Electronic Supplementary Information

Engineering multi-component selenide heterostructures with interfacial electronic interaction for efficient and stable acidic hydrogen evolution reaction electrocatalysis

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1. Experimental section

1.1 Preparation of MXene

MXene was prepared by etching Al atoms in Ti_3AlC_2 as previously reported by Lim et al. First, 1 g of Ti_3AlC_2 was slowly added in HF (30 wt %, 20 mL) solution and stirred continuously at 30 °C for 24 h. The product was washed with distilled water and ethanol several times until the pH of the supernatant was close to neutral. Then, the MXene was dried at 60 °C in Ar atmosphere for 6 h. Afterward, the solid product (MXene) was for further use.

1.2 Preparation of Ru-$MoSe_2$@MXene and Ru-$CoSe_2$@MXene.

For Ru-$MoSe_2$@MXene, First, 1 mmol (79 mg) of Se powder was dispersed in 5 mL N_2H_4•H_2O (80 wt%) and stirred continuously for 1 h (solution A). At the same time, 0.5 mmol (121 mg) Na_2MoO_4•$2H_2O$ and 80 mg of MXene were added to 20 mL DI and stirred, then the obtained mixed solution was ultrasonicated at 30°C for 1 h (solution B). Subsequently, after mixing solution A and solution B, the mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated at 200 °C for 12 h. After naturally cooling to room temperature, the solid product was obtained by centrifuging and washing with distilled water and ethanol several times. Ultimately, the product was dried in a vacuum drying oven for 6 h and then annealed at 600 °C in H_2/Ar (5/95, vol%) atmosphere for 2 h. Then, 30 mg of the synthesized $MoSe_2$/MXene and 0.1 mmol $RuCl_3$•xH_2O were dispersed in 30 mL of a mixed solution (V_{DI}: V_{DMF} = 1:3). Then, the above solution was stirred continuously for 24 h at 30 °C. Afterwards, the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated at 150 °C for 6 h. After it is naturally cooled to room temperature, the mixture is washed with distilled water several times and then dried in a vacuum drying oven at 60 °C for 6 h; The prepared methods of Ru-$CoSe_2$@MXene was similar to that of Ru-$CoSe_2$/$MoSe_2$@MXene except that Ru-$CoSe_2$@MXene does not add molybdenum source.

2. Materials characterizations

The morphology and microstructure of the prepared samples were characterized by field-emission scanning electron microscopy (SEM, S-4800, Hitachi) and X-ray diffraction (XRD, Bruker D8 diffractometer with Cu Kα radiation), transmission electron microscopy (TEM, JEM 2100F, JEOL), X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K-Alpha), Inductively coupled plasma spectrometer (ICP-OES, Agilent 5110), Raman spectrum, (Thermo Fisher, DXR), Electron Paramagnetic Resonance (EPR, Bruker, EMXplus-6/1).

3. Electrochemical measurement

All potentials were treated without iR compensation and converted into a reversible hydrogen electrode (RHE) by the equation: $E_{(vs\ RHE)} = E_{(Ag/AgCl)} + 0.197 + 0.059 \times pH$. The electrolyte is saturated with nitrogen before electrochemical test. Typically, 4 mg of sample was dispersed in a mixture of 325 μL ethanol 125 μL deionized water and 50 μL Nafion solution. Then 5 μL mixture was dripped onto the surface of the glass carbon electrode (GCE) and dried at room temperature. The catalyst loading is 0.6 mg cm^{-2}. Prior to the electrochemical experiment, each catalyst was activated by cyclic voltammetry (CV) until a stable polarization curve was obtained. Linear sweep voltammetry (LSV) polarization curves ranging from 0 to −0.4 V (*vs.* RHE) were obtained at the scan rate of 5 mV s^{-1}. CV cycles were carried out ranging from 0.057 to 0.117 V (*vs.* RHE) at the scan rates of 40, 60, 80, 100, and 120 mV S^{-1}, respectively. The electrochemical impedance spectroscopy (EIS) was carried out at −0.064 V (*vs.* RHE) in the frequency from 100 kHz to 0.1 Hz with an amplitude of 5 mV. The stability test for the HER process was conducted using chronoamperometry at a fixed overpotential of 53 mV (vs. RHE).

