Electronic Supplementary Material (ESI) for RSC Advances.

Efficient Electrocatalytic Reduction of Carbon Dioxide by Metal−doped β_{12}−Borophene Monolayers

Supplemental Information

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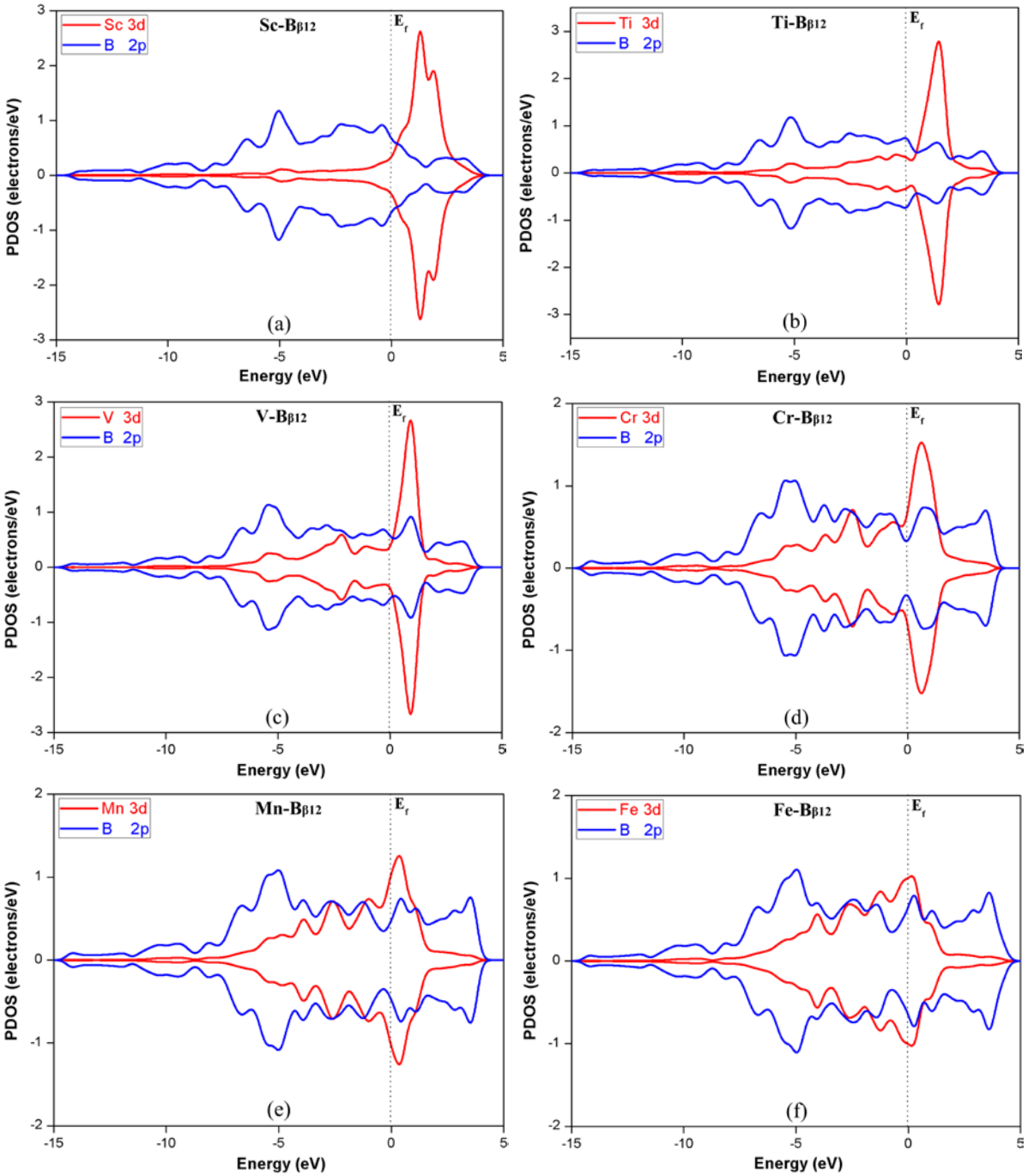
Fig. S1. The PDOS of the first transition metal series TM–$B_{\beta 12}$ monolayers. The dotted line denotes the Fermi level, the red, blue lines represent the 3d orbital of the metal atoms and the 2p orbital of the boron atom which nearest to the metal atoms, respectively.



