Electronic Supplementary Information

Understanding the interaction between transition metal doping and ligand atoms of ZnS and ZnO monolayers to promote CO_2 reduction reaction

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Table S1 Binding energy (E_b), cohesive energy (E_c), and formation energy (E_f) of the TM-ZnS surfaces, total energy of CO_2 adsorbed on the surfaces ($E_{complex}$), CO_2 adsorption energy (E_{ads}), distortion energy (E_{dist}), the total energy of the clean surface before CO_2 adsorption (E_{inital}) and the total energy of the clean surface after CO_2 adsorption (E_{final}) which are the distorting surfaces. The binding energy of the TM-ZnO is given in parenthesis.

TMs	E_b **(eV)**	E_c **(eV)**	E_f **(eV)**	$E_{complex}$ **(eV)**	E_{inital} **(eV)**	E_{final} **(eV)**	E_{dist} **(eV)**	E_{ads} **(eV)**
Sc	-8.79 (-12.3)	-4.42	-3.25	-135.24	-110.55	-111.01	-0.46	-1.26
Ti	-9.24 (-12.5)	-5.81	-3.69	-135.98	-111.38	-110.94	0.43	-2.07
V	-8.63 (-10.8)	-5.89	-3.09	-135.21	-111.91	-111.86	0.05	-0.39
Cr	-7.03 (-9.2)	-4.49	-1.49	-135.81	-112.12	-112.61	-0.49	-0.23
Mn	-7.63 (-9.1)	-4.16	-2.09	-135.98	-112.42	-112.78	-0.36	-0.23
Fe	-7.82 (-9.6)	-5.20	-2.28	-134.34	-110.82	-111.14	-0.32	-0.24
Co	-8.04 (-9.2)	-5.74	-2.50	-132.57	-109.34	-109.35	-0.01	-0.25
Ni	-7.61 (-8.7)	-5.27	-2.07	-131.04	-107.86	-107.86	-0.01	-0.21
Cu	-6.08 (-6.8)	-3.99	-0.54	-129.50	-105.97	-106.30	-0.33	-0.24
ZnS				-128.70	-105.20	-105.52	-0.32	-0.22

The binding energy, formation energy and cohesive energy are defined as

$$E_b = E_{surface\ TM\text{-}ZnS} - E_{surface\ V\text{-}ZnS} - E_{TM}, \quad (1)$$

$$E_c = E_{TM\text{-}bulk/n} - E_{TM}, \quad (2)$$

$$E_f = E_{surface\ TM\text{-}ZnS} - E_{surface\ ZnS} - nE_{TM} + nE_{Zn}, \quad (3)$$

where $E_{surface\ TM\text{-}ZnS}$, $E_{surface\ V\text{-}ZnS}$, $E_{surface\ ZnS}$, E_{TM}, $E_{TM\text{-}bulk}$, E_{TM} and E_{Zn} is total energy of the TM-doped ZnS monolayer, the Zn vacancy on the ZnS surface, the pristine ZnS surface, the isolated gas, the bulk transition metals, the isolated transition metals and the isolated Zn, respectively, where TM is Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu. Additionally, n is the number of transition metals added or removed from the ZnS surface to model the TM-doped ZnS surfaces.[1, 2].

The Gibbs free energy is calculated using the computational hydrogen electrode method proposed by Nørskov *et al.*[3] using the equation

$$G = E + ZPE - TS + \int C_p dT + E_{sol} \quad (4)$$

where E, ZPE, TS, $\int C_p dT$ and E_{sol} are the total electronic energy, the zero-point energy, the entropy correction, the enthalpic temperature correction, and solvation energy correction, respectively. The reaction is studied at 298 K, so vibrational frequency is calculated at 298 K. Table S4 lists energy correction employed for Gibb free energy calculation.

The Gibbs free energy change (ΔG) between the two intermediate states were calculated from the equation below,

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \int C_p dT + \Delta E_{sol} + \Delta G_{pH} + \Delta G_U \quad (5)$$

where ΔE is the electronic energy difference between the two intermediate states. ΔE_{ZPE}, and $T\Delta S$ are the change in zero-point energies and entropic contribution. ΔE_{sol} is the change in solvation energy where -0.2, -0.1, and 0.0 eV is added for the species with OH group direct bond to metal atom, with OH group indirect bond to metal atoms, and the species without OH group, respectively.[4] ΔG_{pH} and ΔG_U are the change variation in the pH of the solution, and the difference in electrode potential of the electrochemical reaction, respectively. $\Delta G_{pH} = 2.303 k_b T pH$, where k_b and pH are the Boltzmann constant, and pH of the solution, accordingly. As this study is assumed to be under highly acidic conditions of pH=0, thus, ΔG_{pH}=0. Moreover, $\Delta G_U = -neU$ where n, e, and U are the number of transferred electrons, the electron charge, and applied potential to the reaction, respectively.[5, 6] For the limiting potential (U_L), it can be obtained following the equation of

$$U_L = -\Delta G_{max}/e \quad (6)$$

where ΔG_{max} is the ΔG of the reaction with the largest free energy change.[1]

Adsorption energy (E_{ads}) of adsorbates and the ZnS and TM-ZnS monolayers for this study is defined as

$$E_{ads} = E_{complex} - E_{surface} - E_{gas} \quad (7)$$

where $E_{complex}$, $E_{surface}$ and E_{gas} are the total energy of the gas adsorbed on the TM-ZnS monolayers, the TM-ZnS clean surfaces, and the isolated gas molecule, respectively.

