## Supporting Information

# Adatom Doping of Transition Metals in ReSe<sub>2</sub> Nanosheets for Enhanced Electrocatalytic Hydrogen Evolution Reaction

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#### I. Experimental Section

*Characterization*. The products were characterized by field-emission transmission electron microscopy (FE TEM, FEI TECNAI G2 200 kV, Jeol JEM 2100F, HVEM). Energy-dispersive X-ray fluorescence spectroscopy (EDX) with elemental maps was measured using a TEM (FEI Talos F200X) operated at 200 kV that equipped with high-brightness Schottky field emission electron source (X-FEG) and Super-X EDS detector system (Bruker Super-X). This EDX has powerful sensitivity and resolution in the low photon energy region. Fast Fourier-transform (FFT) images were generated by the inversion of the TEM images using Digital Micrograph GMS1.4 software (Gatan Inc.). EELS data were acquired using a scanning transmission electron microscope (STEM, JEM-ARM200F, JEOL Ltd) operated at 200 kV with a spherical aberration (Cs) corrector and a Gatan image filter (GIF QuantumER, Gatan Inc.). The electron probe diameter is about 0.25 nm. The energy resolution at the zero-loss peak is typically 0.5 eV. The microscope conditions were optimized for EELS spectrum imaging with a probe size of 1.0 Å.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon Ultima 2) was also used to analyze the composition. High-resolution X-ray diffraction (XRD) patterns were obtained using the 9B and 3D beamlines of the Pohang Light Source (PLS) with monochromatic radiation ( $\lambda = 1.54595$  Å). XRD pattern measurements were also carried out in a Rigaku D/MAX-2500 V/PC using Cu K<sub>a</sub> radiation ( $\lambda = 1.54056$  Å). X-ray photoelectron spectroscopy (XPS) measurements were performed using the 8A1 beam line of the PLS, as well as a laboratory-based spectrometer (Thermo Scientific Theta Probe) using a photon energy of 1486.6 eV (Al K $\alpha$ ). X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Re L<sub>3</sub>-edge and TM K-edge were collected in fluorescence mode using the 10C beam line of the PLS with a ring current of 350 mA at 3.0 GeV. Energy calibration was carried out by simultaneously measuring the reference spectrum

of ReSe<sub>2</sub> and TM foil. Least-squares fits of EXAFS data were performed using the Athena and Artemis software packages, version 0.9.25. Raman spectra were measured with a micro-Raman spectrometer (Horiba ARAMIS IR2), using a diode laser with an excitation wavelength of 532 nm.

*Electrochemical Measurements*. Experiments were carried in a three-electrode cell connected to an electrochemical analyzer (CompactStat, Ivium Technologies). HER electrocatalysis in 0.5 M H<sub>2</sub>SO<sub>4</sub> or 1 M KOH electrolyte was measured using a linear sweeping from 0 to -0.6 V (*vs.* RHE) with a scan rate of 2 mV s<sup>-1</sup>. A saturated calomel electrode (SCE, KCl saturated, Pine Instrument) and Ag/AgCl electrode (saturated with 4 M KCl, Pine Co.) was used as a reference electrode at 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH electrolyte, respectively. A graphite rod (6 mm dia.  $\times$  102 mm long, 99.9995%, Pine Instrument) was used as a counter electrode. The electrolyte was purged with H<sub>2</sub> (ultrahigh grade purity 99.999%) during the measurement.



**Figure E1**. CV curves for the calibration of the potential of reference electrode; SCE electrode at 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH 0) and Ag/AgCl electrode at 1 M KOH (pH 14).

The applied potentials (E) reported in our work were referenced to the reversible hydrogen

electrode (RHE) through standard calibration. We calibrate the potential of the reference electrode vs. standard hydrogen electrode (SHE). Cyclic voltammetry (CV) curves were obtained at a scan rate of 2 mV s<sup>-1</sup>, in the high-purity H<sub>2</sub> saturated electrolyte with a Pt wire as the working electrode, as shown in Figure E1. In 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte (pH 0), the average value of the potential at which the current crossed at zero was -0.278 V. Therefore E (vs. RHE) = E (vs. SCE) + 0.278 V. In 1 M KOH electrolyte (pH 14), the average value of the potential at which the current crossed at zero was -1.007 V. Therefore, E (vs. RHE) = E (vs. Ag/AgCl) + 1.007 V. The overpotential ( $\eta$ ) was defined as E (vs. RHE).

4 mg ReSe<sub>2</sub> sample was mixed with 1 mg carbon black (Vulcan XC-72) dispersed in Nafion (20  $\mu$ L) and isopropyl alcohol (0.98 mL). The catalyst materials (0.39 mg cm<sup>-2</sup>) were deposited on a glassy carbon rotating disk electrode (RDE, area = 0.1641 cm<sup>2</sup>, Pine Instrument),), and a rotation speed of 1600 rpm was used for the linear sweep voltammetry (LSV) measurements. The Pt/C (20 wt.% Pt in Vulcan carbon black, Sigma-Aldrich) tested as reference sample using the same procedure. For chronoamperometric stability test, we fabricated the electrode by depositing the samples (1 mg cm<sup>-2</sup>) on 1 × 1 cm<sup>2</sup> area of hydrophilic/water proof carbon cloth (WIZMAC Co., thickness = 0.35 mm, through-plane resistance = 1 mΩ) that was cut with a size of 1 × 3 cm<sup>2</sup>.

