

Electronic Supplementary Information

Promising engineering strategy for water electro-oxidation iridate catalysts via coordination distortion

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Experiments part

1. Materials preparation

The materials, for research and comparison are prepared according our previous studies, such as IrO_2 ¹, iridium based pyrochlore², hollandite K_xIrO_2 ³ and transition metals doping⁴ are from the alkaline coordination hydrothermal method, iridium based perovskites are prepared form sol-gel method⁵. After the hydrothermal reaction, it will be calcined at a specific temperature to make them crystallinity. The doped materials of stoichiometry $\text{M}_x\text{Ir}_{1-x}\text{O}_y$ are controlled at constant x in each transition metals (Co, Ni and Cu). Here, x is chosen as the value of 0.1 (10% mole ratio) and 0.3 (30% mole ratio). The precursors of transition metals are their respective nitrates ($\text{Co}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$, analytically pure, Shanghai Ling Feng Chemical Reagent Co.,Ltd). The precursors of iridium is the iridium trichloride ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$; analytically pure, TCI (shanghai) Development Co.,Ltd). The variable stoichiometric amounts were mixed into a 40-mL Teflon-lined pressure vessel with 10 mL deionized water and 5 mL 0.5 M aqueous NaOH. The mixture was loaded into an oven to heat the solution to 150°C for 720 min; then, the vessels were cooled naturally at room temperature. The precipitates were suction filtered and washed with deionized water twice to remove other ions. The remaining solid on the filter was dried to dehydration in an oven at 60 °C for 1 h. The dried solid was transferred to a crucible and annealed at 400

°C for 6 h.

2. Electrode preparation and Electrochemical Measurements

The electrodes used for the electrochemical measurements were prepared as follows. First, 6 mg of fresh catalyst powders was dispersed in a solution of 1.5 mL of 2:1 v/v isopropanol/water and 15 μ L of Nafion. Then, the solution was ultrasonicated for approximately 30 min to form a homogeneous ink. Next, 7.5 μ L of ink was deposited on a tailored Ti plate with dimensions of 0.5 cm $\times$ 1.5 cm. The Ti plate was etched for 2 h by 10% (wt %) oxalic acid under near boiling conditions. The deposition process was repeated 5 times to obtain a loading weight of approximately 0.2 mg cm^{-2} .

Electrochemical tests were performed under a three electrode system. Here, a saturated calomel electrode (SCE) was employed as the reference, and a polished and cleaned Pt foil with a 1.5 cm $\times$ 1 cm reaction area was used as the counter electrode. The electrode potential from the SCE scale was converted into the reversible hydrogen electrode (RHE) scale by calibration with $E(\text{RHE}) = E(\text{SCE}) + E_{j=0}$. The over-potential values (η) corrected with the iR were obtained using the following equation: $\eta = E_{\text{Applied}}(\text{RHE}) - iR - 1.229$. The SCE was calibrated with respect to the RHE in all three types of pH solutions using a high purity hydrogen saturated electrolyte with a Pt foil as the working electrode⁶. CVs experiments were performed at a scan rate of 1 mV/s, and the average of the two potentials

at which the current crossed zero was recorded as the thermodynamic potential for the hydrogen electrode reaction. The OER determinations were performed under the 0.1 M perchloric acid (HClO₄, A.R. purity) solution. The working electrodes were cycled at least 5 times until the curves overlapped in the CV experiments; then, the CV data and polarization curves were recorded at the specified scan rate.

3. Materials Characterization

The crystal structure of the catalysts was investigated using powder X-ray diffraction (XRD) with a D/max2550 V apparatus with a Cu-K α radiation source ($\lambda=1.5406$ Å), and the data were recorded over the range of 10 to 80° at the step size of 0.02°. The X-ray absorption (XAS) data of the samples were recorded at room temperature in the transmission mode using ion chambers and the BL14W1 beam line in the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (111) double crystal monochromator. During measurements, the synchrotron was operated at the energy of 3.5 GeV and the current varied between 150-210 mA.

4. TOF calculation:

The TOF values at $\eta=0.323$ V were calculated by assuming that every Ir atom is an active site in catalysts and are given by

$$\text{TOF} = \frac{j A_{\text{geo}}}{4 F n}$$

Here, j is the current density (mA cm^{-2}) at the $\eta=0.323$ V; A_{geo} is the geometric area of electrode is 0.25 cm^2 ; the number 4 means the 4-electron transfer process of OER; F is Faraday's constant with a value of $96485.3 \text{ C mol}^{-1}$; the number n is moles of Ir atom in loading catalysts on electrodes.