Since the surfaces distort after the CO_2 adsorption, the distortion energy of the surfaces should be counted for the CO_2 adsorption. CO_2 adsorption energy (E_{ads}) is calculated using the equation of $E_{ads} = E_{complex} - E_{surface} - E_{CO2} - E_{dist}$ where $E_{complex}$, $E_{surface}$, E_{dist} and E_{CO2} is total energy of CO_2 adsorbed on surfaces, total energy of clean surface distortion energy and total energy of isolated CO_2 gas, respectively. The distortion energy is calculated by $E_{dist} = E_{inital} - E_{final}$ when E_{inital}

is the total energy of the clean surface before CO_2 adsorption while E_{final} is the total energy of the clean surface after CO_2 adsorption then CO_2 gas is removed from the complexes.

Table S2 The total electronic energy (E_{tot}), the zero-point energy (ZPE), the entropy correction (TdS), the enthalpic temperature correction ($\int C_p dT$), solvation energy correction (E_{sol}), chemical potential (μ), Gibb free energy (G), and Gibb free energy change (ΔG) of each intermediate state.

Molecules	**E_{tot} (eV)**	**ZPE (eV)**	**TdS (eV)**	**$\int C_p dT$ (eV)**	**μ (eV)**	**G (eV)**
$H_{2(g)}$	-6.77	0.27	0.40	0.09		-6.81
H	-3.38					-3.40
$CO_{2(g)}$	-22.96	0.31	0.66	0.10		-23.22
$CO_{(g)}$	-14.78	0.14	0.61	0.09		-15.17
$CH_2O_{(g)}$	-22.14	0.71	0.68	0.11		-22.00
$CH_{4(g)}$	-24.04	1.19	0.58	0.11		-23.32
$H_2O_{(l)}$	-14.22	0.57	0.58	0.10	-0.09	-14.22
$HCOOH_{(l)}$	-29.72	0.88	0.77	0.12	-0.22	-29.72
$CH_3OH_{(l)}$	-30.22	1.36	0.74	0.12	-0.07	-29.56

Surfaces	**intermediate states**	**E_{tot} (eV)**	**ZPE (eV)**	**TdS (eV)**	**$\int C_p dT$ (eV)**	**E_{sol} (eV)**	**G (eV)**	**ΔG (eV)**
ZnS	Clean surface	-105.20						
	*H	-107.14	-1.94	0.09	0.09	0.04	-1.90	1.50
	*COOH	-130.79	0.59	0.26	0.11	-0.10	-25.25	1.37
	*OCHO	-131.13	0.62	0.20	0.10		-25.41	1.21
	*CO	-120.56	0.17	0.22	0.09		-15.31	0.50
	*HCOOH	-135.69	0.91	0.26	0.11	-0.10	-29.82	0.20
	*OCH_2O	-132.67	0.80	0.26	0.12		-26.80	3.22
	*COHOH	-135.06	0.94	0.22	0.11	-0.10	-29.14	0.89
	*CHO	-123.23	0.43	0.24	0.10		-17.74	1.47
	*COH	-121.55	0.43	0.16	0.07	-0.10	-16.10	3.11

Surfaces	**intermediate states**	**E_{tot} (eV)**	**ZPE (eV)**	**TdS (eV)**	**$\int C_p dT$ (eV)**	**E_{sol} (eV)**	**G (eV)**	**ΔG (eV)**
	*$HOCH_2O$	-137.89	1.19	0.24	0.12	-0.20	-31.82	1.61
Sc-ZnS	Clean surface	-110.55						
	*H	-115.29	0.14	0.03	0.02		-4.62	-1.22
	*COOH	-139.16	0.61	0.18	0.09	-0.10	-28.19	-1.57
	*OCHO	-140.65	0.63	0.19	0.10		-29.58	-2.96
	*CO	-127.15	0.18	0.20	0.08		-16.54	-0.73
	*HCOOH	-142.55	0.87	0.26	0.12	-0.10	-31.36	-1.34
	*OCH_2O	-142.36	0.85	0.21	0.11		-31.06	-1.04
	*COHOH	-141.18	0.90	0.22	0.10	-0.10	-29.95	0.07
Ti-ZnS	Clean surface	-111.38						
	*H	-115.26	0.15	0.03	0.02		-3.74	-0.34
	*COOH	-139.26	0.62	0.21	0.10	-0.10	-27.47	-0.85
	*OCHO	-140.40	0.62	0.19	0.10		-28.50	-1.88
V-ZnS	Clean surface	-111.91						
	*H	-115.56	0.16	0.02	0.02		-3.49	-0.09
	*COOH	-139.24	0.62	0.20	0.10	-0.10	-26.91	-0.29
	*OCHO	-140.37	0.62	0.20	0.10		-27.93	-1.31
Cr-ZnS	Clean surface	-112.12						
	*H	-115.73	0.16	0.03	0.02		-3.45	-0.05
	*COOH	-139.27	0.62	0.20	0.10	-0.10	-26.72	-0.10
	*OCHO	-140.17	0.63	0.19	0.10		-27.52	-0.90
Mn-ZnS	Clean surface	-112.42						
	*H	-115.59	0.15	0.04	0.02		-3.03	0.37
	*COOH	-139.00	0.61	0.26	0.11	-0.10	-26.22	0.40
	*OCHO	-139.67	0.63	0.18	0.09		-26.69	-0.07
	*CO	-128.12	0.18	0.19	0.09		-15.62	0.19
	*HCOOH	-143.14	0.92	0.34	0.13	-0.10	-30.11	-0.09
	*OCH_2O	-141.77	0.88	0.22	0.10		-28.58	1.45

