed homogeneously (Fig. 2e), consistent with Fig. S3.

The high-resolution TEM (HRTEM) image is used to identify the lattice fringes of IMO. Crystalline lattice distances of 0.35 nm and 0.22 nm correspond to the (040) facet of MoO$_3$ and (111) facet of Ir, respectively (Fig. 2g). Note that facets (040) of MoO$_3$ and (111) of Ir can be obtained at 37.8° and 40.7° from the XRD pattern, consistent with the HRTEM images. Also, the lower peak intensity at 40.7° indicated the Ir with crystal size has good dispersion on the MoO$_3$, facilitating the interaction between Ir and MoO$_3$. Note that graphitic carbon layers can be observed in the edge of IMO, evidenced by the contrast HRTEM images (Fig. 2f, g). There is a conception that the graphitic carbon layers are not active sites for the catalytic reaction and only work for increasing the electron transfer and enhancing the catalytic stability$^{42}$. Graphitic carbon layers are not generally considered for further characterization. According to the morphology and structural characterizations of IMO, we proposed the structure model, including the side view and top view of the heterojunction between the MoO$_3$ (040) and Ir (111) facets (Fig. S5).

Finally, the atomic resolution ABF-STEM (Fig. 2h) and HAADF-STEM (Fig. S6) images (the Ir metal area in the red box in Fig. 2g) were collected.

Spectroscopic characterization. To probe surface compositions and determine the oxidation states, we performed X-ray photoelectron spectroscopy (XPS) analyses. The survey spectra of IMO
and IOMO show the existence of C, Ir, Mo, and O elements, respectively (Fig. S7), consistent with EDS analysis (Fig. S3). To cross-validate our experimental result, the commercial Ir, IrCl₃, and IrO₂ are performed, and the detailed fitting parameter was shown in Table S1. Note that all XPS spectra were calibrated using C 1s at 284.6 eV (Fig. S7). The Ir 4f of IMO has a surprisingly high energy shift compared with that of IOMO, indicating the Ir nanoparticles (NPs) have released the electron due to the low electronegativity (Fig. 3a). To gain insight into this phenomenon, we further analyzed the high-resolution XPS (HR-XPS) of Mo 3d and O 1s (Fig. 3b and Fig. S8). While the Mo⁵⁺ 3d peak is observed clearly from the Mo 3d of IMO, the peak of Mo⁵⁺ 3d (~231.72 eV) is hardly obtained in IOMO (Fig. 3b). Note that O 1s show traditional three peaks that O₅ is lattice oxygen, O₅H is adsorbed hydroxide, and O₅water is adsorbed water (Fig. S8), consistent with previous reports. To further gain insight into the phenomenon, we calculated the charge density difference for investigating the electron transfer over the Ir and MoO₃ in IMO (Fig. 3c, d and Fig. S9). Note that the electrons of Ir are transferred to Mo, as observed from the images of charge density difference. We confirm that the Ir NPs of the IMO has an electron-deficient surface, as evidenced by a higher Ir surface valence state of IMO than that of IOMO and commercial IrO₂ (Fig. 3a and Fig. S10). To prove whether the interfacial Ir atoms binding to MoO₃ or the surface Ir atoms binding to adsorbed oxygen species have higher valence states, the HR-XPS measurement about Ir 4f in IMO is performed with an argon ion etching treated sample, demonstrating zero-valence state of Ir metal in IMO, which is consistent with commercial Ir metal (Fig. S11) and XRD pattern (Fig. 2a). This result confirms that the surface Ir in IMO has a high valence state.

