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Electrocatalytic Reduction of CO_2 by Two−Dimensional Transition Metal Porphyrin Sheets

Supplemental Information

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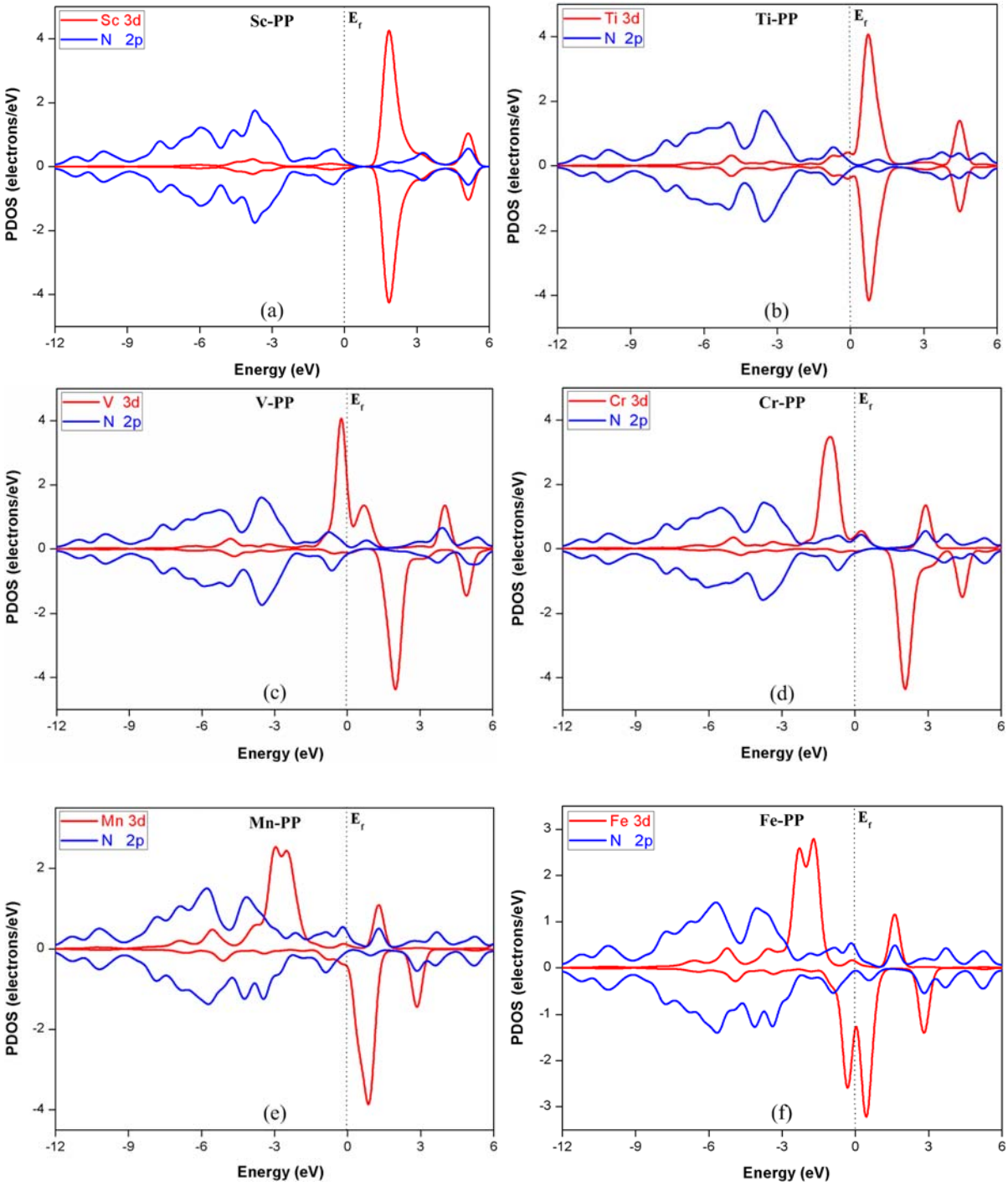
Figure S1. The partial density of states of ten TM–PP monolayers. The dotted line denotes the Fermi level, the red and blue lines represent the 3d orbital of the metal atoms and the 2p orbital of the nitrogen atoms, respectively.



