Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Single Metal Atom Regulated Flexibly by 2D InSe substrate for CO_2 reduction electrocatalyst

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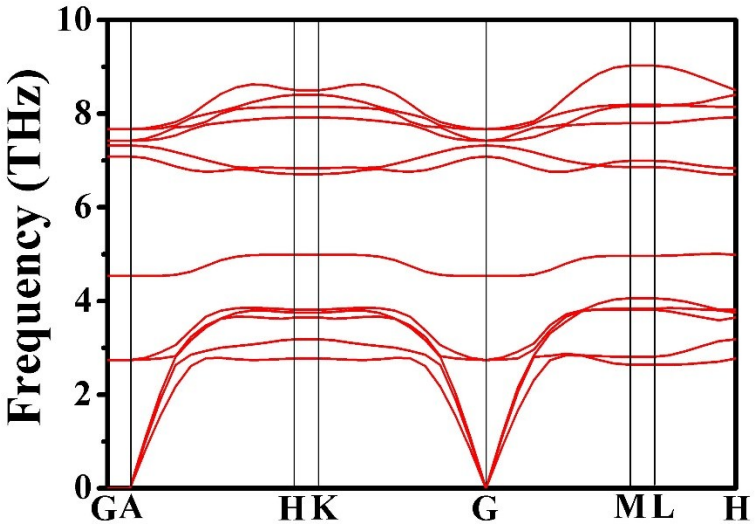

Fig. S1 The phonons dispersion curves of a fully relax 2D InSe monolayer.

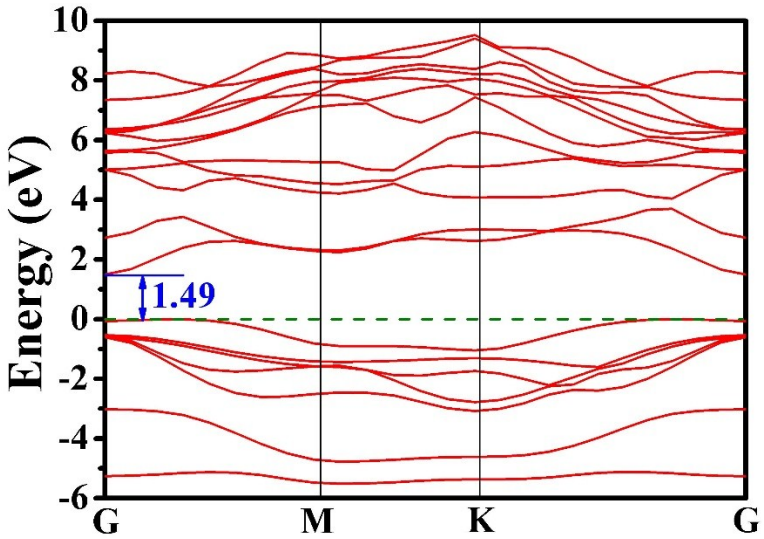

Fig.S2 Band structure of a fully relax 2D InSe monolayer.