Electrochemical impedance spectroscopy (EIS) measurements were carried out for the electrode in an electrolyte by applying an AC voltage of 10 mV in the frequency range of 100 kHz to 0.1 Hz at a bias voltage of -0.15 V (*vs.* RHE). To measure double-layer capacitance *via* CV, a potential range in which no apparent Faradaic processes occur was determined from static CV. This range is 0.1–0.2 V. All measured current in this non-Faradaic potential region is assumed to be due to double-layer capacitance. The charging current,  $i_c$ , is then measured from CVs at multiple scan rates. The working electrode was held at each potential vertex for

10 s before beginning the next sweep. The charging current density ( $i_c$ ) is equal to the product of the scan rate (v) and the electrochemical double-layer capacitance ( $C_{dl}$ ), as given by equation  $i_c = v C_{dl}$ . The difference ( $\Delta J_{0.15}$ ) between the anodic charging and cathodic discharging currents measured at 0.15 V (*vs.* RHE) was used for  $i_c$ . Thus, a plot of  $\Delta J_{0.15}$  as a function of v yields a straight line with a slope equal to 2 × C<sub>dl</sub>. The scan rates were 20–100 mV s<sup>-1</sup>.

*TOF Calculation*. The active site density and per-site turnover frequency (TOF) have been estimated as follows. It should be emphasized that since the nature of the active sites of the catalyst is not clearly understood yet and the real surface area for the nanostructured heterogeneous catalyst is hard to accurately determine, the following result is really just an estimation.



**Figure E2**. CV curves of ReSe<sub>2</sub> samples measured at a scan rate of 50 mV s<sup>-1</sup>, in 0.1 M phosphate buffer solution (pH: 7, Range =  $-0.2 \sim 0.6$  V vs. RHE).

The active sites are determined by calculating the charge (Q) from the CV curves (Figure E2), which was obtained in 0.1 M phosphate buffer solution (pH: 7, Range =  $-0.2 \sim 0.6$  V vs. RHE). While it is difficult to assign the observed peaks to a given redox couple, the integrated

charge over the whole potential range should be proportional to the total number of active sites.

The formula employed to find the number of electrochemically active sites (m) is given by

$$m=rac{Q}{2e}$$
,

where Q is the charge in Coulomb and the factor  $\frac{1}{2}$  is number of electrons taking part in oxidation/reduction process.<sup>S1,S2</sup>

The TOF can be caculated from the total number of hydrogen gas (H<sub>2</sub>) molecules ( $n_{\text{H2}}$ ) turns overs at a required potential as follows.

TOF =  $n_{\text{H2}}/m = J (\text{mA cm}^{-2}) \times 3.12 \times 10^{15} (\text{H}_2 \text{ s}^{-1} \text{ per mA cm}^{-2}) \times \text{electrode area} (= 0.1641 \text{ cm}^2)/m$ , where  $n_{\text{H2}}$  was calculated from the current density (*J*) according to  $n_{\text{H2}} = J (\text{mA cm}^{-2})/1000 \text{ mA} \times 1 (\text{C s}^{-1}) \times 1 \text{ mol e}^{-}/96486 \text{ C} \times 1 \text{ mol H}_2/2 \text{ mol e}^{-} \times 6.022 \times 10^{23} \text{ H}_2 \text{ molecules}/1 \text{ mol H}_2 \times \text{electrode area} = J (\text{mA cm}^{-2}) \times 3.12 \times 10^{15} (\text{H}_2 \text{ s}^{-1}) \times \text{electrode area} (= 0.1641 \text{ cm}^2).$ 

We summarized the results in Table E.

**Table E**. TOF of samples at  $\eta = 0.125$  V, calculated using the density of surface active (*m*).

			pH 0			pH 14			
Samples	<i>Q</i> (mC)	т	$\frac{J}{(\text{mA cm}^{-2})}$	<i>n</i> <sub>H2</sub>	TOF	$\frac{J}{(\text{mA cm}^{-2})}$	<i>n</i> <sub>H2</sub>	TOF	
ReSe <sub>2</sub>	1.895	$5.91 \times 10^{15}$	5.4	$2.76 \times 10^{15}$	0.47	1.4	$7.17 \times 10^{14}$	0.12	
Mn-ReSe <sub>2</sub>	1.971	$6.15 \times 10^{15}$	7.7	$3.94 \times 10^{15}$	0.65	3.0	$1.54 \times 10^{15}$	0.25	
Fe-ReSe <sub>2</sub>	2.607	$8.13 \times 10^{15}$	13.9	$7.12 \times 10^{15}$	0.88	2.3	$1.18 \times 10^{15}$	0.15	
Co-ReSe <sub>2</sub>	2.914	$9.09 \times 10^{15}$	20.2	$1.03 \times 10^{16}$	1.13	7.6	$3.89 \times 10^{15}$	0.42	
Ni-ReSe <sub>2</sub>	2.833	$8.84 \times 10^{15}$	41.0	$2.10 \times 10^{16}$	2.53	14.6	$7.48 \times 10^{15}$	0.91	
Cu-ReSe <sub>2</sub>	2.446	$7.63 \times 10^{15}$	9.4	$4.81 \times 10^{15}$	0.63	4.0	$2.05 \times 10^{15}$	0.27	

*Computational details.* Density functional theory (DFT) calculations were performed with Vienna *Ab initio* Simulation Package (VASP).<sup>S3</sup> The Perdew-Burke-Ernzehof (PBE) exchange correlation functional based on generalized gradient approximation (GGA) was implemented.<sup>S4</sup> We use Hubbard *U* corrections<sup>S5</sup> for 3d orbitals of doped TMs, where *U* values are employed from Ref. S6. The cutoff energy for the plane-wave basis set was chosen 500 eV

and a  $5 \times 5 \times 1$  Monkhorst-Pack *k*-point mesh was used for  $2 \times 2$  ReSe<sub>2</sub> supercell. All structures were relaxed until the force acting on each atom was less than 0.03 eV/Å. The spin-polarized calculations were done for the whole work. To avoid interaction between layers due to periodic boundary conditions, a vacuum with 15 Å thickness was applied.