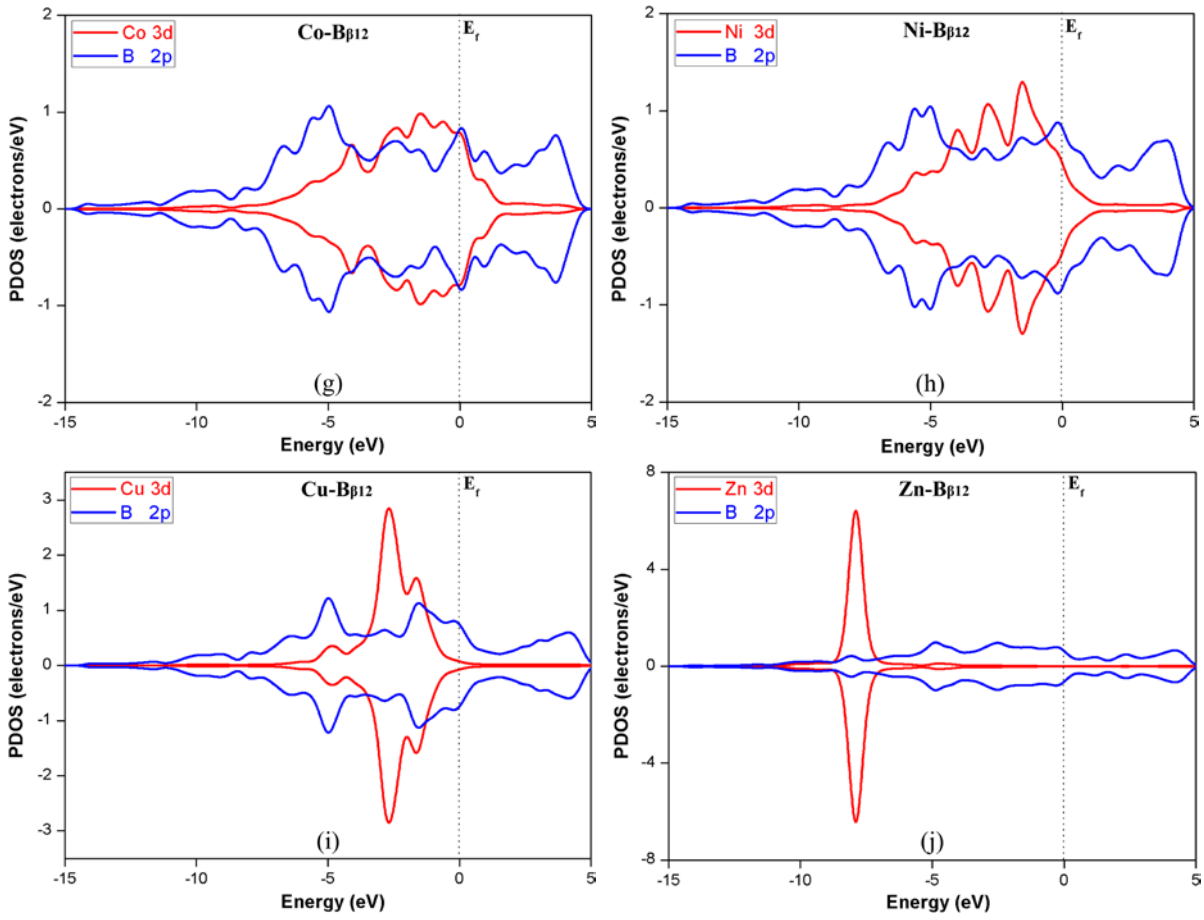

Co 3d
B 2p
Co-Bβ12
E_f
PDOS (electrons/eV)
Energy (eV)
(g)
Ni 3d
B 2p
Ni-Bβ12
E_f
PDOS (electrons/eV)
Energy (eV)
(h)
Cu 3d
B 2p
Cu-Bβ12
E_f
PDOS (electrons/eV)
Energy (eV)
(i)
Zn 3d
B 2p
Zn-Bβ12
E_f
PDOS (electrons/eV)
Energy (eV)
(j)

Fig. S2 The structures and binding energies of Fe atoms with $B_{\beta 12}$ monolayer: (a) Fe_3 cluster, (b) Fe_4 cluster, (c) 3 Fe single atoms and (d) 4 Fe single atoms.