Surfaces	**intermediate states**	**E_{tot} (eV)**	**ZPE (eV)**	**TdS (eV)**	**$\int C_p dT$ (eV)**	**E_{sol} (eV)**	**G (eV)**	**ΔG (eV)**
	*COHOH	-142.05	0.93	0.22	0.11	-0.10	-28.91	1.11
	*CHO	-131.43	0.45	0.13	0.06		-18.62	0.59
	*COH	-130.27	0.47	0.13	0.07	-0.10	-17.54	1.67
	*$HOCH_2O$	-146.60	0.88	0.22	0.10	-0.20	-33.61	-0.19
	*CHOH	-134.53	0.76	0.23	0.10	-0.10	-21.58	1.04
	*CH_2O	-135.56	0.76	0.25	0.11		-22.52	0.10
	*CH_2OH	-139.22	1.09	0.20	0.10	-0.10	-25.91	0.10
	*CH	-123.05	0.34	0.09	0.05		-10.33	1.47
	*CH_3O	-139.59	1.09	0.23	0.10		-26.20	-0.18
	*CH_3OH	-143.80	1.41	0.21	0.10	-0.20	-30.28	-0.85
	*O+CH_4	-142.54	1.28	0.18	0.09		-28.92	0.50
	*CH_2	-127.59	0.59	0.15	0.07		-14.66	0.55
	*CH_3	-132.61	0.93	0.15	0.08		-19.34	-0.73
	*OH+CH_4	-147.60	1.55	0.37	0.16	-0.20	-34.04	-1.21
	*H_2O	-127.62	0.64	0.15	0.07	-0.20	-14.83	-1.93
	*CH_4	-137.03	1.21	0.19	0.08		-23.51	-1.49
Fe-ZnS	Clean surface	-110.82						
	*H	-113.92	0.16	0.04	0.02		-2.95	0.45
	*COOH	-137.49	0.61	0.22	0.10	-0.10	-26.27	0.35
	*OCHO	-138.33	0.62	0.20	0.10		-26.99	-0.37
	*CO	-126.94	0.22	0.14	0.06		-15.98	-0.17
	*HCOOH	-141.37	0.91	0.22	0.11	-0.10	-29.85	0.17
	*OCH_2O	-140.32	0.89	0.18	0.10		-28.70	1.33
	*COHOH	-140.96	0.94	0.20	0.10	-0.10	-29.40	0.63
	*CHO	-130.11	0.43	0.23	0.10		-18.99	0.22
	*COH	-129.05	0.47	0.18	0.09	-0.10	-17.96	1.25
	*$HOCH_2O$	-145.21	1.22	0.22	0.11	-0.20	-33.48	-0.05
	*CHOH	-133.22	0.78	0.19	0.09	-0.10	-21.81	0.80

Surfaces	intermediate states	E_{tot} (eV)	ZPE (eV)	TdS (eV)	$\int C_p dT$ (eV)	E_{sol} (eV)	G (eV)	ΔG (eV)
	*CH_2O	-134.13	0.77	0.19	0.09		-22.64	-0.03
	*CH_2OH	-137.57	1.09	0.21	0.10	-0.10	-25.87	0.15
	*CH	-121.28	0.34	0.09	0.05		-10.16	1.64
	*CH_3O	-138.22	1.07	0.21	0.09		-26.45	-0.43
	*CH_3OH	-142.02	1.41	0.28	0.12	-0.20	-30.14	-0.72
	*O+CH_4	-140.96	1.28	0.29	0.11		-29.03	0.39
	*CH_2	-126.00	0.61	0.13	0.06		-14.64	0.57
	*CH_3	-130.86	0.93	0.14	0.07		-19.18	-0.57
	*OH+CH_4	-146.22	1.54	0.43	0.19	-0.20	-34.30	-1.47
	*H_2O	-125.84	0.65	0.21	0.09	-0.20	-14.70	-1.79
	*CH_4	-135.34	1.21	0.27	0.11		-23.47	-1.46
Co-ZnS	Clean surface	-109.34						
	*H	-112.53	0.17	0.03	0.02		-3.04	0.37
	*COOH	-136.05	0.62	0.23	0.11	-0.10	-26.32	0.30
	*OCHO	-136.14	0.62	0.19	0.10		-26.27	0.35
	*CO	-125.42	0.20	0.17	0.07		-15.98	-0.18
	*HCOOH	-139.80	0.92	0.23	0.10	-0.10	-29.76	0.26
	*OCH_2O	-138.07	0.87	0.19	0.10		-27.95	2.08
	*COHOH	-139.73	0.94	0.21	0.10	-0.10	-29.66	0.36
	*CHO	-128.62	0.46	0.18	0.08		-18.91	0.30
	*COH	-127.36	0.48	0.17	0.08	-0.10	-17.73	1.48
	*$HOCH_2O$	-143.02	1.22	0.23	0.12	-0.20	-32.77	0.66
	*CHOH	-132.10	0.79	0.17	0.09	-0.10	-22.15	0.46
	*CH_2O	-132.22	0.76	0.13	0.07		-22.18	0.43
	*CH_2OH	-136.22	1.10	0.19	0.10	-0.10	-25.98	0.04
	*CH	-119.58	0.33	0.10	0.05		-9.96	1.84
	*CH_3O	-136.16	1.08	0.22	0.10		-25.86	0.16
	*CH_3OH	-140.46	1.41	0.20	0.10	-0.20	-30.01	-0.59