For the thermodynamic analysis of HER catalytic activity, the computational hydrogen electrode model (CHE) model was used.<sup>S7</sup> In CHE model, it is assumed that the chemical potential of hydrogen-electron pair is equal to the half of the chemical potential of hydrogen (H<sub>2</sub>) molecule ( $\mu$ (H<sup>+</sup>) +  $\mu$ (e<sup>-</sup>) = 1/2  $\mu$ (H<sub>2</sub>)) at RHE condition. The H adsorption energy ( $\Delta$ E<sub>H</sub>) was calculated using the following equation:

$$\Delta E_{\rm H} = E({\rm H}^*) - E(^*) - 1/2 \ E({\rm H}_2)$$

where  $E(H^*)$  and  $E(^*)$  are total energies with and without H atom adsorbed on the surface (\*), respectively, and  $E(H_2)$  is the total energy of the H<sub>2</sub> molecule. The H adsorption free energy was obtained by corrections of zero-point energy and entropy term to the H adsorption energy.

$$\Delta G_{\rm H} = \Delta E_{\rm H} + \Delta E_{\rm ZPE} - T\Delta S$$

 $\Delta E_{ZPE}$  is the difference between zero-point energies, and T is defined as 300 K in this study.  $\Delta S$  is the entropy change due to adsorption of the H atom. The calculations of H adsorption were done for all neighboring 6 Se atom sites and TM atom sites, and the most stable ones were chosen.

The HER at alkaline condition was conducted following previous studies.<sup>S8-S10</sup> This involves following key steps:

(1) \* + H<sub>2</sub>O +  $e^- \rightarrow H^* + OH^-$  (Volmer step) (2) H\* + H\*  $\rightarrow$  H<sub>2</sub>( $\uparrow$ ) (Tafel step) or H\* + H<sub>2</sub>O +  $e^- \rightarrow$  \* + OH<sup>-</sup> + H<sub>2</sub>( $\uparrow$ ) (Heyrovsky step) Dividing the first step with including the co-adsorbed OH\* and H\* intermediate:

$$(1-1) * H_2O + e^- \rightarrow H-OH^* + e^-$$

$$(1-2) \operatorname{H-OH}^* + e^- \to \operatorname{H}^* + \operatorname{OH}^-$$

The calculation of H-OH\* was done with both H and OH adsorbed on the surface, and the most stable structure was chosen for the Gibbs free energy change analysis. Assuming the ionization equilibrium of H<sub>2</sub>O in the solution (H<sub>2</sub>O  $\leftrightarrow$  H<sup>+</sup>+ OH<sup>-</sup>), the Gibbs free energy of OH<sup>-</sup> is obtained by  $\mu$ (OH<sup>-</sup>) =  $\mu$ (H<sub>2</sub>O) -  $\mu$ (H<sup>+</sup>), and still, the assumption of the CHE model ( $\mu$ (H<sup>+</sup>) +  $\mu$ (e<sup>-</sup>) = 1/2  $\mu$ (H<sub>2</sub>)) is taken into account.

The Gibbs free energy change calculation is done by following equations:

For the (1-1) step,  $\Delta G_{H-OH^*} = \mu(H-OH^*) - \mu(*) - \mu(H_2O)$ 

For the (1-2) step,  $\Delta G_{H^*} = \mu(H_2O) - 1/2 \ \mu(H_2) + \mu(H^*) - \mu(H-OH^*)$ 

#### **II. Supplementary Tables**

	[TM]/[Re]						
Sample	XPS	EDX	ICP-AES	Avg.			
ReSe <sub>2</sub>	0	0	0	0			
Mn-ReSe <sub>2</sub>	0.052	0.061	0.040	0.051			
Fe-ReSe <sub>2</sub>	0.053	0.054	0.041	0.049			
Co-ReSe <sub>2</sub>	0.054	0.054	0.039	0.049			
Ni-ReSe <sub>2</sub>	0.057	0.046	0.041	0.048			
Cu-ReSe <sub>2</sub>	0.045	0.045	0.041	0.044			

**Table S1**. Composition determined using XPS, EDX, and Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis data of TM-ReSe<sub>2</sub> samples.

	[Se]/[Re]			[Se]/([Re]+[TM])		
Sample	XPS	EDX	Avg.	XPS	EDX	Avg.
ReSe <sub>2</sub>	1.82	1.81	1.82	1.82	1.81	1.82
Mn-ReSe <sub>2</sub>	1.96	1.85	1.91	1.86	1.74	1.80
Fe-ReSe <sub>2</sub>	1.98	1.84	1.91	1.88	1.75	1.82
Co-ReSe <sub>2</sub>	1.98	1.89	1.94	1.87	1.79	1.83
Ni-ReSe <sub>2</sub>	1.96	1.87	1.92	1.85	1.79	1.82
Cu-ReSe <sub>2</sub>	1.92	1.85	1.89	1.83	1.76	1.80

Table S2. Fitting parameters of EXAFS data (Figure 3) for the TM-ReSe<sub>2</sub> samples.