Computational Details

The first-principles calculations were performed using DFT methodologies implemented in the Vienna ab-initio simulation package (VASP)⁷. The generalized gradient approximation (GGA) was used for the exchange–correlation functional in a form suggested by Perdew, Burke, and Ernzerhof (PBE)⁸, and a cutoff energy of 400 eV was used. Electron–ion interactions were treated with the projector augmented wave (PAW) method⁹. Spin-polarized DFT calculations were applied in this study to obtain the lattice parameters, the density of states for IrO_2 , K_xIrO_2 , $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$, $\text{Bi}_2\text{Ir}_2\text{O}_7$, Ca_2IrO_4 and CaIrO_3 unit cell. The all atoms were kept fixed during calculations the unit cell parameter, while the calculate the density of states all atoms were allowed to relax. The force threshold of all the relaxed atoms was set to $0.05 \text{ eV/\AA}$. The Brillouin-zone integration was performed along with a $3 \times 3 \times 3$ Monkhorst-Pack grid for the different unit cell.

In order to calculate the free-energy diagrams of the OER of IrO_2 , Cu doped IrO_2 and $\text{K}_{x \approx 0.25}\text{IrO}_2$. A $6 \times 1 \text{ IrO}_2(110)$ slab with five O-Ir-O units, was prepared for the calculations. The bottom three O-Ir-O layers were fixed

while the top two tri-layers were relaxed. For $\text{K}_{0.25}\text{IrO}_2$, a 1×2 $\text{K}_{x \approx 0.25}\text{IrO}_2(1\bar{1}2)$ surface model with five K layers were used. The top two K layers were allowed to relax. The (001) surfaces were chosen as slab models for $\text{Ir}_{0.7}\text{Cu}_{0.3}\text{O}_8$, these stoichiometric (001) surfaces with 3×1 supercell containing six O-Ir-O layers were optimized with the upper two tri-layers relaxed. The detailed computational method used has been widely described by Nørskov et al¹⁰.

Figures and Tables

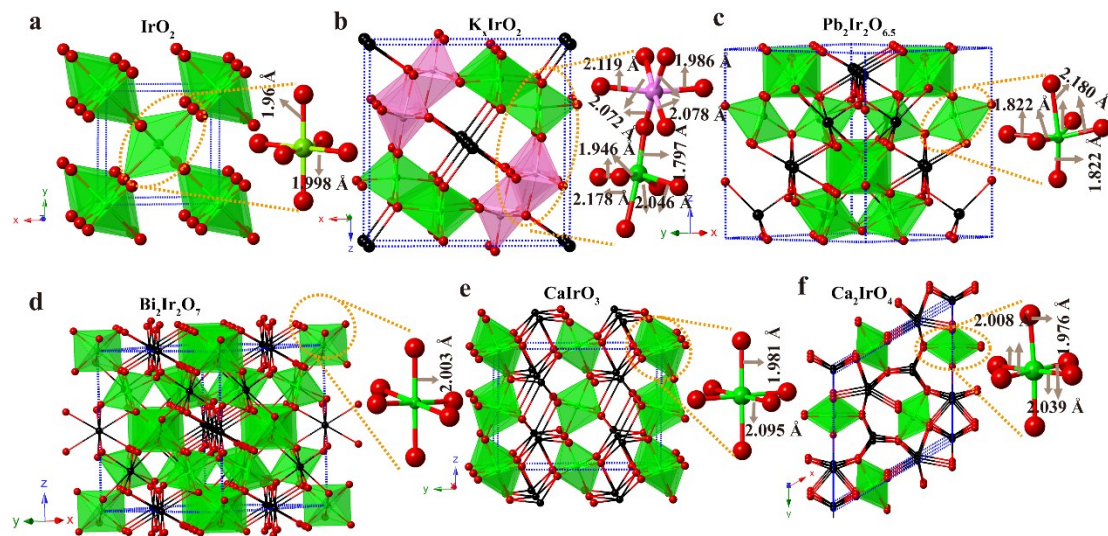


Fig. S1. Crystallographic representations of different iridates. (a) Rutile structure of IrO_2 ; (b) hollandite structure of K_xIrO_2 ; (c) and (d) pyrochlore structure of $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ and $\text{Bi}_2\text{Ir}_2\text{O}_7$; (e) and (f) perovskite structure of CaIrO_3 and Ca_2IrO_4 .

