## **Electronic Supplementary Information (ESI)**

# Competitive adsorption strategy for adsorbed intermediates boosting alkaline hydrogen evolution

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#### 1. Material characterizations

The crystal structures of the samples were identified using powder X-ray diffraction (XRD) (Bruker D8, Cu-Ka). The morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). The energy-dispersive X-ray (EDX) elemental mappings were taken under high-angle angular dark field-scanning TEM (HADDF-STEM) mode. X-ray spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250Xi spectroscope using Al-K $\alpha$  x-rays as the excitation source. The inductively coupled plasma optical-emission spectroscopy (ICP-OES, PerkinElmer) was used to determine the element contents of the samples. Electron paramagnetic resonance (EPR) spectra were performed using a Bruker ESR spectrometer (JES-FA200). Raman spectra of samples were recorded using the confocal Raman spectrometer (LabRAM Aramis) equipped with a 532 nm laser. X-ray absorption near edge structure (XANES) was measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSFR), China. The storage ring of the SSFR was operated at 2.5 GeV with an average current of 200 mA.

In-situ Raman spectroscopy measurements: Raman spectra of samples were recorded using the confocal Raman spectrometer (LabRAM Aramis) equipped with a 532 nm laser. A custom-made electrochemical cell (Gaossunion (China, Tianjin) Photoelectric Technology Co., Ltd.) was used for in-situ experiments, where a fluorine-doped SnO<sub>2</sub> (FTO) substrate coated with the catalyst was used as the working electrode, platinum wire, and an Ag/AgCl electrode as the counter and reference electrodes, respectively. An electrochemical workstation (CHI 760E, Chenhua) was used to apply potentials to the working electrode while Raman spectra were acquired.

In-situ EPR tests: In-situ EPR spectra were measured under controlled electrochemical potentials in a homemade 1 mL reactor Teflon cell with platinum wire and Ag/AgCl electrode as the counter and reference electrodes, respectively. Catalyst loaded on  $1 \times 1$  cm<sup>2</sup> carbon paper was used as the working electrode and 1.0 M KOH saturated with Ar was used as the electrolyte. When reaching the target potential, 20 µL of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) solution was injected into the reactor and 2

the electrolyte in the reactor was extracted for EPR testing after a very short time.

#### 2. Electrochemical measurements

The catalyst ink was prepared by blending the catalyst powder (5 mg) with 50  $\mu$ L of Nafion solution (5 wt%), 450 µL of ethanol and 500 uL of deionized water in an ultrasonic bath. 5 µL of catalyst ink was then pipetted onto the glassy carbon electrode surface. The electrochemical tests were conducted on CHI 760E electrochemical workstation. The Hg/HgO was used as the reference electrode, a graphite rod as the counter electrode, and a glassy carbon electrode as the working electrode. The linear sweep voltammetry (LSV) measurements were taken at a scan rate of 5 mV s<sup>-1</sup> in an Ar-saturated 1 M KOH solution. Potentials were referenced to reversible hydrogen electrode (RHE) using the following equation: E (RHE) = E (Hg/HgO) +  $0.059 \times pH +$ 0.098 V (25 °C). The Tafel slope was obtained from the corresponding LSV curves according to the Tafel equation. The double layer capacitance (C<sub>dl</sub>) was obtained using cyclic voltammetry (CV) scanning from 0.43 to 0.53V (vs. RHE) with different scan rates from 10 to 100 mV s<sup>-1</sup> for HER. The electrochemical impedance spectroscopy (EIS) was conducted at the corresponding potential of 10 mA cm<sup>-2</sup> from LSV curve, with the frequency range of 0.01 Hz to 100 kHz with AC amplitude of 5 mV. The durability was evaluated by comparing LSV curves before and after CV cycling test and chronopotentiometry at the corresponding overpotential of 10 mA cm<sup>-2</sup>. The water splitting test was conducted in the H-type water electrolyzer, using 1 M KOH as the electrolyte and two pools were separated by an anion exchange membrane. The LSV curves were recorded at a scan rate of 5 mV s<sup>-1</sup>. The chronoamperometric measurement was performed at the corresponding potential to deliver a current density of 10 mA cm<sup>-</sup> 2

#### 3. Computational details

We carried out all density functional theory (DFT) calculations in the Vienna ab initio simulation (VASP6.3.0) code. The exchange-correlation is simulated with Perdew-Burke-Ernzerhof (PBE) functional and the ion-electron interactions were described by the projected augmented wave (PAW) method. The Van der Waals (vdWs) interaction <sup>3</sup> was included by using empirical DFT-D3 method. Atoms in the upper two layers of the surface are allowed to move freely while the bottom two layers are fixed to simulate the surface of structure. The Monkhorst-Pack-grid-mesh-based Brillouin zone k-points are set as  $2 \times 2 \times 1$  for RuSe<sub>2</sub> (210) and Mo doped RuSe<sub>2</sub> (210) (molar ratio Mo:Ru=1:3). The convergence criteria are set as  $0.02 \text{ eV } \text{A}^{-1}$  and  $10^{-5} \text{ eV}$  in force and energy, respectively.