Sample (Re K edge)	Scattering Path	R (Å) <sup>a</sup>	$\mathrm{CN}^{\mathrm{b}}$	$\Delta E (eV)^{c}$	$\sigma^2(\text{\AA}^2)^d$
DeCe	Re-Se	2.50	6.0	4.54	0.0059
Kese <sub>2</sub>	Re-Re	ingR (Å) <sup>a</sup> CN <sup>b</sup> ΔE2.506.042.852.072.506.2 ± 0.642.841.8 ± 0.942.506.1 ± 0.542.506.1 ± 0.542.506.0 ± 0.552.506.0 ± 0.552.506.2 ± 0.652.506.2 ± 0.652.506.2 ± 0.542.506.2 ± 0.542.506.2 ± 0.542.852.2 ± 1.362.852.2 ± 1.362.852.2 ± 1.36	7.23	0.0028	
Mn DoSoo	Re-Se	2.50	$6.2\pm0.6$	4.92	0.0061
WIII-KeSe <sub>2</sub>	Re-Re	2.84	$1.8\pm0.9$	4.49	0.0048
Fo DoSo	Re-Se	2.50	$6.1\pm0.5$	4.77	0.0060
re-Rese <sub>2</sub>	Re-Re	ng         R (Å) <sup>a</sup> CN <sup>b</sup> 2.50         6.0           2.85         2.0           2.50 $6.2 \pm 0.6$ 2.84 $1.8 \pm 0.9$ 2.50 $6.1 \pm 0.5$ 2.85 $1.7 \pm 0.7$ 2.50 $6.0 \pm 0.5$ 2.85 $2.2 \pm 1.1$ 2.50 $6.2 \pm 0.6$ 2.84 $2.1 \pm 0.8$ 2.50 $6.2 \pm 0.6$ 2.84 $2.1 \pm 0.8$ 2.50 $6.2 \pm 0.5$ 2.85 $2.2 \pm 1.3$	-6.09	0.0042	
Co PoSo	Re-Se	2.50	$6.0\pm0.5$	5.05	0.0060
Co-Rese <sub>2</sub>	Re-Re	2.85	CN° $\Delta E (eV)^c$ 6.0         4.54           2.0         7.23           6.2 ± 0.6         4.92           1.8 ± 0.9         4.49           6.1 ± 0.5         4.77           1.7 ± 0.7         -6.09           6.0 ± 0.5         5.05           2.2 ± 1.1         7.48           6.2 ± 0.6         5.53           2.1 ± 0.8         4.94           6.2 ± 0.5         4.68           2.2 ± 1.3         6.51           CN <sup>b</sup> $\Delta E (eV)^c$	7.48	0.0034
N. DoSo	Re-Se	2.50	$6.2\pm0.6$	5.53	0.0063
MI-KeSe <sub>2</sub>	Re-Re	2.84	$2.1\pm0.8$	4.94	0.0046
Cu DoSo	Re-Se	2.50	$6.2\pm0.5$	4.68	0.0061
Cu-Rese <sub>2</sub>	Re-Re	2.85	$2.2 \pm 1.3$	6.51	0.0039
Sample (metal K edge)	Scattering Path	R (Å) <sup>a</sup>	$\mathrm{CN}^b$	$\Delta E (\mathrm{eV})^c$	$\sigma^2(\text{\AA}^2)^d$

Co-ReSe <sub>2</sub>	Co-Se	2.38	$4.5 \pm 1.1$	1.51	0.0064
Ni-ReSe <sub>2</sub>	Ni-Se	2.42	$4.2\pm1.3$	1.60	0.0046
Cu DeSer	Cu-Se	2.37	$4.1\pm0.6$	-5.24	0.0064
Cu-KeSe <sub>2</sub>	Cu-O	1.96	$2.5\pm0.3$	5.95	0.0013

<sup>*a*</sup> Distance between scattering atoms. <sup>*b*</sup> Coordination number.

<sup>c</sup> Edge energy shift, representing between the energy grids of experimental and theoretical data.

<sup>*d*</sup> Debye-Waller factor, which measure the static and thermal disorder, is larger for the TM-ReSe<sub>2</sub> samples than ReSe<sub>2</sub>.

Ref. No.	Ref. in Text	Materials	$\eta_{J=10} (mV)$	Tafel slope (mV dec <sup>-1</sup> )	TOF ( $H_2 s^{-1}$ )
S11	22	ReSSe nanodots	84	50.1	
S12	26	Re0.55Mo0.45S2 monolayer	90	56	3.48@300 mV
S13	41	Ni doped MoS <sub>2</sub> @carbon nanofiber	161	81	
S14	42	Co doped MoS <sub>2</sub> /graphene	143	71	1.09@200 mV
S15	43	1% Pd doped MoS <sub>2</sub>	89	62	
S16	44	Mn doped MoSe <sub>2</sub>	167	60	
This work		Ni doped ReSe <sub>2</sub>	82	54	2.53@125 mV

Table S3. Comparison of HER performance (in pH 0) of the previous works in the literatures.

Ref. No.	Ref. in Text	Materials	$\eta_{J=10} (mV)$	Tafel slope (mV dec <sup>-1</sup> )	TOF $(H_2 s^{-1})$
S10	37	Ni doped MoS <sub>2</sub>	98	60	0.32@150mV
S17	40	Co doped MoS <sub>2</sub>	90	50.28	
S18	45	V doped MoS <sub>2</sub>	206	59	
S19	31	ReS <sub>2</sub> /SWCNTs	182		
S20	46	Ni doped WSe <sub>2</sub>	215	109	
This work		Ni doped ReSe <sub>2</sub>	109	81	0.91@125 mV

**Table S5**. Impedance parameters for the equivalent circuit that was shown in Figure S9.

Samples		pH 0			pH 14	
Samples	$R_{s}(\Omega)$	CPE (mF)	$R_{ct}(\Omega)$	$R_{s}(\Omega)$	CPE (mF)	$R_{ct}(\Omega)$
ReSe <sub>2</sub>	5.49	1.24	93.1	5.37	3.52	438

Mn-ReSe <sub>2</sub>	5.71	1.88	63.5	5.41	5.61	176
Fe-ReSe <sub>2</sub>	5.30	3.79	39.5	5.71	1.76	228
Co-ReSe <sub>2</sub>	5.52	5.06	26.7	5.00	5.61	87.0
Ni-ReSe <sub>2</sub>	5.35	9.52	14.6	5.36	8.06	31.4
Cu-ReSe <sub>2</sub>	5.37	2.69	51.0	5.98	7.74	106

#### **III.** Supporting Figures



Figure S1. XRD pattern of TM-ReSe<sub>2</sub> (TM = none, Mn, Fe, Co, Ni, and Cu).