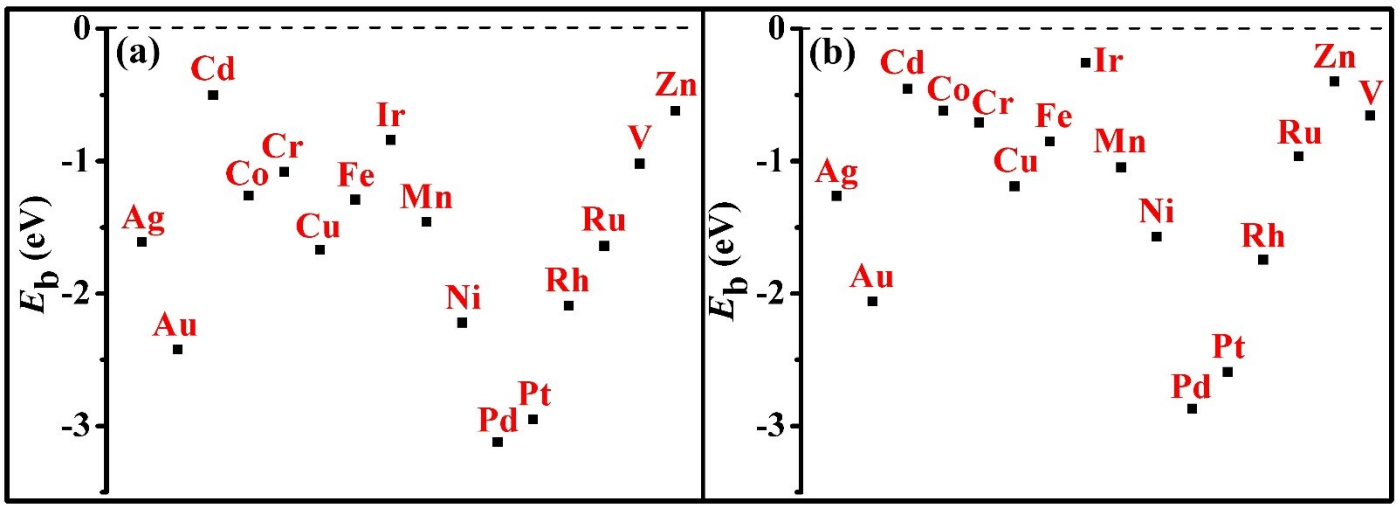

Fig.S3 binding energies of single atoms on mono-Se-vacancy site of InSe referenced to (a) 4-atom and (b) 6-atom metal clusters in vacuum.

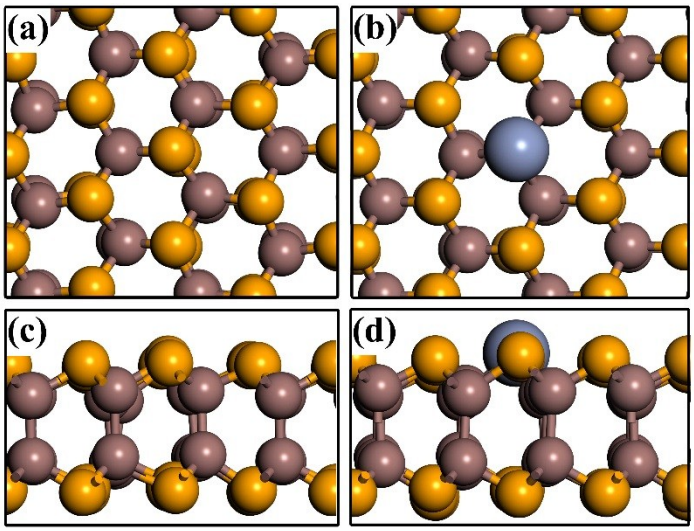

Fig.S4 Snapshots from dynamics simulation of geometrical structures for the (a) top view of 2D InSe monolayer, (b) top view of Cr@2DInSe, (c) side view of 2D InSe monolayer, and (d) side view of Cr@2DInSe, respectively at the temperature of 300K. More snapshots can be obtained from the video named InSedynamics.mp4 and InSeCrdynamics.mp4.