To gain insight into the phase structures of IMO and IOMO, we further utilized the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses for their bulk-average information. The IMO’s Ir L₃-edge absorption edge position is lower than that of IrO₂ (Fig. 4a), indicating metallic Ir NPs properties, consistent with IMO’s XRD pattern (Fig. 2a). Note that Ir L₃-edge of IMO is also positively shifted compared with that of Ir metal foil due to the high electron-deficient surface of IMO. Moreover, the peak of Ir L₃-edge derivative XANES of IMO (Fig. 4b) is located at a low energy position compared with IOMO, implying the metallic
properties of Ir NPs are consistent with XANES and XRD analysis. Fourier-transformed (FT) \( k^2 \)-weighted EXAFS spectra of Ir L3-edge show the prominent peak at 1.65 Å assigned to the Ir-O first coordination shell of IrO2 and the prominent peak at 2.58 Å assigned to the Ir-Ir first coordination shell of Ir NPs (Fig. 4c), which is consistent with previous IrO246 and metallic Ir47. To cross-validate the IMO’s electron-deficient surface, Mo K-edge absorption edge position change (Fig. 4d) was examined as identified by XPS, confirming the electron transfer from Ir element to Mo element. The Mo K-edge absorption of IMO has a shift to low energy, compared to IOMO and MoO3 (Enlarged Fig. 4d), consistent with the Mo3+ 3d peak from XPS, although no noticeable phase change of MoO3 was identified from XRD. Correspondingly, the peak derivative of XANES for Mo K-edge in IMO also shifts to low energy as indicated by the red arrow direction and in comparison to IOMO and MoO3 (Fig. 4e), consistent with Ir L3-edge analysis. Note that the difference between IMO, IOMO, and MoO3 is hardly observed from FT \( k^3 \)-weighted EXAFS spectra of Mo K-edge (Fig. 4f), demonstrating the characteristic peaks of MoO3, which is consistent with previous reports48,49. Generally, it is hard to observe the heterointerface bonding for the heterostructure of IMO from EXAFS spectra50. Thus, EXAFS fitting curves for IMO and IOMO were conducted to study further the coordination information (Fig. S12 and Table S2), indicating Ir-Mo scattering length is around 2.0 Å, consistent with DFT results.

Wavelet transforms (WT) for the Ir L3-edge and Mo K-edge EXAFS analysis are applied to demonstrate the atomic dispersion of IMO and IOMO, respectively (Fig. 4g). The WT of Ir L3-edge related to Ir–Ir bond is detected in Ir-Foil and IMO, confirming the metallic properties of Ir in IMO. In comparison with IMO, as we expected, IOMO has a WT pattern similar with IrO2, consistent with XRD, XANES, EXAFS analyses. Moreover, the WT patterns for IMO and IOMO exhibited a signal similar to that of MoO3, which differs from Mo-Foil. By combining the XAFS results (Ir L3-edge and Mo K-edge) and XPS data analysis, metallic Ir NPs in IMO have unambiguously higher surface oxidation than IrO2 in IOMO. To clarify and expound on the phenomenon, two critical factors of (i) surface oxygen of Ir evidenced from Argon etching XPS (Fig. S11) and (ii) the electron-withdrawing material of MoO3 documented by charge density difference (Fig. 3c) and XAFS spectra (Fig. 4a, d).
Fig. 4 X-ray absorption fine structure (XAFS) characterizations. a XANES survey spectra at the Ir L3-edge for Ir foil, Ir-MoO3, IrO2-MoO3, and IrO2. b Derivative of L3-edge XANES spectra for Ir foil, Ir-MoO3, IrO2-MoO3, and IrO2. c Ir L3-edge X-ray absorption Fourier-transformed (FT) k3-weighted EXAFS spectra in R space. d XANES survey spectra at the Mo K-edge XANES spectra for Ir-MoO3, IrO2-MoO3, and MoO3. e Derivative of L3-edge XANES spectra for Ir-MoO3, IrO2-MoO3, and MoO3. f Mo K-edge X-ray absorption Fourier-transformed (FT) k3-weighted EXAFS spectra in R space. g Wavelet transforms (WT-EXAFS) for Ir-MoO3, IrO2-MoO3, IrO2, MoO3, Ir foil, and Mo foil.
are predominant. The surface oxygen on the Ir NPs can be attributed to the annealing process in the air, which positively promotes the OER activity. Overall, the IMO has an electron-deficient surface for the two reasons: (1) surface oxygen-group on IMO induced the electron transfer from Ir to O; (2) the MoO3 withdraws the electron from Ir NPs, which is the likely center for the formation of oxygen because of a nucleophilic attack by OH or because of H2O forming an O–O bond.