Since the XRD peaks are matched to the reference, all samples are in the 1T'' phase ReSe<sub>2</sub> (JCPDS No. 74-0611; primitive triclinic, a = 6.716 Å, b = 6.602 Å, c = 6.728 Å,  $\alpha = 104.90^{\circ}$ ,  $\beta = 91.820^{\circ}$ ,  $\gamma = 118.94^{\circ}$ ).



**Figure S2**. Raman spectrum of ReSe<sub>2</sub>, Mn-ReSe<sub>2</sub>, Fe-ReSe<sub>2</sub>, Co-ReSe<sub>2</sub>, Ni-ReSe<sub>2</sub>, and Cu-ReSe<sub>2</sub>. The excitation source is 532 nm diode laser.

All samples exhibit the same Raman peaks, corresponding to those of in 1T" phase ReSe<sub>2</sub>. Many peaks arise from the complexity of lattice vibrations in the 1T" phase ReSe<sub>2</sub>, consistently with the previous works.<sup>S21-S24</sup> The peak at 125 cm<sup>-1</sup> is assigned to  $E_g$ -like vibrational mode (in-plane vibration), and the peak at 160 and 174 cm<sup>-1</sup> to  $A_g$ -like vibrational modes (out-of-plane vibration).



**Figure S3.** (a) HRTEM images of TM-ReSe<sub>2</sub> and the histogram showing the thickness distribution of TM-ReSe<sub>2</sub> nanosheets (inset). The average value of thickness is 2.4 nm, corresponding to 3 layers. (b) Atomic force microscopy images show the aggregated sphere of nanosheets, although the samples were sonicated in isopropyl alcohol for 2 h, in order to exfoliate into the nanosheets. A histogram (inset) shows the size distribution of TM-ReSe<sub>2</sub> nanosheets, based on the height profiles. The average size of sphere is 130 nm, which is consistent with the value (150 nm) measured by TEM analysis.



**Figure S4**. (a) TEM images, (b) HAADF-STEM images and EDX elemental mapping, and corresponding EDX spectrum, and (c) SEM EDX spectrum of samples. They all consisted of the flower-like nanosheets. The Re, TM, and Se elements distributed homogeneously in entire sample. The dopants doped with a concentration of 5%. The inset in (a) ReSe<sub>2</sub> shows the histogram for size distribution of flower-like nanoparticles with an average value of 150 nm.







**Figure S5.** Atomically resolved HAADF-STEM images for the basal plane and the corresponding contour plot with intensity profile along the dotted line; (a) Mn-ReSe<sub>2</sub>, (b) Fe-ReSe<sub>2</sub>, (c) Co-ReSe<sub>2</sub>, (d) Ni-ReSe<sub>2</sub>, and (e) Cu-ReSe<sub>2</sub>. The weaker (marked by red circles) and stronger intensities (marked by yellow circles) at the Re sites are due to the substitution and the adatoms of TM, respectively. In the case of Cu-ReSe<sub>2</sub>, the Cu clusters are marked by the yellow triangles. (f) Histogram showing the fraction of adatom that estimated the HAADF-STEM images. We counted at least 100 TM atoms at the substitutional and adatom sites, and round the value; 25%, 40%, 75%, 90%, and 100% for Mn, Fe, Co, Ni, and Cu, respectively.



**Figure S6**. XPS 2*p* peak of samples and the references: (a) Fe-ReSe<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>; (b) Co-ReSe<sub>2</sub>, CoO, Co<sub>3</sub>O<sub>4</sub>; (c) Ni-ReSe<sub>2</sub> and NiO; (d) Cu-ReSe<sub>2</sub>, Cu<sub>2</sub>O, and CuO.

The  $2p_{3/2}$  and  $2p_{1/2}$  peaks of samples are resolved into two or three bands; M1(red), M2 (green), and M3 (blue). The M1 band is assigned to the TM-Se bond. The M1 band appeared at the same position of their neutral state (M<sup>0</sup>), 639.0 eV for Mn, 707. 0 eV for Fe, 778.3 eV for Co, 852.7 eV for Ni, and 932.7 eV for Cu. The M2 band is assigned to the TM-O bonds exposed as dangling bonds, and the M3 band to their satellite peaks. The M1 peak of Fe-, Co-, and Ni-ReSe<sub>2</sub> was not observed from the oxide reference samples. In contrast, the Cu-ReSe<sub>2</sub> shows the similar peak feature as that of Cu<sub>2</sub>O, suggesting that the Cu clusters in the ReSe<sub>2</sub> are oxidized to form the oxide like Cu<sub>2</sub>O.





**Figure S7**. XRD pattern of 20% TM doped ReSe<sub>2</sub> (TM = Mn, Fe, Co, Ni, and Cu), HAADF-STEM image and EDX elemental mapping/spectrum.