4. Supporting Figures

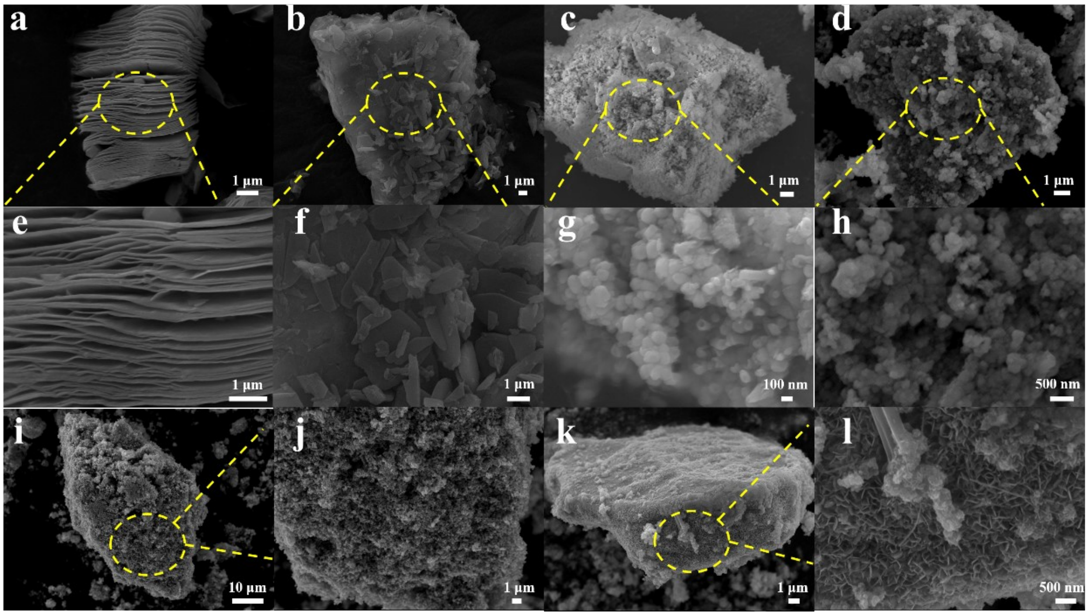

Fig. S1. (a, e) The SEM images of MXene, (b, f) 2D CoMOF@MXene, (c, g) $CoSe_2$@MXene, (d, h) $CoSe_2/MoSe_2$@MXene, (i, j) Ru-$CoSe_2$@MXene, and (k, l) Ru-$MoSe_2$@MXene in lower and higher magnifications.