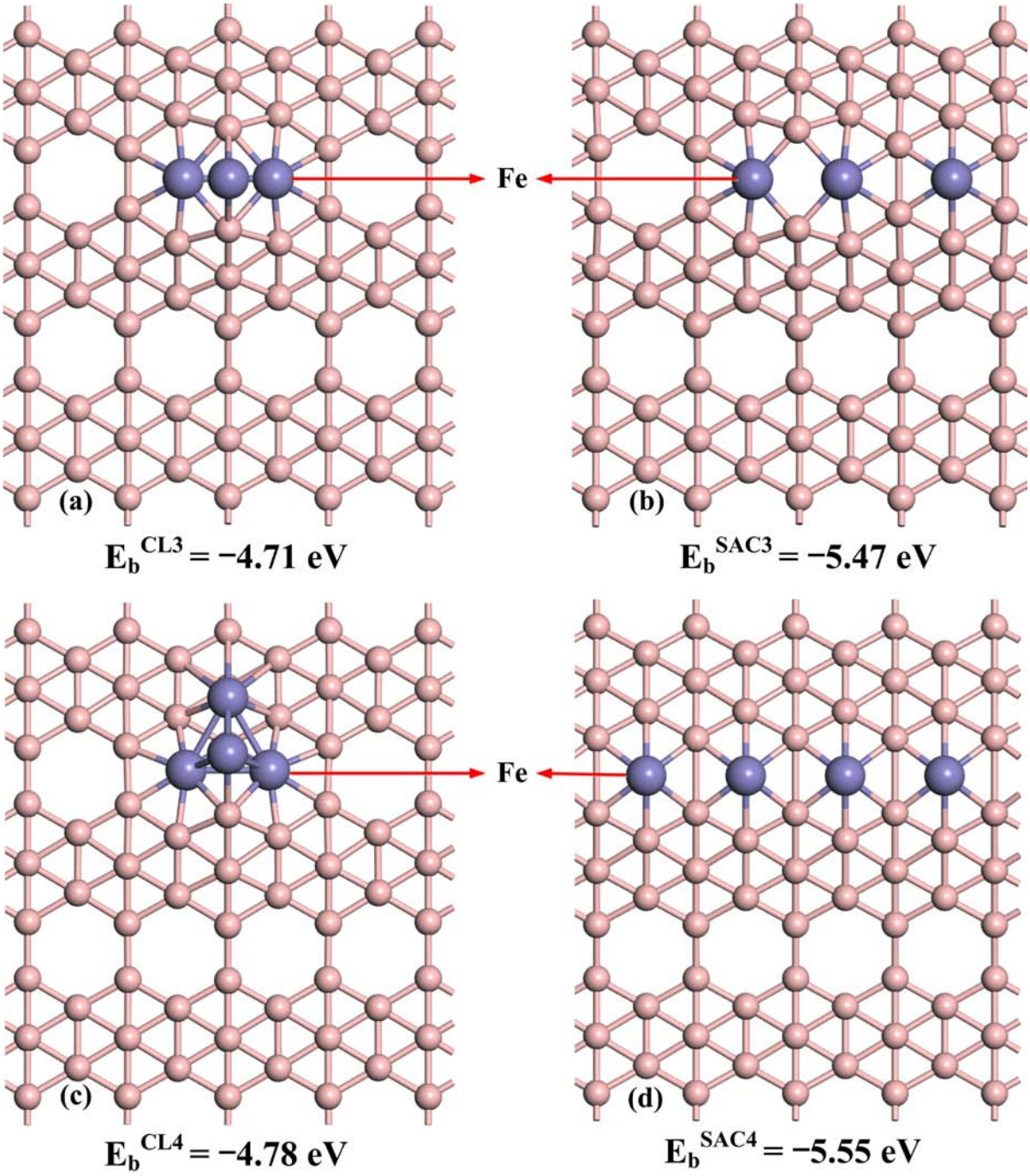


Table S1. E_b^{SAC1}, E_b^{SAC3} and E_b^{SAC4} are the binding energies of single, three and four metal atoms with $B_{\beta 12}$ monolayer, respectively. E_b^{CL3} and E_b^{CL4} are the binding energies of the metal clusters (three and four transition metals) with $B_{\beta 12}$ monolayer, respectively. E_c are the cohesive energies of TM bulks, where TM are the metal atoms of the first transition metal series.