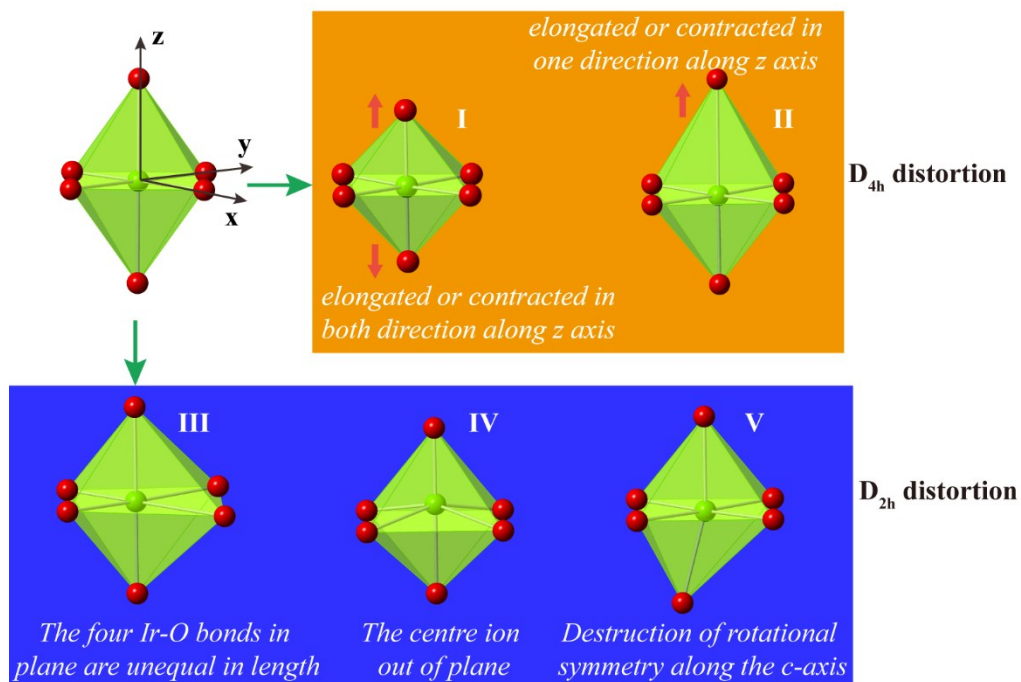


Fig. S2. MO_6 coordination distortion types. Commonly, it includes D_{4h} and D_{2h} distortion.

Table S1. The descriptor and mathematical expression of different distortion types in MO₆ coordination.

Distortion type	Parameters ϵ	Descriptor	Mathematical expression*	
I	ϵ_1	The Ir-O bond length between z axis (d_a) and xy plane (d_p) are not equal	$2(d_{a1}+d_{a2})/(d_{p1}+d_{p2}+d_{p3}+d_{p4})$	D _{4h}
II	ϵ_2	The Ir-O bond length in z axis are not equal	d_{a1}/d_{a2}	
III	ϵ_3	The Ir-O bond length in xy plane are not equal	$2d_{p1}/2d_{p2}$	
IV	ϵ_4	The centre ion is not in the xy plane	$(d_{a1}+d_{a2})/2d_{a2}$	D _{2h}
V	ϵ_5	The O-Ir-O angle in the z axis is not 180°	$\sin(180^\circ/2)/\sin(\varphi_{O-Ir-O}/2)$	

*, d_a -the Ir-O bond length in z axis; d_p -the Ir-O bond length in xy plane; φ_{O-Ir-O} -the O-Ir-O angle along the z axis. In order to avoid cancellation when parameters are multiplied, all parameters are greater than or equal to 1 except ϵ_1 .

According to above discussion, the distortion of IrO₆ can be given by fellow equation:

$$\Gamma = \prod \epsilon_i \quad (i=1,2,\dots,5).$$

Table S2. The distortion parameters of IrO₆ coordination in different materials

Materials	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	Distortion parameters Γ
IrO ₂	0.98098	1	1	1	1	0.98098
K _x IrO ₂ -1	0.99574	1.21202	1.10601	1.05139	1.00089	1.40464
K _x IrO ₂ -2	0.98916	1.06697	1.03348	1.0029	1.00391	1.09817
Pb ₂ Ir ₂ O _{6.5}	1	1.19649	1.09824	1.19649	1.01274	1.59226
Bi ₂ Ir ₂ O ₇	1	1	1	1	1	1
CaIrO ₃	0.94558	1	1	1	1	0.94559
Ca ₂ IrO ₄	0.97653	1	1	1.01544	1.00048	0.99207