The free energy calculation of species adsorption ( $\Delta G$ ) is based on following model:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} + \Delta H_{0 \to T} - T\Delta S + G_{\text{U}}$$
<sup>(1)</sup>

Herein,  $\Delta E$ ,  $\Delta E_{ZPE}$ , and  $\Delta S$  represent the changes of electronic energy, zero-point energy, and entropy, respectively, that are caused by adsorption of intermediate. The  $\Delta H_{0\rightarrow T}$  refers to the change in enthalpy when heating from 0 K to T K. The entropy of H<sup>+</sup> + e<sup>-</sup> pair is approximately regarded as half of H<sub>2</sub> entropy in standard condition.

### 4. Supplementary Figures



**Fig. S1** XRD patterns of c-RuSe<sub>2</sub> at different annealing temperatures and standard data of c-RuSe<sub>2</sub> (PDF #80-0670).



Fig. S2 Raman spectrum of the as-prepared RuSe<sub>2</sub>-500 °C.



Fig. S3 HER polarization curves in 1 M KOH at a scan rate of 5 mV s<sup>-1</sup> for Mo-doped RuSe<sub>2</sub> (different Mo to Ru ratios) and pristine RuSe<sub>2</sub>.



Fig. S4 FE-SEM image of pristine RuSe<sub>2</sub>.



Fig. S5. Survey XPS spectrum of pure RuSe<sub>2</sub>.



Fig. S6 CV curves of (a) Mo-RuSe<sub>2</sub> and (b) RuSe<sub>2</sub> with various scan rates from 10 to 100 mV s<sup>-1</sup> in 1.0 M KOH.



Fig. S7 The LSV curves normalized by the electrochemically active surface area.



Fig. S8 FE-SEM image of Mo-RuSe<sub>2</sub> after chronopotentiometry test of 16 h.



**Fig. S9** (a) HER polarization curve of Mo-RuSe<sub>2</sub> in 1 M KOH at a scan rate of 5 mV s<sup>-1</sup>. (b) Plot of current density versus time with a constant potential of 0.24V versus RHE.



**Fig. S10** Polarization curves (a,c) and Tafel plots (b,d) under a temperature range of 20-40 °C for Mo-RuSe<sub>2</sub> and pure RuSe<sub>2</sub>, respectively.



Fig. S11 The optimal theoretical structures of RuSe<sub>2</sub> (a), H<sub>2</sub>O\* (b) and OH\*+H\* (c) on RuSe<sub>2</sub>.



Fig. S12 (a) XRD pattern and (b) corresponding elemental mapping images of Mo,Se-RuO<sub>2</sub>.

**Synthesis of Mo, Se-RuO<sub>2</sub> sample:** The as-prepared Mo-RuSe<sub>2</sub> amorphous precursor powder was transferred to a quartz tube and annealed in the air atmosphere at 400 °C for 2 h, along with the temperature ramp rate of 5 °C min<sup>-1</sup>, and finally the Mo, Se-RuO<sub>2</sub> sample was obtained.

Sample	Feeding radio of Ru/Mo/Se	Atomic ratio of Ru/Mo/Se
RuSe <sub>2</sub>	1/x/2.1	1/x/2.051
Mo-RuSe <sub>2</sub> -0.12	0.875/0.125/2.1	0.863/0.137/2.043
Mo-RuSe <sub>2</sub> -0.17	0.833/0.167/2.1	0.821/0.179/2.048
Mo-RuSe <sub>2</sub> -0.25	0.75/0.25/2.1	0.729/0.271/2.057
Mo-RuSe <sub>2</sub> -0.33	0.667/0.333/1	0.624/0.375/2.032

Table S1. Feeding radios and atomic ratios of Ru/Mo/Se in different samples.

**Table S2.** The HER activity comparison of Mo-RuSe<sub>2</sub> with some reported TMD- and Ru-based HER catalysts in alkaline media.

Catalyst	Overpotential @10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Ref.
Mo-RuSe <sub>2</sub>	27	39	This work
Ru-ZIF-900	52	78	J. Mater. Chem. A, 2020, 8, 3203
h-RuSe <sub>2</sub>	34	95	Angew. Chem. Int. Ed. 2021, 60, 7013
Au-Ru NWs	50	30.8	Nat. Chem. 2018, 10, 456
Ru-MC	27	25	ChemElectroChem 2022, 9, e202101580.
RuP/CoNiP <sub>4</sub> O <sub>12</sub> /CC	27	10	Applied Catalysis B: Environmental 2023, 328, 122447.
Ru/Co@OG	13	22.8	Angew. Chem. Int. Ed. 2021, 60, 16044.
$Ru_2P/Ir_2P$	23.2	30.7	Adv. Energy Mater. 2024, 14, 2401426
Ir-Ru@C	13	29.6	Applied Catalysis B: Environment and Energy 2024, 358, 124422
$Pt-Ru/RuO_2$	18	18.5	Nat. Commun. 2024, 15, 1447
Ru-MoS <sub>2</sub>	50	62	Adv. Sci. 2019, 6, 1900090
Co-Ru-MoS <sub>2</sub>	52	55	Small 2020, 16, 2000081
Ni <sub>5</sub> P <sub>4</sub> -Ru	54	52	Adv. Mater. 2020, 32, 1906972
M-MoS <sub>2</sub>	210	60.7	ACS Nano 2024, 18, 10312
RhSe <sub>2</sub>	81.6	39	Adv. Mater. 2021, 33, 2007894