**Electrochemical OER performance.** IMO outperforms other OER catalysts previously reported in the literature, including benchmark catalysts such as RuO2 (10 mA cm−2 at ~293 mV, similar to the previous studies) and Ir (10 mA cm−2 at ~328 mV, similar to the previous studies). The OER catalytic activity of IMO is significantly higher, as evidenced by the overpotential (η) of ~156 mV under the same current density (10 mA cm−2, Fig. 5a, b). Remarkably, due to the unique electron-deficient surface structures (Fig. 5c), IMO exhibits the best OER efficiency with the ultra-low η as compared to recently reported literature. Tafel slopes are derived from the polarization curves to provide deeper insights into the OER mechanism (Fig. 5d). The Tafel slope of IMO is 48 mV dec−1, which is remarkably lower than the state-of-the-art RuO2 at 75 mV dec−1, consistent with the previous reports and Ir at 71 mV dec−1, consistent with the previous reports. All measured values of Tafel slope is lower than 120 mV dec−1 and we can conclude surface species formed in the step just before the rate-determining step is not predominant. Due to the high coverage of active species at empty sites that decrease the value of Tafel slope, the low Tafel slope of IMO can be attributed to a large number of oxygen species on surface Ir in IMO. The absorbed oxygen species not only provide the high valence state surface of Ir in IMO but also reduce the value of Tafel slope, which accelerates the process of OER and increases the OER efficiency. The fast electron transfer kinetics process during the OER reaction is consistent with the metallic nature of Ir NPs with graphitic carbon.
support. The current density differences show that the double-layer capacitance ($C_{DL}$) is a function of the scan rate (Fig. S13). As a result, the $C_{DL}$ of IMO at $\sim 8.0$ mF cm$^{-2}$ is higher than that of IOMO at $\sim 6.4$ mF cm$^{-2}$, indicating IMO has a high total electrochemical active surface area, which facilitates the electrochemical process of OER. Nyquist plots of IMO (Fig. S14) show a low electrolyte resistance (Rs) and charge transfer resistance (Rct) compared to IOMO catalysts, implying a fast ion transfer and quickly electron processes at the catalytic-electrolyte interface, consistent with the fast electron transfer kinetics process identified by Tafel slope. Faradaic efficiency of IMO is estimated by measuring the produced O$_2$ gas using a water displacement method, demonstrating nearly 100% Faradaic efficiency (Fig. S15 and Table S3). To assess the intrinsic catalytic efficiency, we first perform the mass activity based on the total deposited catalysts amount, indicating the superior mass activity of IMO (Fig. S16a). To further quantify the catalytic efficiency of Ir metal, mass activity is evaluated by normalizing the amount of Ir. IMO delivers a high mass activity of $\sim 178.9$ mA/mgIr at an overpotential of 200 mV, which is about two times higher than that of IOMO and about 600 times higher than that of Ir metal (Fig. S16b). Furthermore, turnover frequency (TOF) is performed (Fig. S17), consistent with the result of mass activity. Remarkably, the TOF of IMO reaches 5.2 s$^{-1}$ at an overpotential of 200 mV, 40 times higher than that of Ir metal, indicating its excellent intrinsic activity due to the highly electron-deficient surface of Ir metal in IMO, which is promising for practical usage.