Surfaces	**intermediate states**	**E_{tot} (eV)**	**ZPE (eV)**	**TdS (eV)**	**$\int C_p dT$ (eV)**	**E_{sol} (eV)**	**G (eV)**	**ΔG (eV)**
	*O+CH_4	-139.19	1.26	0.26	0.12		-28.73	0.69
	*CH_2	-124.50	0.62	0.12	0.06		-14.60	0.60
	*CH_3	-129.50	0.94	0.14	0.07		-19.28	-0.67
	*OH+CH_4	-144.06	1.54	0.37	0.17	-0.20	-33.59	-0.76
	*H_2O	-124.27	0.65	0.13	0.07	-0.20	-14.55	-1.64
	*CH_4	-133.55	1.21	0.19	0.08		-23.11	-1.10
Ni-ZnS	Clean surface	-107.86						
	*H	-111.22	0.225	0.013	0.010		-3.15	0.26
	*COOH	-134.59	0.62	0.22	-0.10	-0.10	-26.54	0.08
	*OCHO	-134.32	0.62	0.20	0.10		-25.95	0.67
Cu-ZnS	Clean surface	-105.97						
	*H	-110.34	0.23	0.01	0.01		-4.14	-0.74
	*COOH	-132.73	0.56	0.22	0.10	-0.10	-26.41	0.21
	*OCHO	-132.24	0.62	0.19	0.10		-25.74	0.88
	*CO	-121.64	0.19	0.13	0.06		-15.55	0.25
	*HCOOH	-136.84	0.91	0.27	0.12	-0.10	-30.21	-0.19
	*OCH_2O	-134.74	0.93	0.14	0.08		-27.89	2.14
	*COHOH	-136.20	0.92	0.20	0.10	-0.10	-29.50	0.52
	*CHO	-125.68	0.50	0.16	0.08		-19.29	-0.08
	*COH	-123.52	0.46	0.17	0.09	-0.10	-17.27	1.94
	*$HOCH_2O$	-138.99	1.21	0.23	0.12	-0.20	-32.12	1.31
	*CHOH	-128.58	0.79	0.14	0.08	-0.10	-21.98	0.63
	*CH_2O	-128.74	0.74	0.26	0.10		-22.19	0.43
	*CH_2OH	-132.88	1.10	0.21	0.10	-0.10	-26.02	0.00
	*CH	-117.25	0.39	0.04	0.03		-10.91	0.89
	*CH_3O	-132.01	1.06	0.23	0.11		-25.10	0.92
	*CH_3OH	-136.88	1.37	0.23	0.09	-0.20	-29.86	-0.44
	*O+CH_4	-136.25	1.28	0.27	0.12		-29.16	0.26

Surfaces	intermediate states	E_{tot} (eV)	ZPE (eV)	TdS (eV)	$\int C_p dT$ (eV)	E_{sol} (eV)	G (eV)	ΔG (eV)
	*CH_2	-122.02	0.68	0.07	0.04		-15.39	-0.18
	*CH_3	-125.90	0.95	0.16	0.07		-19.06	-0.45
	*OH+CH_4	-139.97	1.55	0.35	0.16	-0.20	-32.83	-0.01
	*H_2O	-121.01	0.65	0.18	0.09	-0.20	-14.68	-1.77
	*CH_4	-130.50	1.21	0.20	0.08		-23.44	-1.43

Table S3 Magnetic moment and total energy of Cu-ZnS, Ti-ZnO, V-ZnO and Cr-ZnO when the float and integer magnetic moment.

Surfaces	Magnetic moment (μ_B)	Total energy (eV)
Cu-ZnS	1.00	-105.98 (E_{min})
	0.68	-105.97
Ti-ZnO	0.68	-145.85 (E_{min})
	1.00	-145.84
V-ZnO	2.24	-145.26
	2.00	-145.26
Cr-ZnO	3.77	-145.47 (E_{min})
	3.00	-145.39
	4.00	-145.45

Table S4 Total magnetic moment obtained from OSZICAR ($M_s^{OSZICAR}$) and total energy (E_{tot}) for the high spin (HS) and the low spin (LS) states. The spin state providing the lower energy is labeled by E_{min}.

TM	$M_s^{OSZICAR}$ for HS (μ_B)	E_{tot} for HS (eV)	$M_s^{OSZICAR}$ for LS (μ_B)	E_{tot} for LS (eV)
Sc	0.80	-110.55 (E_{min})		
Ti	1.99	-111.38 (E_{min})	0.00	-110.29

V	3.00	-111.91 (E_{min})	1.00	-111.17
Cr	4.00	-112.12 (E_{min})	0.00	-110.91
Mn	5.00	-112.42 (E_{min})	1.00	-110.14
Fe	4.00	-110.82 (E_{min})	0.00	-109.26
Co	3.00	-109.34 (E_{min})	1.00	-108.71
Ni	2.00	-107.86 (E_{min})	0.00	-107.13
Cu	0.68	-105.97 (E_{min})	1.00	-105.97
Zn	0.00	-105.20 (E_{min})		

Table S5 Desorption free energy, G_{des}, and adsorption free energy, G_{ads}, for CO, HCOOH, CH_2O, CH_3OH and H_2O products.

surfaces	***G*$_{des}$(eV)**					***G*$_{ads}$(eV)**				
	$HCOOH_{(l)}$	**$CO_{(g)}$**	**$CH_2O_{(g)}$**	**$CH_3OH_{(l)}$**	**$H_2O_{(l)}$**	**$HCOOH_{(l)}$**	**$CO_{(g)}$**	**$CH_2O_{(g)}$**	**$CH_3OH_{(l)}$**	**$H_2O_{(l)}$**
ZnS	0.11	0.14				-0.11	-0.14			
Sc-ZnS	1.65	1.37	2.39	1.25	1.16	-1.65	-1.37	-2.39	-1.25	-1.16
Mn-ZnS	0.39	0.45	0.51	0.72	0.62	-0.39	-0.45	-0.51	-0.72	-0.62
Fe-ZnS	0.13	0.81	0.64	0.58	0.48	-0.13	-0.81	-0.64	-0.58	-0.48
Co-ZnS	0.05	0.82	0.18	0.45	0.33	-0.05	-0.82	-0.18	-0.45	-0.33
Cu-ZnS	0.49	0.39	0.19	0.31	0.46	-0.49	-0.39	-0.19	-0.31	-0.46

$G_{ads} = -G_{des}$ when G_{ads} is calculated using an equation of $G_{ads} = G_{complex} - G_{product}$ where $G_{complex}$ and $G_{product}$ are the free energy of the species adsorbed on the surface and the isolated products, respectively.