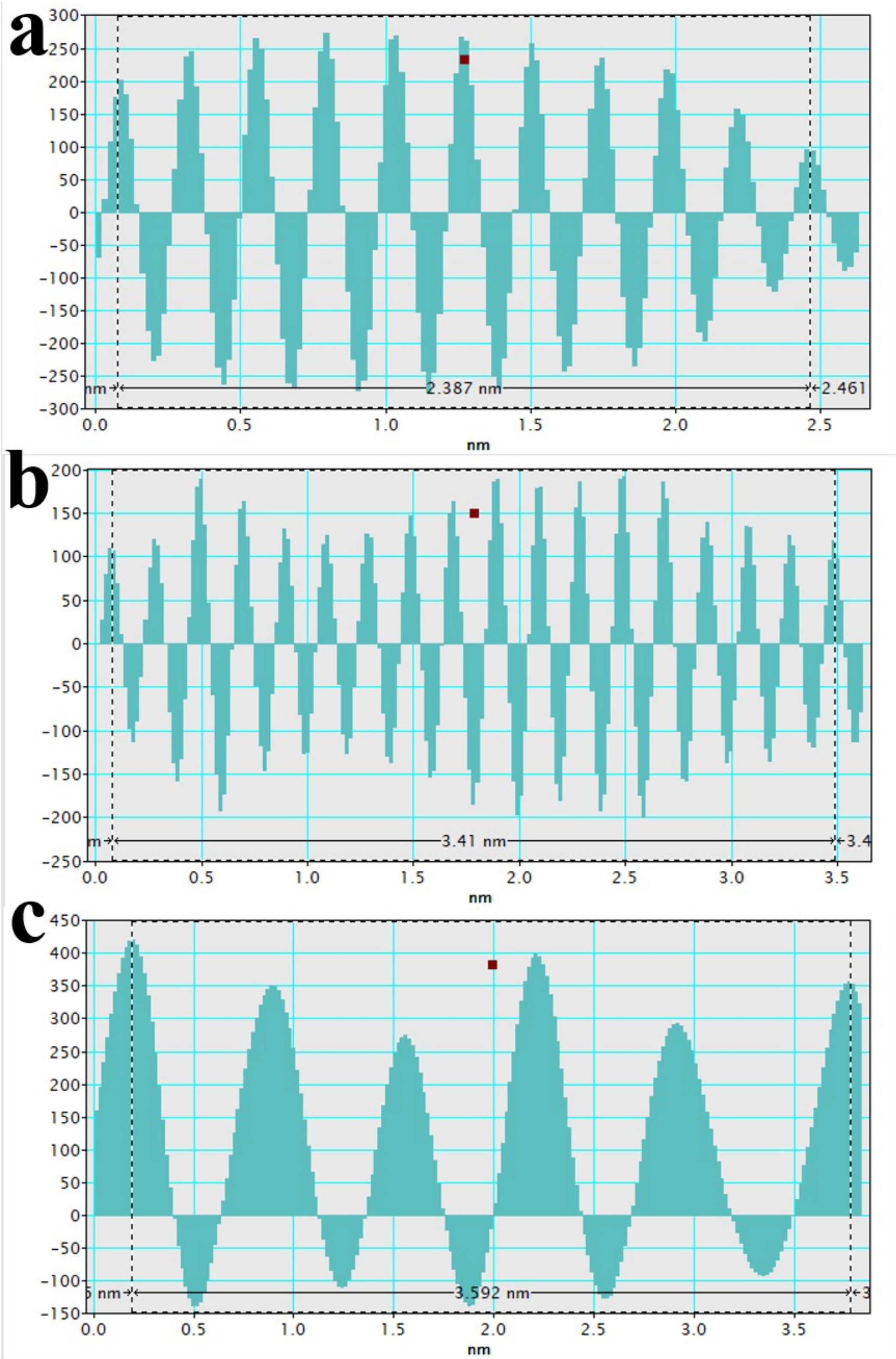

Fig. S2. The corresponding profile images of g 1 (a), g 2 (b) and g 3 (c).

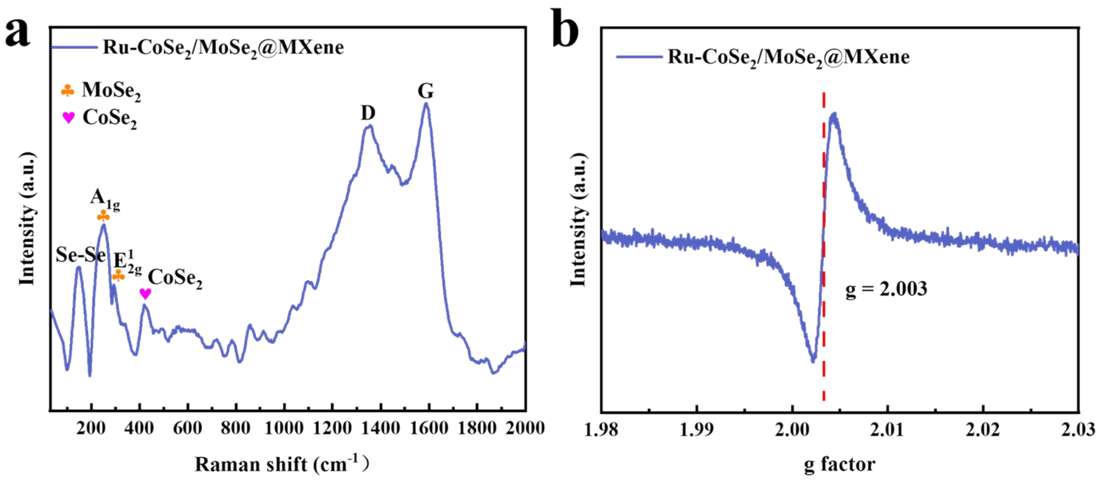

Fig. S3. (a) Raman spectroscopy and (b) EPR signals of Ru-$CoSe_2$/$MoSe_2$@MXene