To evaluate the catalysts' durability, the chronopotentiometry curves of IMO, Ir, and RuO$_2$ were collected over 48 h. For IMO, no tremendous loss occurred at the constant anodic current density of 10 mA cm$^{-2}$ under 0.5 M H$_2$SO$_4$. By comparison, Ir and RuO$_2$ were found to be unstable with $\eta$ increasing fast within few hours (Fig. 5e). Further, the chronopotentiometry test at a high current density of 100 mA cm$^{-2}$ for 48 h demonstrates the exceptional stability of IMO, which is promising for practical usage (Fig. S18). Note that the activity and stability generally show the trade-off relationship. Thanks to the Mo$^{5+}$ existence in the MoO$_3$, the catalysts of IMO exhibited excellent durability compared with IOMO. To gain insight into the mechanism, we measure the XPS spectra after the OER experiment. The energy state of the Ir, Mo, and O undergo a minor high-energy shift after the OER process, indicating that these elements lose the electron during the OER (Fig. S19 and Table S4). Note that the surface structure of the IMO is still preserved well after the OER reaction, since the synergic effect of the high surface state of Ir with the help of the Mo$^{5+}$ can withstand resistance in an oxidation state (Fig. S19a). However, the surface structure of IOMO can be corroded during the OER process because the ratio of lattice oxygen ($O_L$) decreases compared with that in fresh of IOMO (Fig. S19b), which is the origin of the instability for IOMO in comparison with IMO.

Theoretical investigation for active sites using DFT. Inspired by the unique structure with the electron-deficient surface that benefits the OER efficiency as demonstrated using in situ and ex situ x-ray spectroscopies, we further investigate the catalytic activity by means of DFT. Firstly, we check the favorite sites for HO$^*$ adsorption at various IMO sites since the HO$^*$ is the first intermediate formed in the OER (Fig. 6a). The interfacial site (A site) between the MoO$_3$ and Ir, the Ir edge site (B site), the Ir hollow site (C site), and the Ir top site (D site) are calculated as favorable for adsorption energy of HO$^*$, demonstrating the sites A, B, and C are favorable for the HO$^*$ adsorption compared with the D site (Fig. 6b). Note that the D site on IMO is unstable during the optimized process, which prevents the D site from becoming the active site for the OER process. Additionally, note that the same trend of oxygen adsorption is observed and the D site on IMO shows the bond distance of 2.72 Å (Fig. S20), indicating that the D site is not a favorable site for oxygen adsorption.

To gain insight into the OER mechanism of IMO by considering its boosting OER efficiency, the various amount of surface oxygen species was considered (Figs. S22–26). As a result, the Ir metallic surface with 8 surface oxygen atoms has the highest formation energy ($\sim 1.74$ eV/atom) compared to other metal surfaces, oxygen atoms ($\sim 1.63$ eV/atom for seven surface oxygen, $\sim 1.62$ eV/atom for nine surface oxygen, $\sim 1.42$ eV/atom for ten surface oxygen). As we expected, the IMO with seven surface oxygen atoms (O-7) models shows the low OER energy barriers by reducing the energy barriers compared with the IMO (Fig. 6c and Fig. S27). In addition, to break the scaling relation between HO$^{\cdot}$ and HO$^{\bullet}$ the proton dissociation pathway (PDP) is suggested for the models IMO (O-8). As a result, PDP indicates the lowest energy barrier when the proton transfers to the neighbor surface oxygen compared to the relative other OER pathway, and the corresponding configurations are illustrated (Fig. 6c), which is consistent with the experimental results of low overpotential and Tafel slope. These results significantly demonstrate that the surface oxygen participates in the OER reaction as a proton acceptor, powerfully uncovering the origin of IMO's excellent catalytic OER performance, which opens up an avenue for designing highly efficient catalysts.

By following data-driven and high-throughput simulation guidance for the coupled Ir-Mo system as a promising acid-stable catalyst, we designed and fabricated the electron-deficient surface of IMO catalysts using a pot economy and one-pot electrospinning strategy. Ir 4f of IMO has a high energy shift from the HR-XPS measurement compared to that of IOMO due to the surface oxygen and electron-withdrawing substrate, as cross-validated from the DFT simulation (charge density difference) and XAFS spectra. To our knowledge, as a result, IMO shows the high stability with superior OER catalytic performance compared with the benchmark catalysts (Ir and RuO$_2$) up to date, because the energetic effect of the high surface state of Ir with the help of the Mo$^{5+}$ can withstand resistance in an oxidation state. Further, the active catalytic origin of OER was uncovered by means of DFT simulation. The proton dissociation mechanism was suggested while the neighbor surface oxygen works as a proton acceptor. This study not only uncovers the rational design of IMO for superior catalytic performance by creating an electron-deficient surface, but also reveal the general and unique strategy—PVP with following annealing process to fabricate the metal–metal oxide (Ir-MoO$_3$, Ru-MoO$_3$, Rh-MoO$_3$, and Au-MoO$_4$) heterostructures—for guiding other metal-semiconductor design.