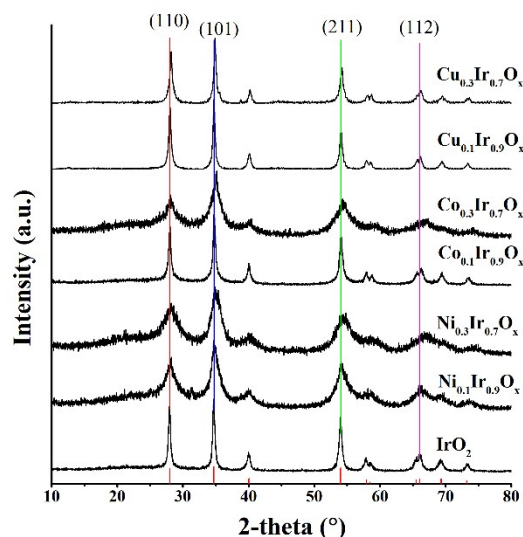


Fig.S3. The XRD patterns of prepared doped samples. The vertical red line on the bottom is the standard diffraction positions of IrO_2 . From XRD, the small doped amount of 10% mole ratio do not arise the peaks positions change. But it obvious when increase the doped amount.

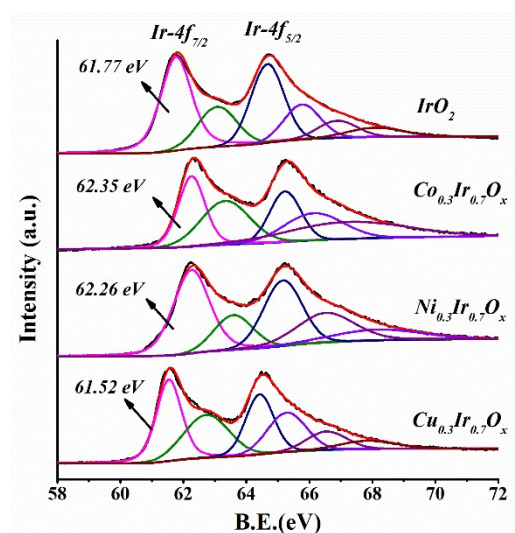


Fig. S4. Ir-4f XPS spectra of different elements doped samples. In order to observe the binding energy variations, we chose the doped amount of 30% mole ratio to comparison. The binding energy of Ir-4f_{7/2} is close to 61.77 eV in here, and is consistent with reports of 61.7 eV for pure IrO_2 .

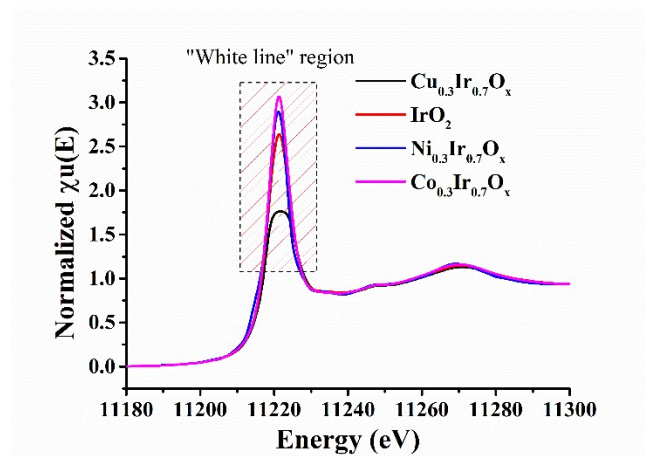


Fig. S5. Ir-L_{III} edge XANES of prepared doped samples. The “white line” intensity of the Ir-L_{III} edge in XANES can be used to evaluate the 5d orbital electrons’ occupation states, because the greater electrons occupied in 5d orbitals, the intensity of “white line” will be decreased. The intensity of $\text{Cu}_{0.3}\text{Ir}_{0.7}\text{O}_x$ has the lowest intensity, while Co and Ni present higher intensity than pure IrO_2 . Thus, 3d transition metals doped will give rise to change of Ir valence state, but no linear relationship been observed. This is agreement with the observation of Ir-4f XPS.