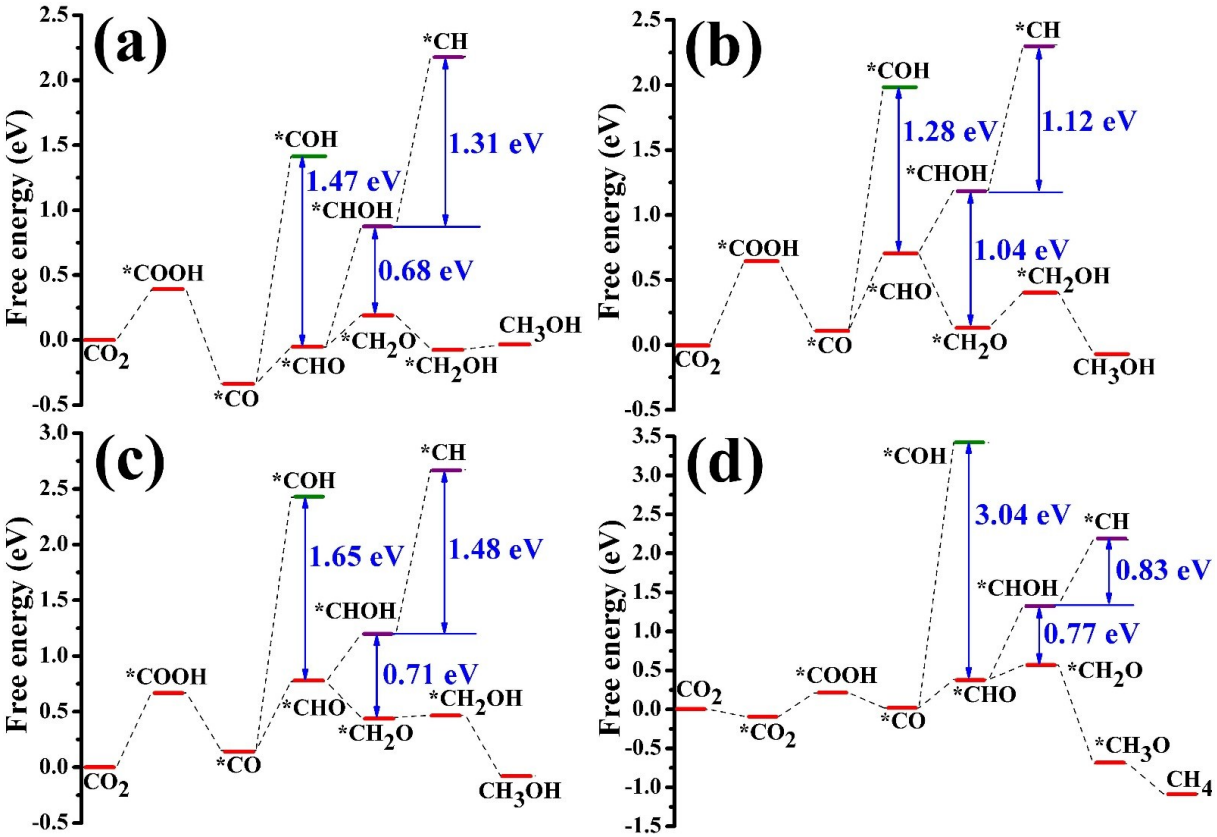

Fig. S5 Free energy profiles of CRR on (a) Rh@2DInSe, (b) Mn@2DInSe, (c) Cu@2DInSe, and (d) Cr@2DInSe at zero applied voltage (vs RHE) and 298.15K.