Table S6 Magnetic monument (M_s) of each species adsorbed on Mn-ZnS surface in the vacuum with 3d-orbital and oxidation state of the Mn atom as well as number of electrons (no. of e^-) and total energy (E_{tot}) of each complex, where M_{Mn} is the magnetization of Mn atom.

Protonation step	**Intermediated states**	**M_s (μ_B)**	**M_{Mn} (μ_B)**	**3d-orbital of Mn**	**Oxidation states**	**E_{tot} (eV)**
Mn-ZnS surface		5.00	4.19	$3d^5$	2^+	-112.42
1^{st} (H^++e^-)	*COOH	4.00	3.64	$3d^4$	3^+	-139.00
	*OCHO	4.00	3.58	$3d^4$	3^+	-139.67
2^{nd} (H^++e^-)	*HCOOH	5.00	4.28	$3d^5$	2^+	-143.14
	*OCH_2O	3.00	2.77	$3d^3$	4^+	-141.77
	*$CO+H_2O_{(l)}$	5.00	4.07	$3d^5$	2^+	-142.34
	*COHOH	3.00	2.84	$3d^5$	2^+	-142.05
3^{rd} (H^++e^-)	*$COH+H_2O_{(l)}$	2.00	2.10	$3d^6$	1^+	-144.49
	*$CHO+H_2O_{(l)}$	4.00	3.63	$3d^4$	3^+	-145.65
	*$HOCH_2O$	4.00	3.56	$3d^4$	3^+	-146.60
4^{th} (H^++e^-)	*CHOH	3.00	3.00	$3d^5$	2^+	-134.53
	*CH_2O	5.00	4.25	$3d^5$	2^+	-135.56
5^{th} (H^++e^-)	*CH_2OH	4.00	3.69	$3d^4$	3^+	-139.22
	*CH_3O	4.00	3.53	$3d^4$	3^+	-139.59
6^{th} (H^++e^-)	*CH_3OH	5.00	4.28	$3d^5$	2^+	-143.80
	*$O+CH_4$	5.00	4.24	$3d^5$	2^+	-142.54
7^{th} (H^++e^-)	*$OH+CH_4$	4.00	3.55	$3d^4$	3^+	-147.41
	*OH	4.00	3.55	$3d^4$	3^+	-147.60
8^{th} (H^++e^-)	*H_2O	5.00	4.28	$3d^5$	2^+	-127.62
	*CH_4	5.00	4.26	$3d^5$	2^+	-137.03