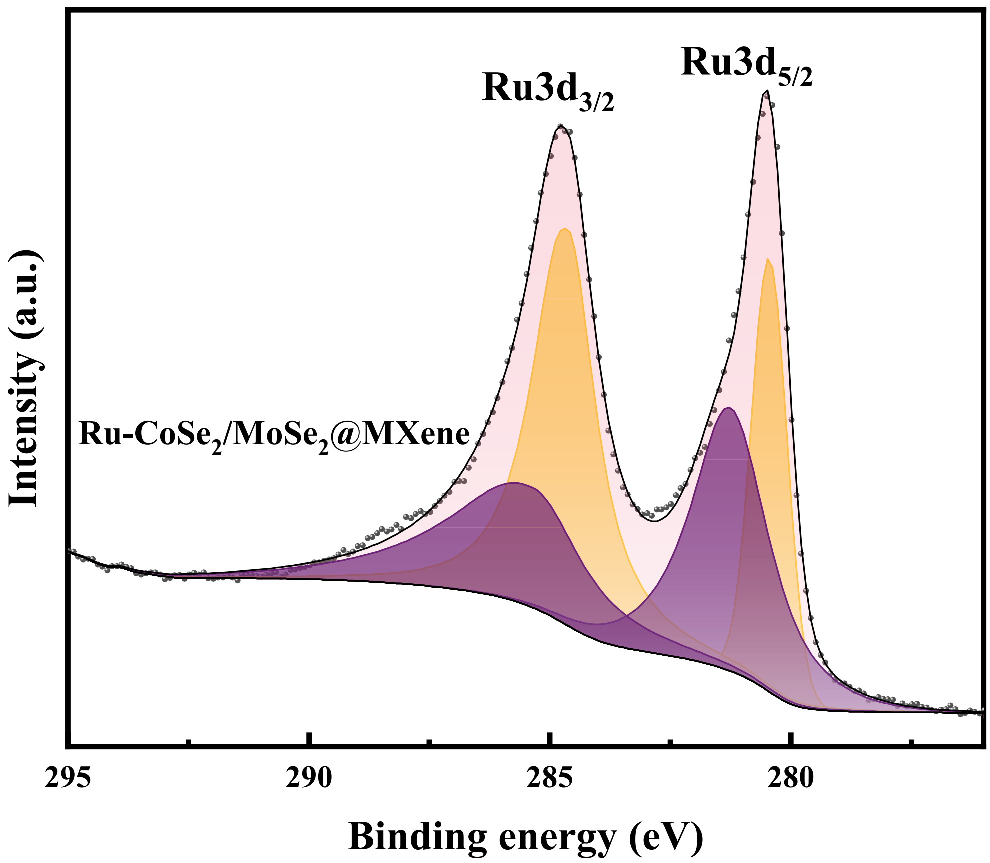

Fig. S4. XPS spectrum of Ru 3d.

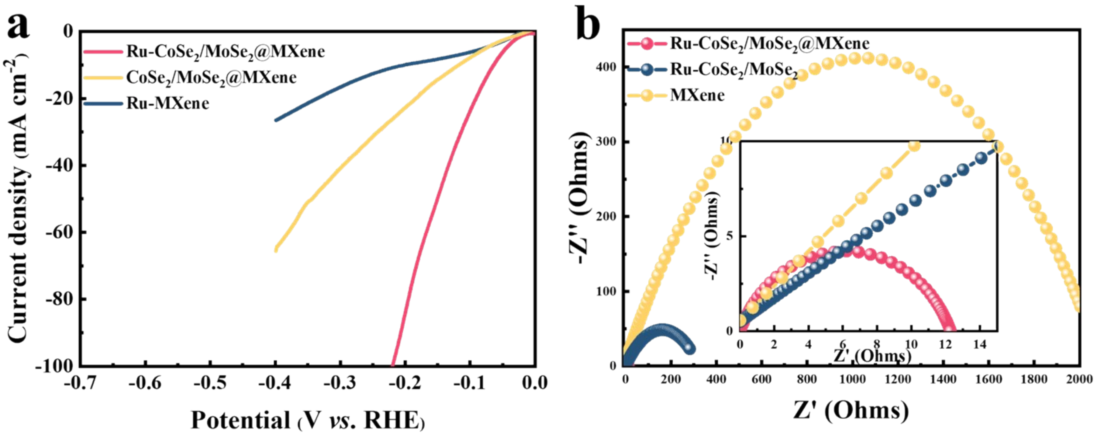

Fig. S5. (a) LSV curves of Ru-$CoSe_2$/$MoSe_2$@MXene, $CoSe_2$/$MoSe_2$@MXene, and Ru-MXene. (b) Nyquist plots of Ru-$CoSe_2$/$MoSe_2$@MXene, Ru-$CoSe_2$/$MoSe_2$, and MXene.