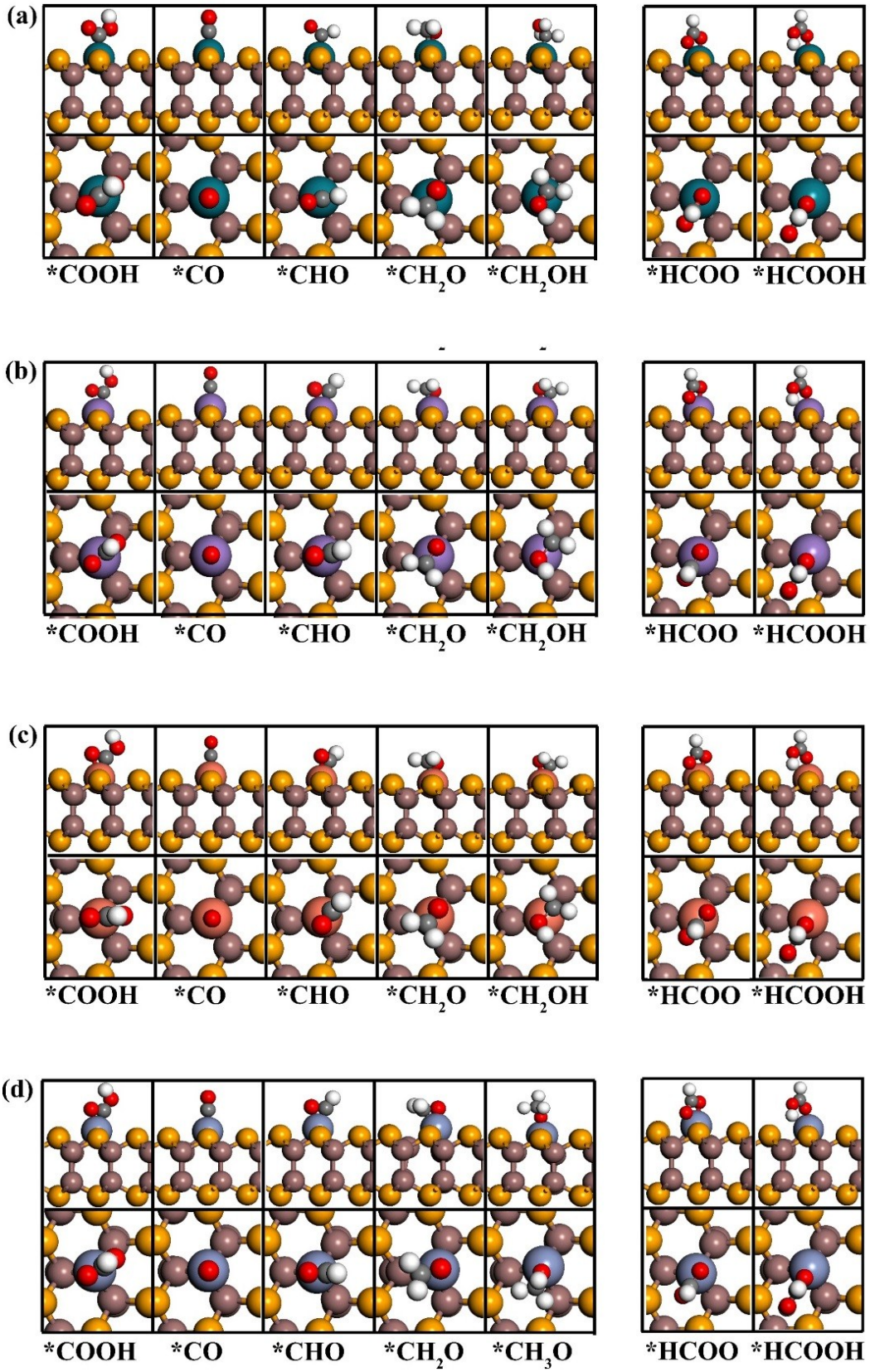

Fig. S6 Configurations of the intermediates along the reaction path on the active sites of (a) Rh@2DInSe, (b) Mn@2DInSe, (c) Cu@2DInSe, and (d) Cr@2DInSe.