Methods
Computational details. All of our DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [57–59]. The projector-augmented wave (PAW) method was employed to describe the ion-electron interaction [60,61]. The exchange-correlation function was depicted by the generalized gradient approximation in the form of Perdew–Burke–Ernzerhof (GGA-PBE) functional [62]. The electronic wave functions were expanded using a plane-wave basis with 400 eV cutoff energy. Monkhorst-Pack $k$ points mesh sizes of 2 x 2 x 1 were used for...
geometric optimizations and self-consistent total energy calculations. All the structures were optimized with the convergence criteria of $10^{-4}$ eV/Å in force and $10^{-6}$ eV per atom in energy. A 15 Å vacuum space in the $z$-direction was applied to avoid interactions between adjacent periodic images.

The thermodynamic model of water oxidation proposed by Norskov and co-workers, which is composed of four electrochemical steps, each of which constitutes one proton transfer, was used in this work. The following electron reaction paths are considered for the oxygen evolution reaction (OER) process:

1. $\text{H}_2\text{O}(l) + \text{HO}^* \rightleftharpoons \text{HOO}^* + \text{H}^+ + \text{e}^- (\Delta G_1)$,
2. $\text{HO}^* \rightleftharpoons \text{O}^* + \text{H}^+ + \text{e}^- (\Delta G_2)$,
3. $\text{O}^* + \text{H}_2\text{O}(l) \rightleftharpoons (\text{H}^+)\text{HOO}^* + \text{H}^+ + \text{e}^- (\Delta G_3)$,
4. $\text{HOO}^* \rightleftharpoons \text{O}_2(g) + \text{H}^+ + \text{e}^- (\Delta G_4)$,

where * represents an active site on the Ir-MoO$_3$ surface. O*, OH*, and OOH* are intermediates adsorbed on the active site.

Molecular O$_2$ energy is indirectly obtained from the experimental Gibbs free energy formation of water oxidation equation at standard conditions $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2$, $\Delta G = -4.92$ eV to avoid the calculation of oxygen molecule O$_2$ by DFT. For the ideal case in which $\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4 = 0$, the equilibrium potential to produce oxygen is $(eU - k_B T \ln(10) \times p\text{H})/e = 1.23$ V. Practically, the catalytic activity of the above process is controlled by the rate-determining step (RDS), which has the maximum free energies of adsorption ($\Delta G_{\text{RDS}}$).

Synthesis of MoO$_3$ composite. MoO$_3$ was prepared by means of a facile electrospinning method in the presence of ammonium molybdate (para) tetrahydrate, and polyvinylpyrrolidone (1.2 g, PVP, average M.W. 130,000), followed by high-temperature pyrolysis. Specifically, 1 mmol ammonium molybdate (para) tetrahydrate and 1.2 g of PVP were added to a mixed solvent of dimethylformamide (5 mL DMF) and alcohol (5 mL EtOH) with stirring at 80-degree for 12 h. The mixed solution was added into a 10 mL plastic syringe with a 25-gauge stainless-steel needle. The applied direct current voltage and distance between the needle and the aluminum-foil-wrapped collector were fixed at 15 kV and 12 cm, respectively. The flow rate of the mixed solution was maintained at 10 µL min$^{-1}$. The as-

Fig. 6 DFT computational modeling and investigation of IMO active site. a The optimal sites for the HO* adsorption on the interfacial site (A site) between the MoO$_3$ and Ir, Ir’s edge site (B site), Ir’s hollow site (C site), and Ir’s top site (D site). b The corresponding adsorption energies of the four sites in a. c Relative energy profiles and the simplified surface structures of various reaction species as the arrow define. d The configuration of HOO* for site B after relaxation. e The configuration of HOO* for site A after relaxation. f The configuration of HOO* for site C after relaxation. Color code: The red, gold, and violet balls represent the O, Ir, and Mo atoms, respectively.
prepared materials were annealed at 500 °C for 3 h in the air at a heating rate of 5 °C min⁻¹. Finally, MoO₃ was collected.