All samples are in the 1T" phase ReSe<sub>2</sub> (JCPDS No. 74-0611; primitive triclinic, a = 6.716 Å,

b = 6.602 Å, c = 6.728 Å,  $\alpha = 104.90^{\circ}$ ,  $\beta = 91.820^{\circ}$ ,  $\gamma = 118.94^{\circ}$ ). The reference peaks of orthorhombic phase FeSe<sub>2</sub> (JCPDS No. 21-0432; Pnnm [58], a = 4.800 Å, b = 5.776 Å, c = 3.585 Å), orthorhombic phase CoSe<sub>2</sub> (JCPDS No. 10-0408; Pmnn [58], a = 3.60 Å, b = 4.84 Å, c = 5.72 Å), orthorhombic phase NiSe<sub>2</sub> (JCPDS No. 18-0886; Pnnm [58], a = 4.89 Å, b = 5.96 Å, c = 3.67 Å), and primitive cubic phase Cu<sub>7</sub>Se<sub>4</sub> (JCPDS No. 26-0557; P. a = 11.41 Å) are plotted. The Mn-ReSe<sub>2</sub> shows only ReSe<sub>2</sub> peaks, indicating that Mn fully substituted into the ReSe<sub>2</sub>. However, the Fe-, Co-, Ni-, and Cu-ReSe<sub>2</sub> shows the additional peaks matched to those of TM selenide, indicating the TMs precipitated to produce FeSe<sub>2</sub>, CoSe<sub>2</sub>, NiSe<sub>2</sub>, and Cu<sub>7</sub>Se<sub>4</sub>, respectively.

The nanosheet morphology remains the same for the higher doping concentration. The EDX mapping and spectrum of Mn-ReSe<sub>2</sub> show that the Re, Mn, and Se atoms distribute homogeneously over the entire samples with 20% Mn concentration. For Fe-ReSe<sub>2</sub>, the distribution of Re and Fe atoms is homogeneous in the region of (i), but inhomogeneous in the region of (ii), which consisted of the Fe rich region. In the case of Co-ReSe<sub>2</sub> and Ni-ReSe<sub>2</sub>, the higher concentration (20%) of TM exists separately from the 5%-doped ReSe<sub>2</sub>.



Figure S8. (a) XRD patterns of Ni-ReSe<sub>2</sub> shows that the 1T" phase ReSe<sub>2</sub> (JCPDS No. 74-0611; primitive triclinic, a = 6.716 Å, b = 6.602 Å, c = 6.728 Å,  $\alpha = 104.90^{\circ}$ ,  $\beta = 91.820^{\circ}$ ,  $\gamma =$ 118.94°) maintains after 12 h CA test of HER in 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH 0) and 1 M KOH (pH 14). (b) Raman spectrum of Ni-ReSe<sub>2</sub> before/after HER. The excitation source is 532 nm diode laser. All samples exhibit the same Raman peaks, corresponding to those of in 1T" phase ReSe<sub>2</sub>. The peak at 125  $\text{cm}^{-1}$  is assigned to E<sub>g</sub>-like vibrational mode (in-plane vibration), and the peak at 160 and 174 cm<sup>-1</sup> peaks to Ag-like modes (out-of-plane vibration). (c) HAADF-STEM image and EDX elemental mapping/spectrum of Ni-ReSe2. The nanosheet morphology remains the same after HER. The EDX mapping and spectrum show that the Re, Ni, and Se atoms distribute homogeneously over the entire samples with 5% Ni doping concentration, which remains the same as that of before. (d) XPS data of Ni-ReSe<sub>2</sub> before/after CA test. Before the test, the Re  $4f_{7/2}$  and  $4f_{5/2}$  peaks show only Re-Se bonding structure peak (Re1). After the test, each peak was resolved into two bands (Re1 and Re2) using a Voigt function. The  $4f_{7/2}$  peak consists of two bands at 41.6 (R1 band) and 42.1 (R2 band), which are assigned to the Re-Se and defects, respectively. The R2 band is newly formed probably due to the deposition of electrolyte. The feature of Se 3d and Ni 2p peaks remains the same after HER. All data shows the same electronic structures after HER.



**Figure S9**. (a) Chronoamperometric (CA) responses of ReSe<sub>2</sub> at  $\eta_{J=10}$  for 12 h in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH. The degradation in pH 0 and pH 14 is 4% and 21% respectively, indicating that the stability is lower than that of Ni-ReSe<sub>2</sub>. (b) XRD patterns of ReSe<sub>2</sub> shows that the 1T" phase ReSe<sub>2</sub> (JCPDS No. 74-0611; primitive triclinic, *a* = 6.716 Å, *b* = 6.602 Å, *c* = 6.728 Å,  $\alpha = 104.90^{\circ}$ ,  $\beta = 91.820^{\circ}$ ,  $\gamma = 118.94^{\circ}$ ) maintains after 12 h CA test of HER in 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH 0) and 1 M KOH (pH 14). (c) Raman spectrum of ReSe<sub>2</sub> before/after CA lest. The excitation source is 532 nm diode laser. All samples exhibit the same Raman peaks, corresponding to those of in 1T" phase ReSe<sub>2</sub>. The peak at 125 cm<sup>-1</sup> is assigned to E<sub>g</sub>-like vibrational mode (in-plane vibration), and the peak at 160 and 174 cm<sup>-1</sup> peaks to A<sub>g</sub>-like modes (out-of-plane vibration). (d) SEM and EDX spectrum of samples. They all consisted of the flower-like nanosheets. The Re and Se elements distributed homogeneously in entire sample. (e) XPS data of ReSe<sub>2</sub> before/after HER, which is similar except the Re2 peak formation (after HER) due to deposition of electrolyte. All data shows the same electronic structures after HER.