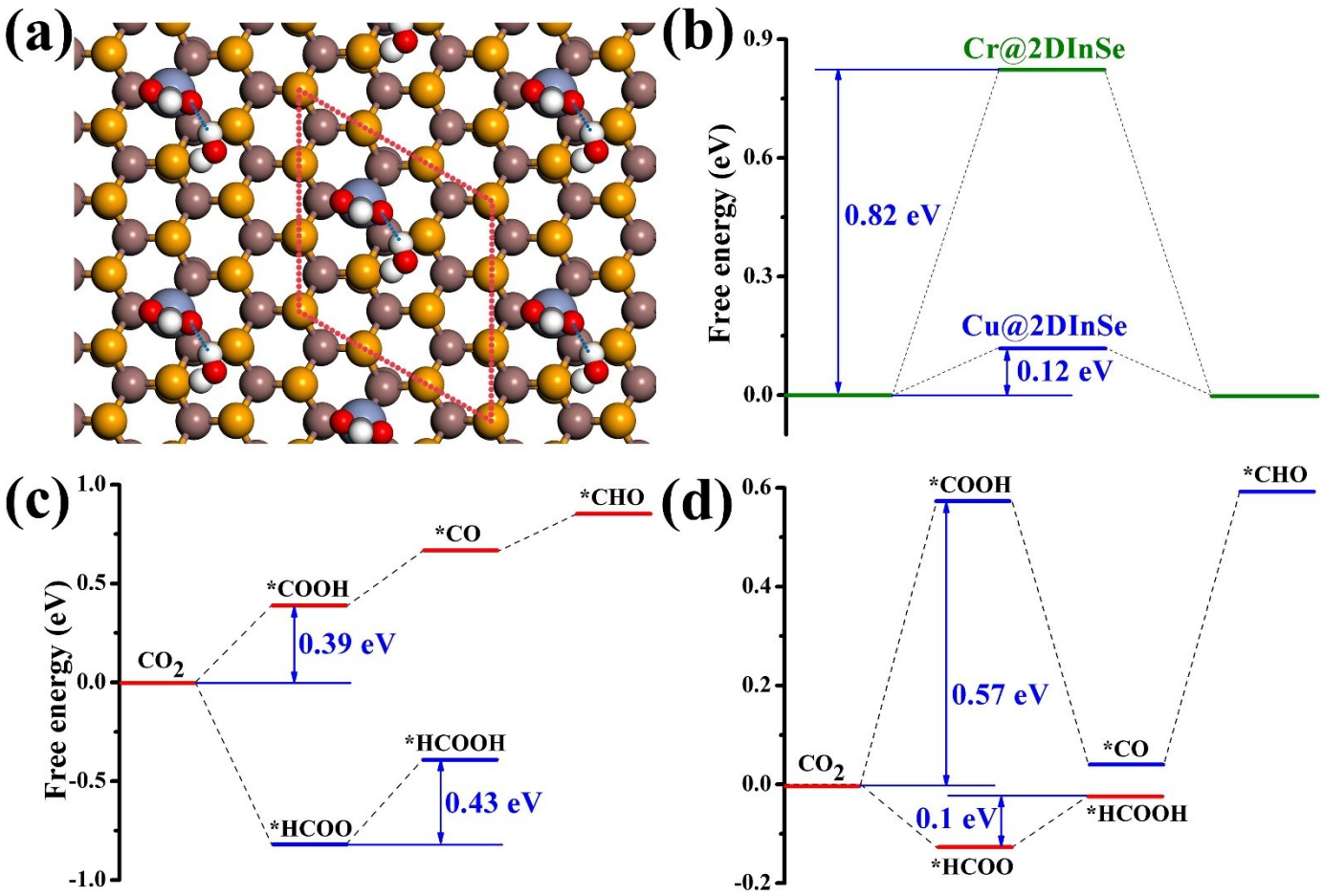

Fig. S7 (a) Configuration of HCOO adsorption on Cr@2DInSe with one water molecule. The blue dashed line denotes hydrogen bond; Free energy profiles of (b) HER on Cr@2DInSe and Cr@2DInSe; Free energy profiles of CRR on (c) Cr@2DInSe and (d) Cu@2DInSe.

Table S1 The adsorption energies (E_{ad}) of different intermediates. 1-16 denotes different M@2DInSe systems. 17-26 denotes different transition metal systems.

