Table S1 ΔG_{H^*} values and $Logi_0$ values of 12 kinds of S/Se-TM@VSSe as HER catalysts.

SACs	ΔG_{H^*}(eV)	$Log(i_0/Acm^{-2})$
S-Cu@VSSe	0.71	-11.65
S-Ru@VSSe	0.70	-11.53
S-Rh@VSSe	0.32	-5.10
S-Os@VSSe	-0.10	-1.62
S-Ir@VSSe	0.76	-12.53
S-Pt@VSSe	0.07	-0.85
Se-Cu@VSSe	1.38	-23.03
Se-Ru@VSSe	0.63	-10.27
Se-Rh@VSSe	0.37	-5.90
Se-Os@VSSe	-0.16	-2.73
Se-Ir@VSSe	-0.06	-1.11
Se-Pt@VSSe	-0.22	-3.67

Table S2 The values of ΔG_{OH^*}, ΔG_{O^*}, ΔG_{OOH^*}, η^{OER} and η^{ORR}

SACs	ΔG_{OH^*}(eV)	ΔG_{O^*}(eV)	ΔG_{OOH^*}(eV)	η^{OER}(V)	η^{ORR}(V)
S-Cu@VSSe	0.58	3.29	3.75	1.48	0.77
S-Ru@VSSe	0.60	0.89	3.72	1.60	0.93
S-Rh@VSSe	0.70	2.18	3.64	0.26	0.53
S-Os@VSSe	0.26	1.13	3.19	0.83	0.97
S-Ir@VSSe	0.75	1.65	3.88	1.01	0.48
S-Pt@VSSe	0.66	2.33	3.94	0.44	0.57
Se-Cu@VSSe	0.61	2.35	4.23	0.66	0.62
Se-Ru@VSSe	0.69	1.14	3.66	1.29	0.78
Se-Rh@VSSe	0.91	2.70	3.80	0.56	3.22
Se-Os@VSSe	0.45	1.13	3.36	1.00	0.78
Se-Ir@VSSe	0.54	2.22	3.63	0.45	0.69
Se-Pt@VSSe	0.58	2.71	3.50	0.90	0.65

Table S3 D-band center position values of 12 SACs

SACs	d-band Center Position(eV)
S-Cu@VSSe	-0.80
S-Ru@VSSe	-0.56
S-Rh@VSSe	-0.64
S-Os@VSSe	-0.63
S-Ir@VSSe	-0.66
S-Pt@VSSe	-0.68
Se-Cu@VSSe	-0.85
Se-Ru@VSSe	-0.58
Se-Rh@VSSe	-0.67
Se-Os@VSSe	-0.59
Se-Ir@VSSe	-0.69
Se-Pt@VSSe	-0.80

Table S4 The value of the energy reduction of a single TM atom in the 1-site or 3-site configuration of S/Se-TM@VSSe with 7 TM atoms

SACs	1-site	3-site
S-Rh@VSSe	-6.27	-2.30
S-Os@VSSe	-9.80	-5.57
S-Ir@VSSe	-7.79	-4.58
S-Pt@VSSe	-5.50	-3.34
Se-Rh@VSSe	-6.44	-3.09
Se-Os@VSSe	-9.64	-4.70
Se-Ir@VSSe	-8.11	-4.46

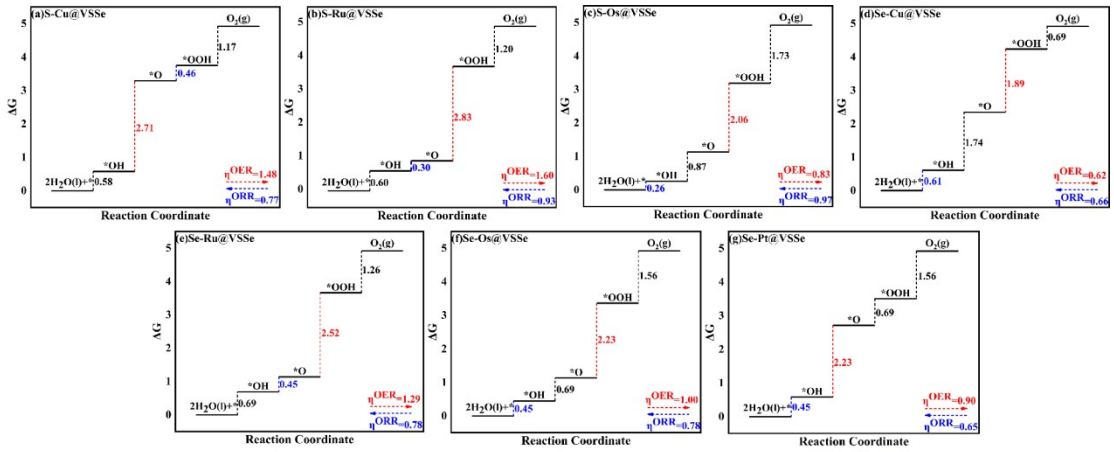

Fig.S1 OER/ORR free energy step chart at U= 0 V: (a) S-Cu@VSSe, (b) S-Ru@VSSe, (c) S-Os@VSSe, (d) Se-Cu@VSSe, (e) Se-Ru@VSSe, (f) Se-Os@VSSe, (g) Se-Pt@VSSe. OER determination steps are marked with red, whereas ORR determination steps are highlighted with blue fonts. A red arrow indicates the OER direction and a blue arrow indicates the ORR direction.