Figure S10. HER LSV curves of the samples with or without 10 mM KSCN in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Thiocyanate ion (SCN<sup>-</sup>) was used to block the TM active sites, since SCN<sup>-</sup> is known to poison the metal sites.<sup>S25</sup> The addition of 10 mM SCN<sup>-</sup> resulted in an increase of onset overpotential of TM-ReSe<sub>2</sub>, close to that of undoped ReSe<sub>2</sub>. Therefore, the enhanced HER activity of the TM-ReSe<sub>2</sub> catalyst is attributed to the TM adatom.



**Figure S11**. Nyquist plots for EIS measurements of ReSe<sub>2</sub>, Mn-ReSe<sub>2</sub>, Fe-ReSe<sub>2</sub>, Co-ReSe<sub>2</sub>, Ni-ReSe<sub>2</sub>, and Cu-ReSe<sub>2</sub>, using the frequency in the range from 100 kHz to 0.1 Hz at a representative potential of -0.10 V (at pH 0) and -0.15 V (*vs.* RHE) at pH 14. The modified Randles circuit for fitting is shown.

Electrochemical impedance spectroscopy (EIS) measurements of the samples were performed using a 100 kHz–0.1 Hz frequency range and an amplitude of 10 mV at  $\eta = 0.10$  and 0.15 V. In the high-frequency limit and under non-Faradaic conditions, the electrochemical system is approximated by the modified Randles circuit shown in the inset, where  $R_s$  denotes the solution resistance, CPE is a constant-phase element related to the double-layer capacitance, and  $R_{ct}$  is the charge-transfer resistance from any residual Faradaic processes. A semicircle in the lowfrequency region of the Nyquist plots represents the charge transfer process, with the diameter of the semicircle reflecting the charge-transfer resistance. The real (Z') and negative imaginary (-Z'') components of the impedance are plotted on the x and y axes, respectively. The simulation of the EIS spectra using an equivalent circuit model allowed us to determine the charge transfer resistance,  $R_{ct}$ , which is a key parameter for characterizing the catalyst-electrolyte charge transfer process. The  $R_{ct}$  values follow an order consistent with the HER performance. The fitting parameters are summarized in Table S5.



**Figure S12**. Cyclic voltammetry (CV) curves of ReSe<sub>2</sub>, Mn-ReSe<sub>2</sub>, Fe-ReSe<sub>2</sub>, Co-ReSe<sub>2</sub>, Ni-ReSe<sub>2</sub>, and Cu-ReSe<sub>2</sub>, in a non-Faradaic region (0.1-0.2 V *vs*. RHE), at 20-100 mV s<sup>-1</sup> scan rates (with a step of 20 mV s<sup>-1</sup>) and in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (b) 1 M KOH. Difference ( $\Delta J$ ) between the anodic charging and cathodic discharging currents measured at 0.15 V (*vs*. RHE at pH 0) and 0.05 (*vs*. RHE at pH 14) and plotted as a function of the scan rate. The value in parenthesis represents the C<sub>dl</sub>, obtained by the half of the linear slope.

The  $C_{dl}$  value increases with TM doping, following the sequence of HER performance. Therefore, the double-layer capacitance determines the HER catalytic activity of samples. The  $C_{dl}$  (mF cm<sup>-2</sup>) value of TM-ReSe<sub>2</sub> is summarized as follows.

pН	ReSe <sub>2</sub>	Mn- ReSe <sub>2</sub>	Fe-ReSe <sub>2</sub>	Co-ReSe <sub>2</sub>	Ni-ReSe <sub>2</sub>	Cu-ReSe <sub>2</sub>
0	3.1	6.3	7.7	9.4	10.0	4.8
14	8.5	15.6	11.2	23.3	23.9	16.3



Substitution model (TM <sub>Re</sub> )									
Re site	Mn <sub>Re</sub>	Fe <sub>Re</sub>	Co <sub>Re</sub>	Ni <sub>Re</sub>	Cu <sub>Re</sub>				
1 (= 3)	-322.07 (0.59)	-320.80 (0.46)	-319.77 (0.46)	-316.92 (0.51)	-316.42 (0.50)				
2 (= 4)	-322.66 (0)	-321.26 (0)	-320.23 (0)	-317.43 (0)	-316.96 (0)				

Adatom model (TM <sub>ad</sub> )					
Re site	Mn <sub>ad</sub>	Fe <sub>ad</sub>	Co <sub>ad</sub>	Ni <sub>ad</sub>	Cu <sub>ad</sub>
1	-334.37 (0.09)	-331.54 (1.24)	-331.78 (0.10)	-329.78 (0)	-329.82 (0.08)
2	-334.46 (0)	-332.78 (0)	-331.88 (0)	-329.78 (0)	-329.90 (0)
3	-333.50 (0.96)	-332.49 (0.29)	-331.62 (0.26)	-329.61 (0.17)	-329.57 (0.33)
4	-334.01 (0.51)	-332.20 (0.58)	-331.41 (0.47)	-329.61 (0.17)	-329.38 (0.52)

Figure S13. Configuration of the substitution  $(TM_{Re})$  and the adatom  $(TM_{ad})$  model for four different Re sites (marked by  $1 \sim 4$ ) and corresponding total energy (in eV). The values in parenthesis correspond to the relative energy to the most stable configuration (site 2).



Figure S14. The most stable structures of TM-ReSe<sub>2</sub> for the substitution ( $TM_{Re}$ ) and adatom ( $TM_{ad}$ ) models. The grey and green balls represent Re and Se atoms, and other colored balls represent TM atoms.



Figure S15. Energy diagram for the migration of  $TM_{ad}$  to  $TM_{Re}$  and corresponding the structures.