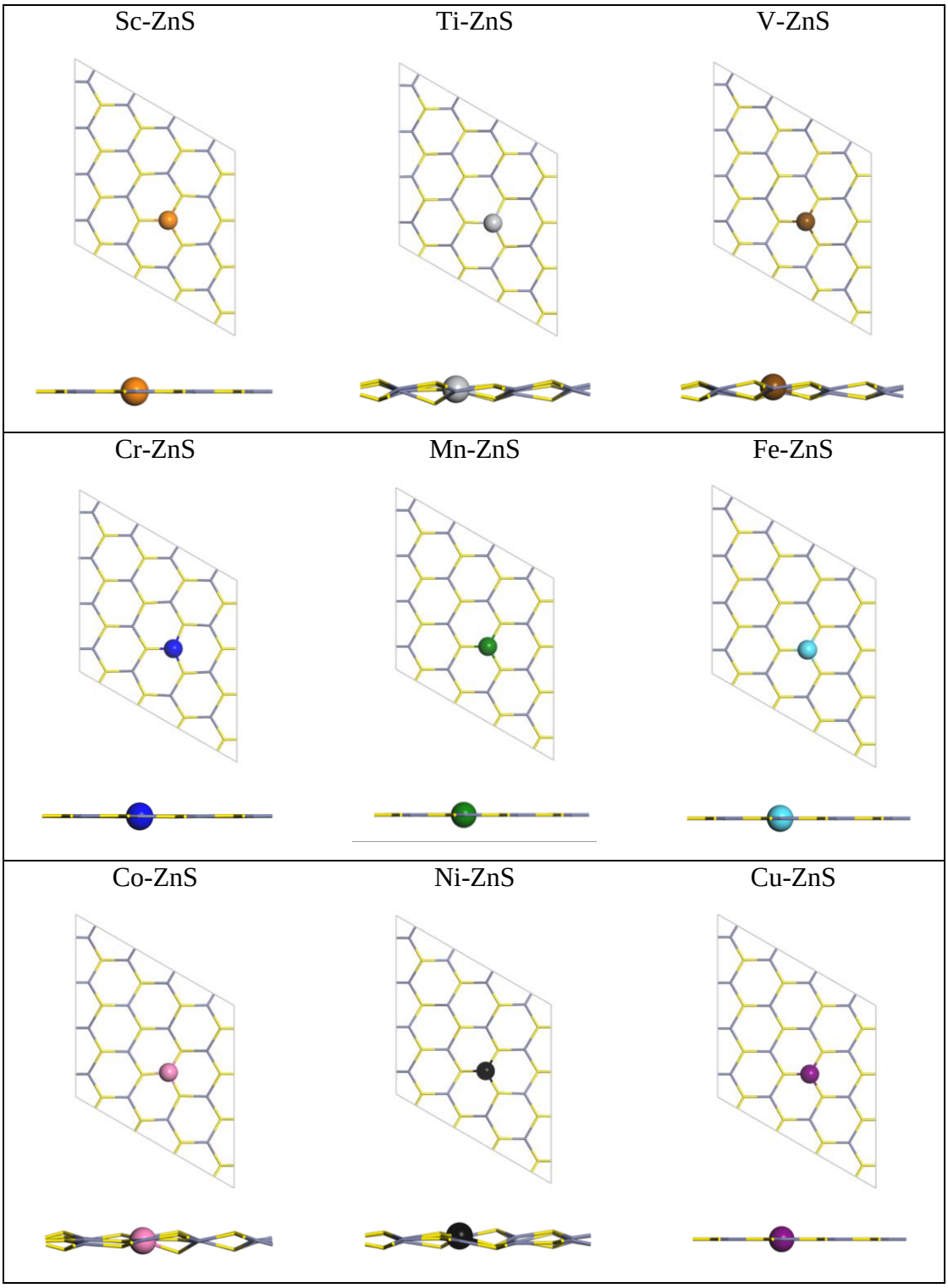


Figure S1 The TM-ZnS structures where TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu atoms where flint, yellow, orange, light grey, brown, dark blue, green, light blue, pink, black and purple balls are Zn, S, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu atoms, respectively.

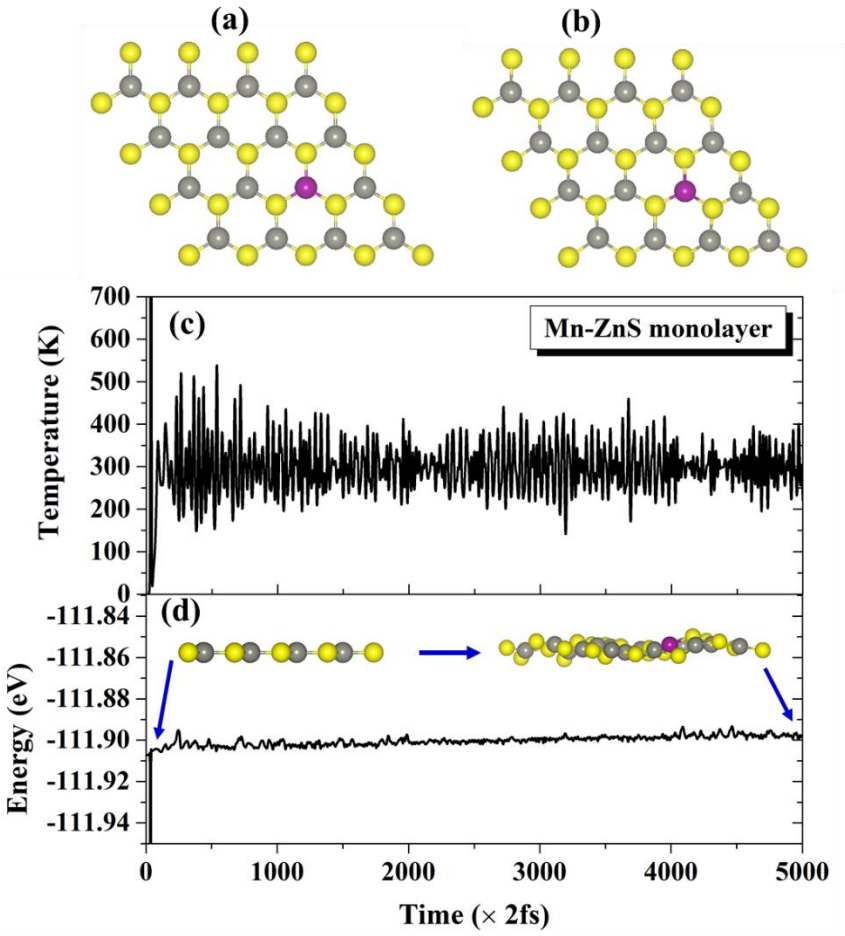


Figure S2 AIMD simulation of Mn-ZnS monolayer is calculated at 300 K for 10 ps with a time step of 2 fs. Top view of the surface at (a) starting time and (b) after the dynamic calculation for 10 ps. (c) temperature variation and (d) energy change during the calculation with side view of the surface starting time and 10 ps. Grey, purple and yellow balls are Zn, Mn and S atoms, respectively.