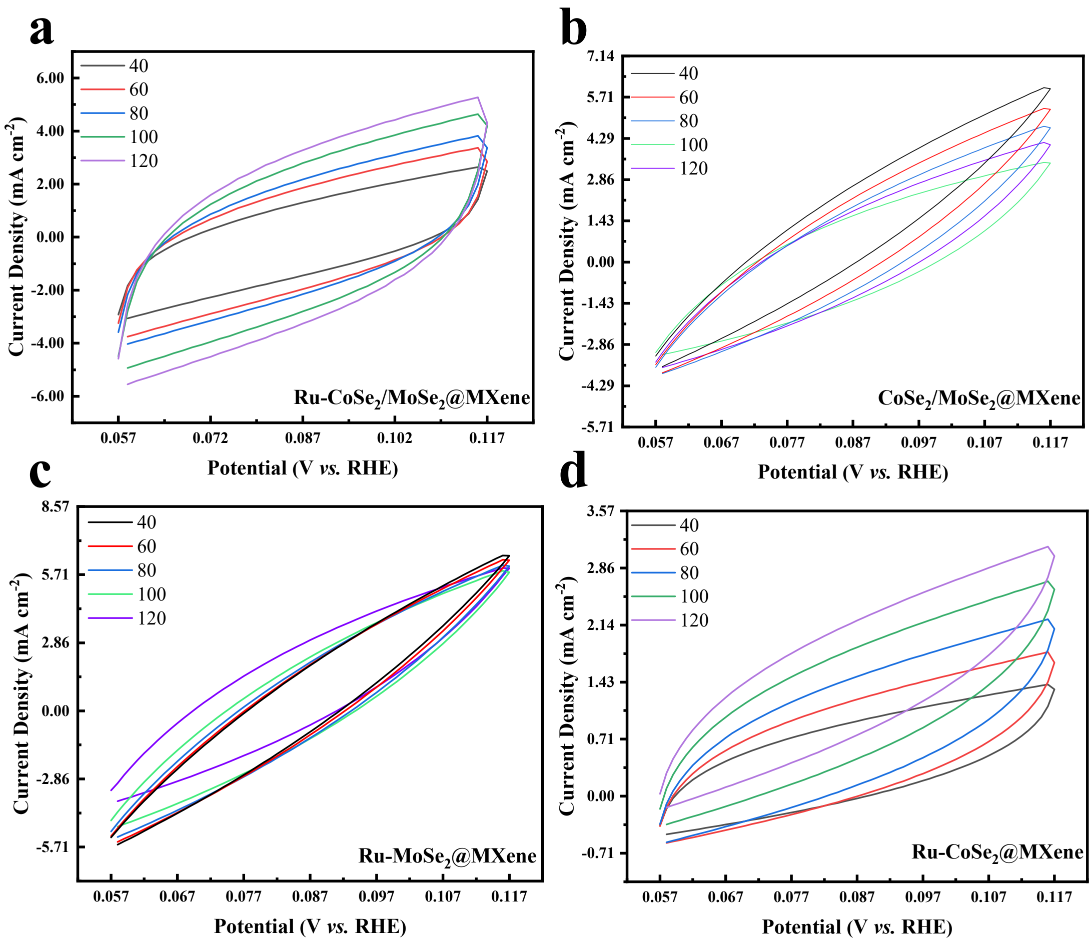

Fig. S6. (a) The CV curves of Ru-CoSe$_2$/MoSe$_2$@MXene, (b) CoSe$_2$/MoSe$_2$@MXene, (c) Ru-MoSe$_2$@MXene and (d) Ru-CoSe$_2$/MoSe$_2$@MXene.