We calculated the activation barrier for the reaction path that involved the structure evolution from the adatom to the substitution. The initial structure (i) is specified by the adatom model (TM<sub>ad</sub>). In the activated complex (ii), one Re atom is missed and the TM atom was placed at a sufficiently large distance from the surface. The final state (iii) corresponds to the substitution model (TM<sub>Re</sub>). Since the Cu<sub>Re</sub> is less stable the Cu<sub>ad</sub>, the adatom is exceptionally preferred. The next favorable of the adatom model is Ni-ReSe<sub>2</sub>, since the Ni<sub>Re</sub> is slightly stable than Ni<sub>ad</sub>. The activation energy is mainly determined by producing the Re vacancy from the adatom model, which requires more energy as the TM goes from Mn to Fe and Co. The lower activation energy makes it easier to form the substitution model, so the substitution becomes more favored following the sequence of Mn > Fe > Co. Overall, the adatom becomes more favored for Co, Ni, and Cu, which is consistent with the experimental results.



**Figure S16**. The most stable structures with H adsorbed (H\*) on TM-ReSe<sub>2</sub> for the substitution and adatom models and corresponding  $\Delta G_{H*}$  value. In the substitution model, the H atom attached on top of Se atoms near TM atoms (Se<sup>NN</sup>). In the adatom model, the H atom attached on top of the TM atoms by forming the TM<sub>ad</sub>-H bond. Grey and green balls represent Re and Se atoms, and other colored balls represent TM atoms.



**Figure S17.**  $\Delta G_{H^*}$  (eV) calculated for four different Ni<sub>ad</sub> sites (position 1~4) of Ni<sub>ad</sub>-ReSe<sub>2</sub>. The  $\Delta G_{H^*}$  values at distinct doping sites are similar, varying from -0.14 eV to -0.02 eV.



**Figure S18**. The most stable structures of (a) ReSe<sub>2</sub>, (b) Co<sub>ad</sub>-ReSe<sub>2</sub>, and (c) Ni<sub>ad</sub>-ReSe<sub>2</sub> with one Se vacancy at the upside and their corresponding H adsorbed model.

For the H atom attached on top of Re atom of ReSe<sub>2</sub>, the  $\Delta G_{H^*}$  is 0.17 eV. In the Co<sub>ad</sub>-ReSe<sub>2</sub> and Ni<sub>ad</sub>-ReSe<sub>2</sub>, the H atom attached on top of the TM atoms by forming the TM-H bond;  $\Delta G_{H^*}$  = -0.05 eV and 0.06 eV, respectively. Grey, blue, yellow, and green balls represent Re, Co, Ni, and Se atoms. The red ball and the dotted circle represent the H atom and the Se vacancy, respectively.



**Figure S19**. The H\*-adsorption intermediate for the ReSe<sub>2</sub> edge site and corresponding  $\Delta G_{H*}$  value (eV). We used a stripe model, where the stable termination is determined in Re-rich condition because HER environment is highly reductive. The  $\Delta G_{H*}$  is 0.45 eV for the most stable edge formed with 50% Se coverage.



**Figure S20**. The most stable structures with H-OH adsorbed (H-OH\*) on TM-ReSe<sub>2</sub> for the substitution and adatom models. The grey, green, purple, and red balls represent Re, Se, O, and H atoms, and the other colored balls represent TM atoms.



**Figure S21**. The Gibbs free energy change for HER path at pH 14 for  $TM_{Re}$  and  $TM_{ad}$  models. The actual values of  $\Delta G_{H-OH*}$  for each TMs are labeled.

To explain the HER catalytic activity at pH 14, one more intermediate step was calculated (see Experimental section above for details). In alkaline conditions, the water dissociation step occurs first, and then the generation of hydrogen molecule follows. The intermediate for water dissociation step was introduced, with modeling of co-adsorbed OH\* and H\*, and its Gibbs free energy change is denoted as  $\Delta G_{H-OH*}$ . Assuming the water dissociation step is the rate determining step, the HER catalytic activity would follow the  $\Delta G_{H-OH*}$  value. The  $\Delta G_{H-OH*}$  value of TM<sub>ad</sub> is closer to 0 eV than that of TM<sub>Re</sub>, indicating that the catalytic activity of TM<sub>ad</sub> determines the HER performance. The  $|\Delta G_{H-OH*}|$  value decreases following the order: Co > Mn > Ni > Cu > Fe, while the experiment shows Ni > Co > Cu > Mn > Fe. In particular, Fe<sub>ad</sub>-ReSe<sub>2</sub> exhibited the most negative value of  $\Delta G_{H-OH*}$  (-1.85 eV), which is consistent with the experimental result. In the case of Mn<sub>ad</sub>-ReSe<sub>2</sub>, the lower fraction of adatoms could not show HER activity as good as that predicted by calculation. In the same context, the highest fraction of adatom in Ni-ReSe<sub>2</sub> would enhance the HER performance. Overall, if the fraction of adatom is considered, the  $\Delta G_{H-OH*}$  can be correlated with the experimental results.



**Figure S22**. Partial charge plot for (a)  $Ni_{Re}$  and (b)  $Ni_{ad}$  without (left) and with (right) H\*. The partial charge is represented by the blue translucent area. The grey, green, and yellow balls represent Re, Se, and Ni, respectively.



**Figure S23**. Spin-resolved total and partial DOS of (a) Mn, (b) Fe, (c) Co, and (d) Cu. Each includes 2 plots: PDOS without (left) and with (right) hydrogen atom. Fermi level ( $E_F$ ) is presented by the dotted line, and all energies are offset by the vacuum level ( $E_{vac}$ ). The partial DOS projected on TM (red), Se<sup>NN</sup> (nearest neighboring Se atoms, blue), and H (green) are amplified by 5, 5, and 40 times, respectively.

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