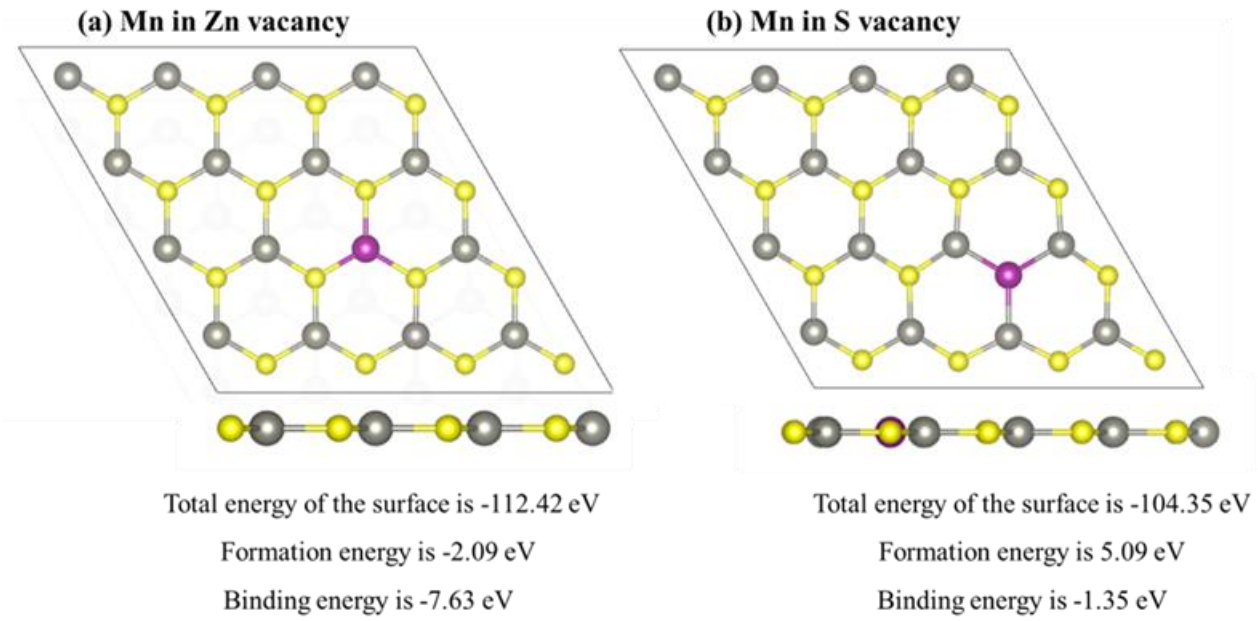


Figure S3 Geometry of Mn doping to Zn vacancy and S vacancy of ZnS monolayer, the formation energy, and the binding energy. The binding and formation energies are calculated using equations (1) and (3) mentioned above.

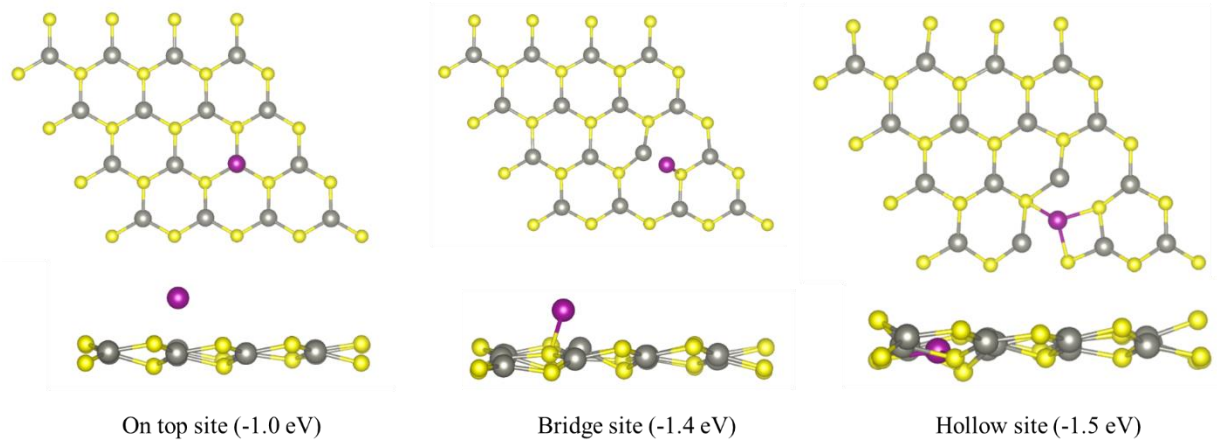


Figure S4 Geometry of Mn doping to pristine ZnS monolayer at different sites and the binding energy. The binding energy is calculated using equation (1) mentioned above.