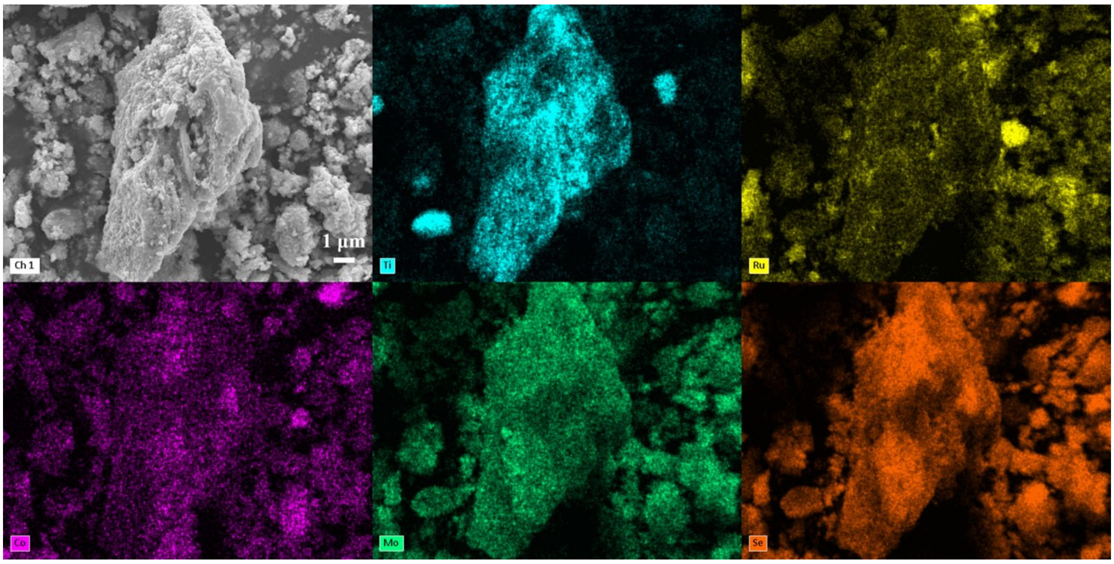

Fig. S7. The SEM image and the corresponding elemental mappings of Ru-$CoSe_2$/$MoSe_2$@MXene

Table S1. ICP-OES analysis of Ru-$CoSe_2$/$MoSe_2$@MXene.

Test number	Samplin g quantity m_0	Constant volume V_0	Test element	Test element solution concentration C_0	Dilution multiple f	Element concentration of original solution C_1	Sample element content C_x	Sample element content W
	g	mL		mg/mL		mg/mL	mg/kg	%
1	0.0529	25.0000	Ru	4.6500	10	46.4997	21975.2679	2.1975
2	0.0529	25.0000	Ru	4.6609	10	46.6088	22026.8382	2.2027
3	0.0529	25.0000	Ru	4.6690	10	46.6897	22065.0854	2.2065
Average								2.2022

Table S2. The HER performance comparison of Ru-$CoSe_2$/$MoSe_2$@MXene with other reported electrocatalyst.

Electrocatalysts	**η_{10} (mV)**	**Tafel (mV dec^{-1})**	**R_{ct} (Ω)**	**References**
Fe-S-MoS_2/CFP	160	80	67	[1]
MoS_{2-x}–NbS_x	159	53	1.4	[2]
$IrNiO_x/WO_3$	18	64.28	5	[3]
$BC_{Mo900-1}$	30	33	35.10	[4]
$NiMoO_4/MoS_2/Ni_3S_2$/NF-1.7	72	32	1.57	[5]
Ru@2H-MoS_2	167	77.5	135	[6]
Ru-NBC	40	40.82	13.6	[7]
1T-$MoSe_2$/TiC-C	106	32	50	[8]
Ni_2P/Ni_5P_4@CC	87	74	11.9	[9]
Rh/MoO_3	49	45	0.106	[10]
WSe_2–CuO	141	80	5.5	[11]
Ru-$CoSe_2$/$MoSe_2$@MXene	64	48.98	12.29	This work

Table S3. ICP-OES analysis of Ru-$CoSe_2$/$MoSe_2$@MXene after i-t test.

Test number	Sampling quantity m_0	Constant volume V_0	Test element	Test element solution concentration C_0	Dilution multiple f	Element concentration of original solution C_1	Sample element content C_x	Sample element content W
	g	mL		mg/mL		mg/mL	mg/kg	%
1	0.0117	25	Ru	1.4032	10	14.0319	29982.7564	2.9983
2	0.0117	25	Ru	1.3890	10	13.8900	29679.4173	2.9679
3	0.0117	25	Ru	1.3733	10	13.7330	29343.9359	2.9344
Average								2.9668

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