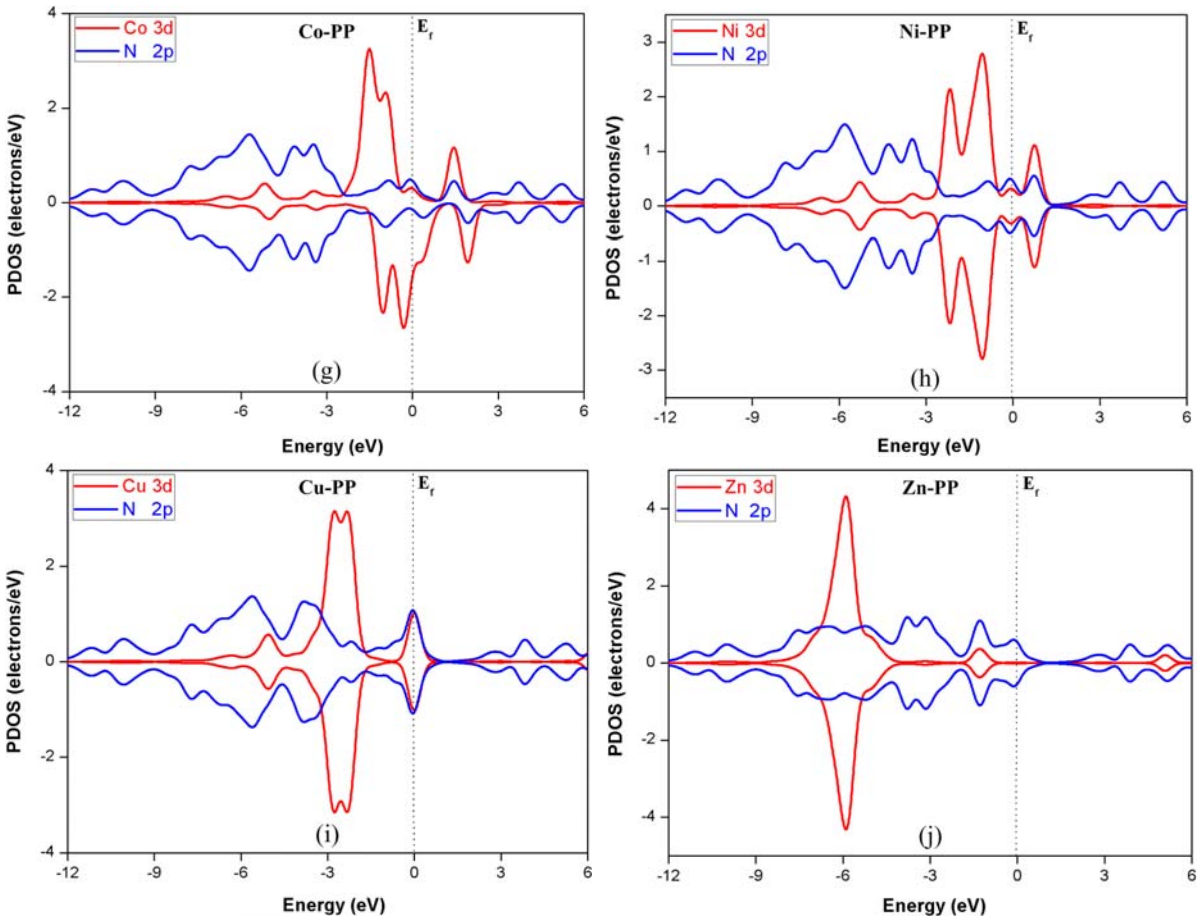

Co 3d
N 2p
Co-PP
E_f
PDOS (electrons/eV)
Energy (eV)
(g)
Ni 3d
N 2p
Ni-PP
E_f
PDOS (electrons/eV)
Energy (eV)
(h)
Cu 3d
N 2p
Cu-PP
E_f
PDOS (electrons/eV)
Energy (eV)
(i)
Zn 3d
N 2p
Zn-PP
E_f
PDOS (electrons/eV)
Energy (eV)
(j)

Table. S1 Properties of TM−PP monolayers: Cohesive energy (E_c) of TM bulk, binding energy (E_b) between TM and PP, and formation energy (E_f).

TM−PP	E_b / eV	E_c / eV	E_f / eV
Sc	–12.111	–4.518	–5.922
Ti	–11.467	–5.282	–5.279
V	–10.466	–5.632	–4.277
Cr	–9.399	–4.547	–3.210
Mn	–9.340	–4.247	–3.151
Fe	–9.699	–5.283	–3.510
Co	–9.713	–5.633	–3.524
Ni	–8.735	–4.644	–2.547
Cu	–6.951	–3.857	–0.763
Zn	–5.688	–1.402	0.501

[1]E_b is the binding energy of metal atoms on the PP, which is calculated by $E_b = E_{TM-PP} - E_{TM} - E_{PP}$, where the E_{TM-PP}, E_{TM} and E_{PP} are the energies of TM−PP, PP and metal atoms.

[2]E_c is the cohesive energy of the bulk metals, which is calculated by $E_c = (E_{TM(bulk)} - nE_{TM})/n$, where the $E_{TM(bulk)}$ is the energy of metal crystal, E_{TM} is the energy of a single metal atom, and n is the number of metal atoms in the crystal.