	E_{ad} (eV)						
	*CO_2	*COOH	*CO	*CHO	*CH_2O	*CH_3O	*CH_2OH
1	-0.06	-2.17	-1.08	-2			
2	-0.08	-2.27	-0.62	-1.79			
3	-0.36	-3.16	-1.84	-3.4			
4	-0.33	-2.75	-1.38	-3.06	-0.93	-2.16	-2.82
5	-0.17	-1.79	-0.93	-1.64			
6	-0.19	-2.07	-0.7	-1.56			
7	-0.25	-3.45	-1.98	-3.52			
8	-0.18	-2.37	-0.53				
9	-0.44	-2.65	-1.19	-2.35	-1.26	-3.17	-2.41
10	-0.48	-2.91	-1.03	-2.54	-1.45	-3.42	-2.55
11	-0.56	-2.93	-1.46	-2.91			
12	-0.54	-2.9	-1.88	-2.83			
13	-0.49	-3.01	-1.71	-3.03			
14	-0.34	-2.39	-1.42	-2.3			
15	-0.24	-2.47	-1.11	-2.04	-0.78	-2.77	-2.34
16	-0.24	-2.43	-0.77	-1.96			
17		-1.76	-0.15				
18		-1.81	-0.17				
19		-2.05	-0.44				
20		-2.11	-0.56				
21		-2.5	-1.25				
22		-3.24	-2.07				
23		-3.31	-2.17				
24		-3.29	-2.24				
25		-4.47	-2.57				
26		-4.32	-3.81				

1: Pt@2DInSe; 2: Au@2DInSe; 3: Ru@2DInSe; 4: Rh@2DInSe; 5: Pd@2DInSe; 6: Ag@2DInSe; 7: Ir@2DInSe; 8: Cd@2DInSe; 9: Mn@2DInSe; 10: Cr@2DInSe; 11: V@2DInSe; 12: Fe@2DInSe; 13: Co@2DInSe; 14: Ni@2DInSe; 15: Cu@2DInSe; 16: Zn@2DInSe; 17: Cd; 18: Zn; 19: Ag; 20: Au; 21: Cu; 22: Co; 23: Pt; 24: Ni; 25: Cr; 26:Sc

Table S2 Reaction free energies (G_r) of different reaction steps in various systems. a-i denote different reaction steps. 1-5 denote different M@2DInSe systems.

	G_r (eV)														
	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**	**n**	**o**
1	0.39	-0.72	0.28	0.24	0.25	0.16	-0.26	0.03	-0.48	0.63	-0.74	0.12	-0.03	0.03	0.12
2	0.63	-0.52	0.60	-0.58	-0.62	0.37	0.28	-0.46	0.43	-0.52	0.17	0.42	0.48	-0.48	0.06
3	0.67	-0.52	0.62	-0.28	-0.51	0.91	0.02	-0.54	-0.02	-0.37	0.11	0.02	0.22	-0.22	0.07
4	0.33	-0.19	0.36	0.19	-1.27	-0.38	-0.33	-0.30	0.63	-0.72	0.41	0.53	0.43	-0.43	-0.09
5	0.78	-0.28	0.50												

1: Mn@2DInSe; 2: Cu@2DInSe; 3: Rh@2DInSe; 4: Cr@2DInSe; 5: Zn@2DInSe

a: *CO_2 (CO_2) + H^+ + e^- → *COOH; b: *COOH + H^+ + e^- → *CO + H_2O; c: *CO + H^+ +e^- → *CHO; d: *CHO + H^+ + e^- → *CH_2O; e: *CH_2O + H^+ + e^- → *CH_3O; f: *CH_3O + H^+ + e^- → CH_4; g: *CH_2O + H^+ + e^- → *CH_2OH; h: *CH_2OH + H^+ + e^- → CH_3OH; i: *CH_3O + H^+ + e^- → CH_3OH; j: *CO_2 + H^+ + e^- → *HCOO; k: *HCOO + H^+ + e^- → *HCOOH; l: *HCOOH → * + HCOOH; m: * + H^+ + e^- → *H; n: *H + H^+ + e^- → H_2; o: * + CO_2 →*CO_2

Table S3 Contribution of zero point energies (ZPE) to the reaction free energy of different reaction steps in various systems. a-i denote different reaction steps. 1-5 denote different M@2DInSe systems.