Table S3. Ir-L_{III} edge EXAFS fitting parameters for prepared materials.^a

Catalysts	<i>c</i> axis length (Å)	Ir-Ir shell 2 (Å)	σ^2	R_{factor}
IrO₂	3.159	3.565	0.00402	0.00103
Cu-0.1	3.149	3.564	0.00491	0.00113
Cu-0.3	3.143	3.564	0.00345	0.00124
Ni-0.1	3.145	3.553	0.00806	0.00143
Ni-0.3	3.142	3.550	0.00366	0.00162
Co-0.1	3.146	3.551	0.00652	0.00127
Co-0.3	3.141	3.550	0.00311	0.00144

^a) Fitting parameters for prepared catalysts; fit range $2 < k < 14$, $2.4 < R < 4.4$; number of independent points = 14. The coordination number (N) are constant for different samples in the same path scattering during the fitting. The “c-axis length” (N=2) and “Ir-Ir shell 2” (N=8) are the fitting target; σ^2 , Debye–Waller factor; R_{factor} , goodness of fit.

Table S4. The lattice parameters of prepared transition metals doped IrO₂.*

Materials	c-axis (Å)	a-axis (Å)	d _p (Å)	d _a (Å)	d _p /d _a
IrO ₂	3.159	4.517	1.9992	1.9668	0.9837
Cu-0.1	3.149	4.505	1.9927	1.9642	0.9857
Cu-0.3	3.143	4.502	1.9887	1.9641	0.9876
Ni-0.1	3.145	4.503	1.9902	1.9644	0.9870
Ni-0.3	3.142	4.502	1.9882	1.9648	0.9883
Co-0.1	3.146	4.504	1.9910	1.9645	0.9866
Co-0.3	3.141	4.498	1.9876	1.9625	0.9874

*Lattice parameters are obtained from the fit of EXAFS.

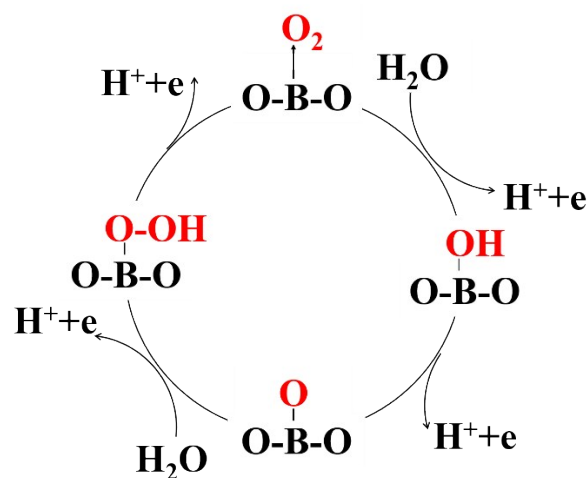


Fig.S6. The possible mechanism of OER process in acid condition.

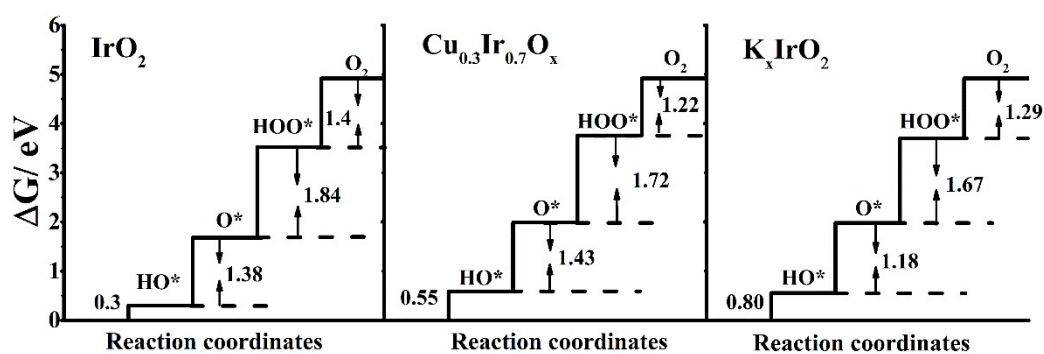


Fig.S7. The calculated free-energy diagrams for the OER of IrO₂, Cu_{0.3}Ir_{0.7}O_x and K_xIrO₂. From the energy variations of each step, it can clearly find that the third step of Ir-OOH* is the RDS for OER.

Table S6. Summary of electrical conductivity of different materials.

Materials	Conductivity (S cm ⁻¹) at room temperature	References
IrO ₂	433~8300	11
K _x IrO ₂	~70	12
Pb ₂ Ir ₂ O _{6.5}	2800-3000	13
Bi ₂ Ir ₂ O ₇	660-700	14
CaIrO ₃	~0.1	15
Ca ₂ IrO ₄	~100	15

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