**Synthesis of IrO₂ and MoO₃ composite (IMO).** IMO was prepared by means of a facile electrospinning method in the presence of ammonium molybdate (para) tetrahydrate, and polyvinylpyrrolidone (1.2 g, PVP, average M.W. 130,000), followed by high-temperature pyrolysis. Specifically, 1 mmol IrO₂, 1 mmol ammonium molybdate (para) tetrahydrate, and 1.2 g of PVP were added to a mixed solvent of dimethylformamide (5 mL DMF) and alcohol (5 mL EtOH) with stirring at 80-degree for 12 h. The mixed solution was added into a 10 mL plastic syringe with a 25-gauge stainless-steel needle. The applied direct current voltage and distance between the needle and the aluminum-foil-wrapped collector were fixed at 15 kV and 12 cm, respectively. The flow rate of the mixed solution was maintained at 10 µL min⁻¹. The as-prepared materials were annealed at 500 °C for 3 h in the air at a heating rate of 5 °C min⁻¹. Finally, IMO was collected. Note that the Ru-MoO₃, Rh-MoO₃, and Au-MoO₃ were prepared by the same method with the replacement of the appropriate metal oxides.

**Synthesis of IrO₂ and MoO₃ composite (IOMO).** IOMO was prepared by means of a facile electrospinning method in the presence of ammonium molybdate (para) tetrahydrate, and polyvinylpyrrolidone (1.2 g, PVP, average M.W. 130,000), followed by high-temperature pyrolysis. Specifically, 1 mmol ammonium molybdate (para) tetrahydrate and 1.2 g of PVP were added to a mixed solvent of dimethylformamide (5 mL DMF) and alcohol (5 mL EtOH) with stirring at 80-degree for 12 h. The mixed solution was added into a 10 mL plastic syringe with a 25-gauge stainless-steel needle. The applied direct current voltage and distance between the needle and the aluminum-foil-wrapped collector were fixed at 15 kV and 12 cm, respectively. The flow rate of the mixed solution was maintained at 10 µL min⁻¹. The as-prepared materials were annealed at 500 °C for 3 h in the air at a heating rate of 5 °C min⁻¹. Finally, IMO was collected.

**Electrochemical measurements.** All electrochemical tests were carried out using a VMP3 electrochemical workstation (Biologic Science Instruments, France). To prepare the working electrode, we sonicated a mixture of 5 mg of catalyst, 0.5 mL of DI water, 0.49 mL of ethanol, and 10 µL of 5 wt% NaCl solution using a standard three-electrode cell. All potentials were converted to the RHE scale using the equation

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH}
\]

where \(E_{\text{Ag/AgCl}}\) is the standard potential of Ag/AgCl reference electrode at room temperature. All measurements were carried out in 0.5 M H₂SO₄ saturated 0.5 M H₂SO₄ solution using a standard three-electrode cell. All experiments were conducted in an ambient condition at 298 K.

**Data availability**

The data supporting the findings of this study are available within the paper and its Supplementary Materials. The raw data used in this work are available from the corresponding author upon reasonable request.

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Author contributions
X.L and H.L conceived the idea and directed the project. X.L. design and synthesize the experimental synthesis, XAFS and analysis. A.K. help the OER performance measure-. T.Y. help the SEM measurement. X.S. help the XPS analysis. M.L. help the XRD analysis. X.L. and H.L. write the draft. All authors discuss the results.

Competing interests
The authors declare no competing interests.

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