	ΔE_{ZPE} (eV)														
	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**	**n**	**o**
1	0.18	-0.02	0.21	0.13	0.19	-0.09	0.22	0.07	0.1	0.19	0.13	-0.06	0.00	0.00	0.04
2	0.20	0.04	0.12	0.06	0.32	-0.12	0.32	0.05	0.05	0.18	0.15	-0.22	0.04	-0.04	0.05
3	0.20	0.03	0.12	0.12	0.25	-0.01	0.27	0.05	0.07	0.14	0.15	-0.08	0.11	-0.11	0.09
4	0.19	-0.03	0.19	0.32	-0.02	0.02	0.00	0.12	0.14	0.19	0.18	-0.07	0.00	0.00	0.00
5	0.24	-0.01	0.14												

1: Rh@2DInSe; 2: Mn@2DInSe; 3: Cu@2DInSe; 4: Cr@2DInSe; 5: Zn@2DInSe

a: $*CO_2$ (CO_2) + H^+ + e^- → $*COOH$; b: $*COOH + H^+ + e^-$ → $*CO + H_2O$; c: $*CO + H^+ + e^-$ → $*CHO$; d: $*CHO + H^+ + e^-$ → $*CH_2O$; e: $*CH_2O + H^+ + e^-$ → $*CH_3O$; f: $*CH_3O + H^+ + e^-$ → CH_4; g: $*CH_2O + H^+ + e^-$ → $*CH_2OH$; h: $*CH_2OH + H^+ + e^-$ → CH_3OH; i: $*CH_3O + H^+ + e^-$ → CH_3OH; j: $*CO_2 + H^+ + e^-$ → $*HCOO$; k: $*HCOO + H^+ + e^-$ → $*HCOOH$; l: $*HCOOH$ → * + HCOOH; m: * + H^+ + e^- → *H; n: *H + H^+ + e^- → H_2; o: * + CO_2 →$*CO_2$

Table S4 Contribution of enthalpic temperature correction (TS) to different reaction steps in various systems. a-i denote different reaction steps. 1-5 denote different M@2DInSe systems.

	-ΔTS (eV)														
	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**	**n**	**o**
1	0.24	-0.55	0.36	0.07	0.32	-0.24	0.32	-0.46	-0.46	0.32	0.12	-0.82	0.05	-0.05	0.41
2	0.27	-0.44	0.20	0.41	-0.01	-0.16	0.01	-0.52	-0.50	0.28	0.25	-0.76	0.20	-0.20	0.45
3	0.22	-0.39	0.20	0.26	0.26	-0.47	0.22	-0.53	-0.57	0.32	0.09	-0.92	0.22	-0.22	0.40
4	0.26	-0.52	0.30	0.07	-0.26	-0.29	-0.33	-0.54	-0.62	0.34	0.25	-0.93	0.16	-0.16	0.37
5	0.26	-0.45	0.18												

1: Rh@2DInSe; 2: Mn@2DInSe; 3: Cu@2DInSe; 4: Cr@2DInSe; 5: Zn@2DInSe

a: $*CO_2 + H^+ + e^-$ → $*COOH$; b: $*COOH + H^+ + e^-$ → $*CO + H_2O$; c: $*CO + H^+ + e^-$ → $*CHO$; d: $*CHO + H^+ + e^-$ → $*CH_2O$; e: $*CH_2O + H^+ + e^-$ → $*CH_3O$; f: $*CH_3O + H^+ + e^-$ → CH_4; g: $*CH_2O + H^+ + e^-$ → $*CH_2OH$; h: $*CH_2OH + H^+ + e^-$ → CH_3OH; i: $*CH_3O + H^+ + e^-$ → CH_3OH; j: $*CO_2 + H^+ + e^-$ → $*HCOO$; k: $*HCOO + H^+ + e^-$ → $*HCOOH$; l: $*HCOOH$ → * + HCOOH; m: * + H^+ + e^- → *H; n: *H + H^+ + e^- → H_2; o: * + CO_2 →$*CO_2$