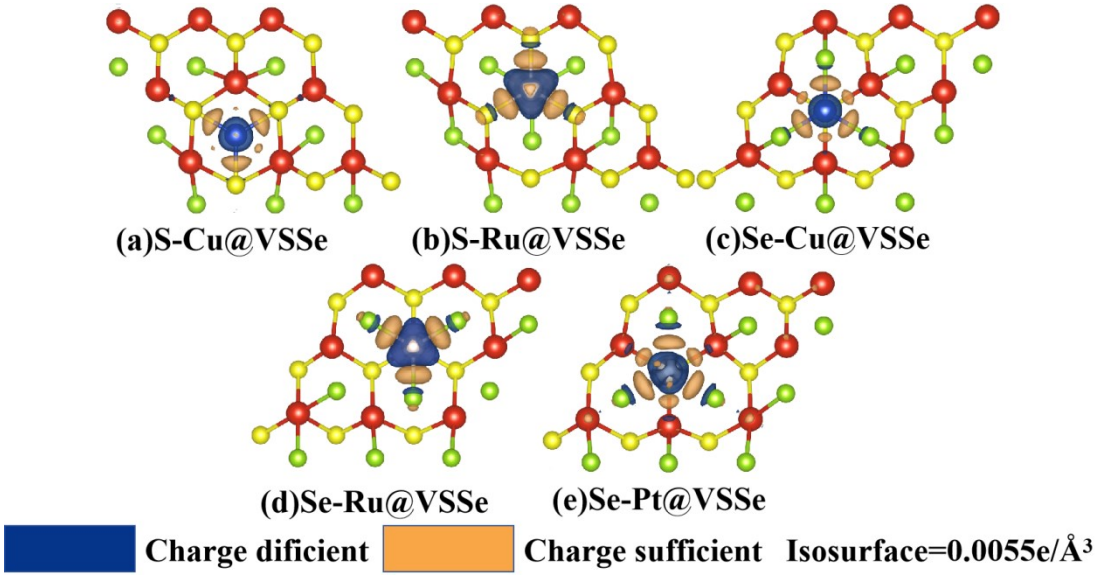

Fig.S2 Charge density difference plots for (a) S-Cu@VSSe, (b) S-Ru@VSSe, (c) Se-Cu@VSSe,

(d) Se-Ru@VSSe, (e) Se-Pt@VSSe, where isosurface level is set to 0.0055 e/A^{-3}

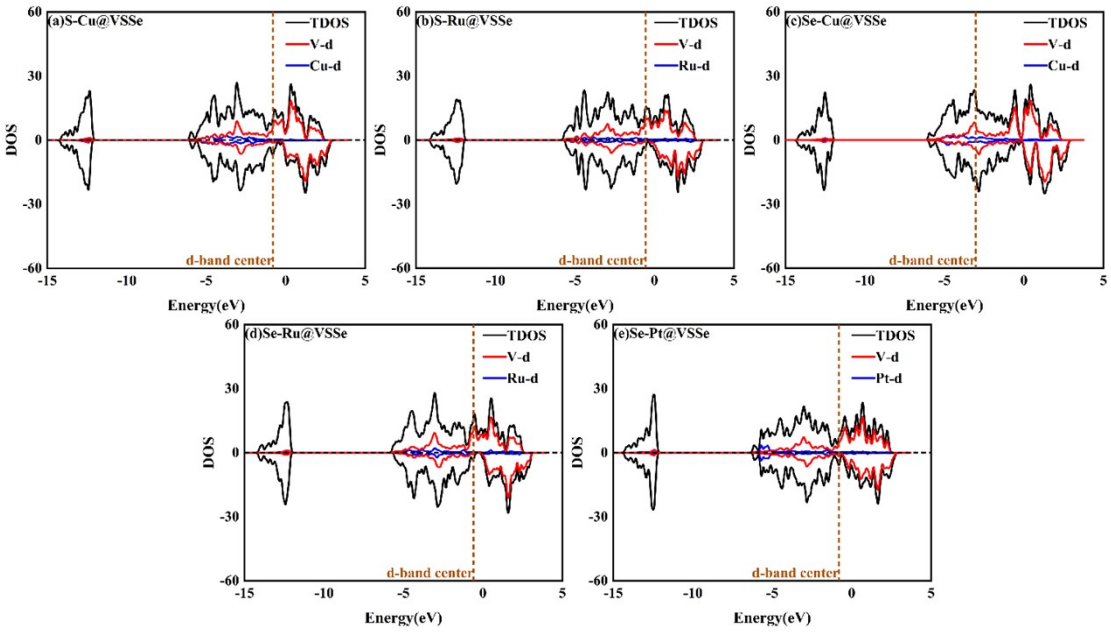

Fig.S3 PDOS diagrams of (a) S-Cu@VSSe, (b) S-Ru@VSSe, (c) Se-Cu@VSSe, (d) Se-Ru@VSSe, (e) Se-Pt@VSSe, where the dotted brown line indicates the center of the d-band.