[3]E_f is the formation energy of TM−PP, which is calculated by $E_f = E_{TM-PP} - n_{TM}\mu_{TM} - n_C\mu_C - n_N\mu_N$, where the E_{TM-PP} are the energies of TM−PP, n_{TM}, n_C and n_N are the number of TM, C, and N atoms, respectively. μ_{TM}, μ_C and μ_N are the chemical potentials of TM, C and N, which are obtained from the single atom of transition metal, graphene, and N_2, respectively.

Table S2 Gibbs free energy change of the first protonation step in the CO_2 reduction reaction (CRR) and H_2 evolution reaction (HER) on the TM–PP in eV.

TM–PP	ΔG_{H^*}	ΔG_{C^*OOH}	ΔG_{O^*CHO}
Sc	1.076	0.390	–0.756
Ti	0.066	–0.441	–1.311
V	0.148	–0.165	–0.954
Cr	0.397	0.116	–0.186
Mn	0.509	0.242	0.288
Fe	0.296	–0.031	0.287
Co	0.199	–0.113	–0.153
Ni	1.148	0.840	1.065
Cu	1.964	1.245	1.062
Zn	1.709	1.346	0.702

Table S3 Adsorption Energy (E_{ads}) of different CO_2 reduction products and the bond length between metal atoms and the carbon or oxygen atoms ($R_{TM-C/TM-O}$).

TM–PP		CO	HCOOH	HCHO	CH_3OH	CH_4
Sc–PP	$R_{Sc-C/Sc-O}$ / Å	2.395	2.159	2.169	2.134	2.499
	E_{ads} / eV	−0.529	−1.004	−1.021	−1.277	−0.322
Ti–PP	$R_{Ti-C/Ti-O}$ / Å	2.075	2.053	2.007	2.069	2.365
	E_{ads} / eV	−1.409	−1.282	−1.412	−1.592	−0.523
V–PP	$R_{V-C/V-O}$ / Å	1.975	2.020	1.969	2.008	2.470
	E_{ads} / eV	−1.431	−1.087	−1.258	−1.306	−0.368
Cr–PP	$R_{Cr-C/Cr-O}$ / Å	1.862	2.035	1.973	2.036	3.098
	E_{ads} / eV	−0.993	−0.435	−0.585	−0.656	−0.233
Mn–PP	$R_{Mn-C/Mn-O}$ / Å	2.150	2.268	2.274	2.204	3.065
	E_{ads} / eV	−0.474	−0.458	−0.564	−0.675	−0.258
Fe–PP	$R_{Fe-C/Fe-O}$ / Å	1.712	2.218	2.212	2.211	3.002
	E_{ads} / eV	−1.383	−0.473	−0.596	−0.779	−0.268
Co–PP	$R_{Co-C/Co-O}$ / Å	1.784	2.186	2.159	2.182	3.536
	E_{ads} / eV	−0.889	−0.344	−0.492	−0.652	−0.176
Ni–PP	$R_{Ni-C/Ni-O}$ / Å	2.077	2.929	2.870	2.696	3.199
	E_{ads} / eV	0.012	−0.104	−0.215	−0.314	−0.212
Cu–PP	$R_{Cu-C/Cu-O}$ / Å	2.850	2.563	2.581	2.441	3.144
	E_{ads} / eV	−0.251	−0.250	−0.274	−0.496	−0.311
Zn–PP	$R_{Zn-C/Zn-O}$ / Å	2.385	2.261	2.280	2.208	3.052
	E_{ads} / eV	−0.264	−0.357	−0.455	−0.657	−0.235

Table S4 Adsorption Energies (E_{ads}) of the intermediates in the potential determining steps of CRR on the TM–PP monolayers: C*O (for Mn and V), C*H_2OH (for Ti), O*CHOH (for Cr, Fe and Co), C*OOH (for Sc and Ni) and O*CHO (for Cu and Zn). The bond length between metal atom and the carbon atom or the oxygen atom ($R_{TM-C/TM-O}$).

TM–PP	**Sc–PP**	**Ti–PP**	**V–PP**	**Cr–PP**	**Mn–PP**
$R_{TM-C/TM-O}$ / Å	2.193	2.133	1.975	2.235	2.150
E_{ads} / eV	−1.620	−2.306	−1.431	−0.435	−0.474
TM–PP	**Fe–PP**	**Co–PP**	**Ni–PP**	**Cu–PP**	**Zn–PP**
$R_{TM-C/TM-O}$ / Å	2.218	2.186	1.961	2.073	2.106
E_{ads} / eV	−0.473	−0.344	−1.238	−1.172	−1.536