TM−$B_{\beta 12}$	E_b^{SAC1} / eV	E_b^{CL3} / eV	E_b^{SAC3} / eV	E_b^{CL4} / eV	E_b^{SAC4} / eV	E_c / eV
Sc	−6.16	−4.24	−5.54	−4.63	−5.66	−4.57
Ti	−6.07	−5.30	−6.59	−5.46	−7.00	−5.56
V	−4.44	−4.70	−5.66	−4.70	−6.03	−5.51
Cr	−2.95	−3.30	−4.07	−3.23	−4.45	−4.37
Mn	−3.41	−3.62	−4.12	−3.35	−4.36	−4.23
Fe	−4.71	−4.71	−5.47	−4.78	−5.55	−5.33
Co	−4.97	−5.09	−5.83	−4.77	−5.93	−5.59
Ni	−4.42	−4.93	−5.47	−4.61	−5.66	−5.02
Cu	−3.08	−2.81	−2.93	−2.93	−3.00	−3.76
Zn	−1.17	−0.89	−0.82	−0.89	0.28	−1.54

[1]E_b are the binding energies of metal atoms with the $B_{\beta 12}$ monolayer, which is calculated by: $E_b = (E_{TMn-B\beta 12} - nE_{TM} - E_{B\beta 12}) / n$, where the $E_{TMn-B\beta 12}$, E_{TM} and $E_{B\beta 12}$ are the energies of TM_n–$B_{\beta 12}$, metal atoms and $B_{\beta 12}$ monolayer, and n is the number of metal atoms.

[2]E_c are the cohesive energies of transition 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 single metal atom and n is the number of metal atoms in the crystal.

Table S2. The 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–$B_{\beta12}$.

TM−$B_{\beta12}$	**ΔG_H / eV**	**ΔG_{C*OOH} / eV**	**ΔG_{O*CHO} / eV**
Sc	0.725	−0.155	−1.046
Ti	0.515	−0.472	−1.279
V	0.185	−0.800	−1.507
Cr	−0.026	−0.769	−1.266
Mn	−0.168	−0.557	−0.828
Fe	−0.130	−0.510	−0.406
Co	0.035	−0.378	−0.250
Ni	0.450	−0.308	−0.439
Cu	0.709	0.246	−0.304
Zn	−0.101	−0.202	−0.665

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

TM–$B_{\beta12}$		CO	HCOOH	HCHO	CH_3OH	CH_4
Sc	$R_{Sc-C/Sc-O}$ / Å	2.455	2.146	2.110	2.161	3.975
	E_{ads} / eV	−0.403	−1.024	−0.968	−1.247	0.015
Ti	$R_{Ti-C/Ti-O}$ / Å	2.126	2.064	2.043	2.069	2.352
	E_{ads} / eV	−1.085	−1.243	−1.137	−1.391	−0.414
V	$R_{V-C/V-O}$ / Å	1.994	2.002	1.939	2.009	2.388
	E_{ads} / eV	−1.421	−1.347	−1.342	−1.502	−0.508
Cr	$R_{Cr-C/Cr-O}$ / Å	1.909	2.004	1.936	1.998	2.371
	E_{ads} / eV	−1.952	−1.277	−1.305	−1.360	−0.486
Mn	$R_{Mn-C/Mn-O}$ / Å	1.821	2.006	1.945	2.000	2.375
	E_{ads} / eV	−2.244	−1.105	−1.187	−1.159	−0.522
Fe	$R_{Fe-C/Fe-O}$ / Å	1.711	2.026	1.951	2.052	2.478
	E_{ads} / eV	−2.172	−0.876	−0.937	−1.002	−0.364
Co	$R_{Co-C/Co-O}$ / Å	1.748	2.043	1.977	2.065	3.602
	E_{ads} / eV	−2.002	−0.784	−0.729	−0.811	−0.392
Ni	$R_{Ni-C/Ni-O}$ / Å	1.759	1.959	1.895	1.978	2.993
	E_{ads} / eV	−1.822	−0.863	−0.929	−0.975	−0.119
Cu	$R_{Cu-C/Cu-O}$ / Å	1.847	2.026	2.005	2.038	2.327
	E_{ads} / eV	−1.393	−0.871	−0.828	−1.012	−0.379
Zn	$R_{Zn-C/Zn-O}$ / Å	1.996	2.023	2.022	2.019	2.413
	E_{ads} / eV	−0.919	−1.011	−0.914	−1.204	−0.288