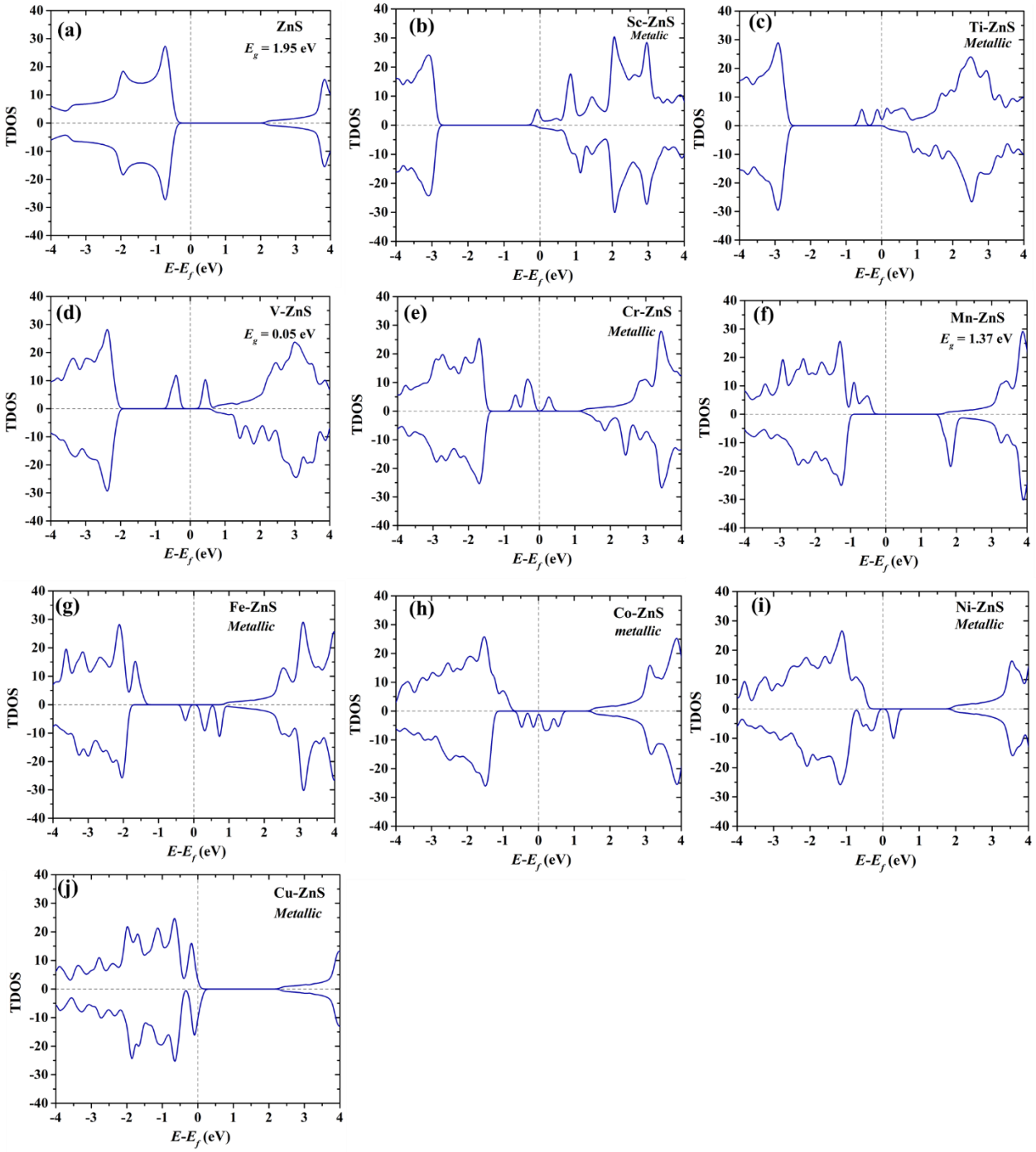


Figure S5 Total DOS (TDOS) of bare (a) ZnS, (b) Sc-ZnS, (c) Ti-ZnS, (d) V-ZnS, (e) Cr-ZnS, (f) Mn-ZnS, (g) Fe-ZnS, (h) Co-ZnS, (i) Ni-ZnS and (j) Ni-ZnS monolayers.

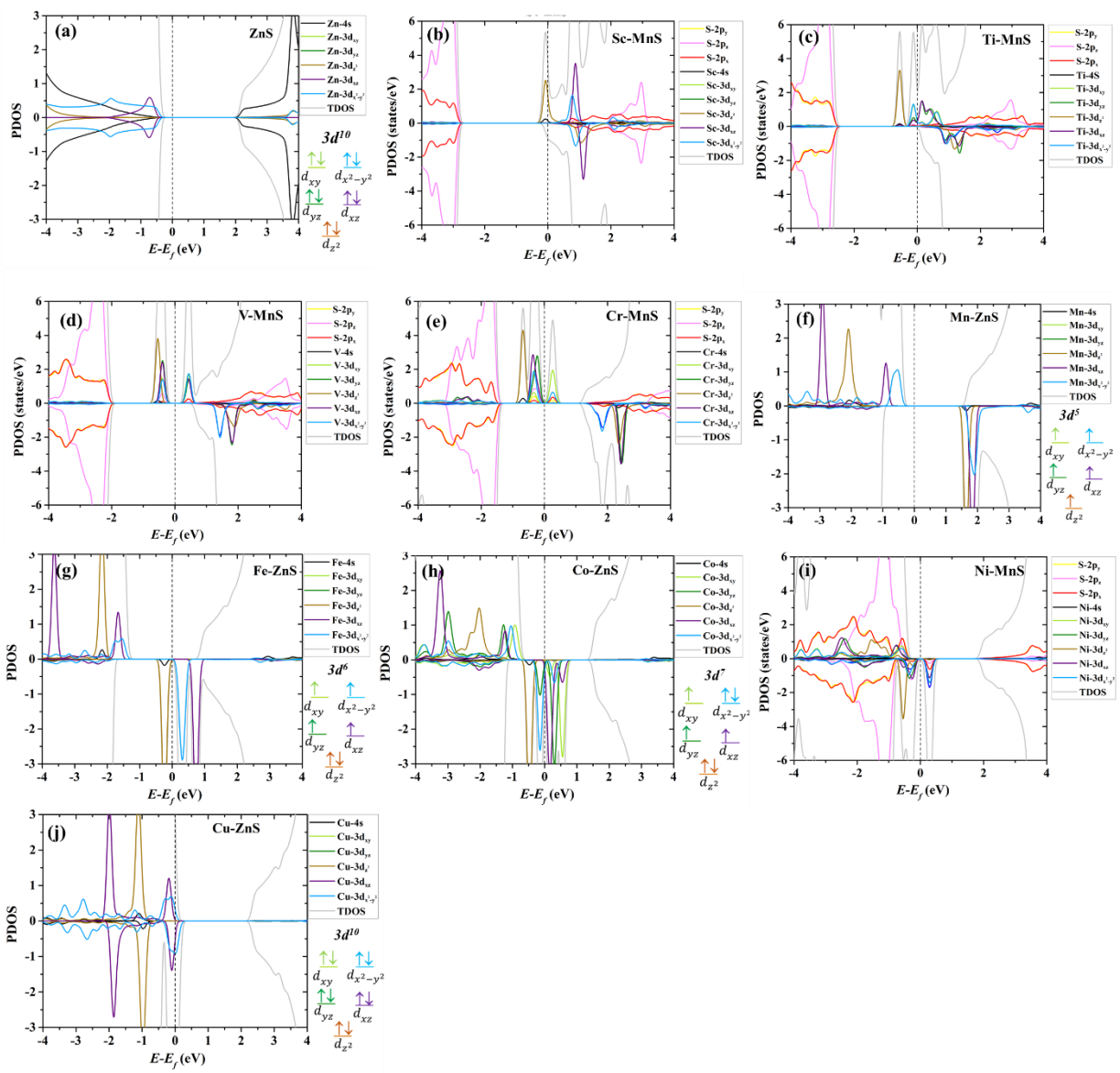


Figure S6 Projected DOS (PDOS) as well as *3d* orbital configuration of (a) ZnS, (b) Sc-ZnS, (c) Ti-ZnS, (d) V-ZnS, (e) Cr-ZnS, (f) Mn-ZnS, (g) Fe-ZnS, (h) Co-ZnS, (i) Ni-ZnS and (j) Ni-ZnS.

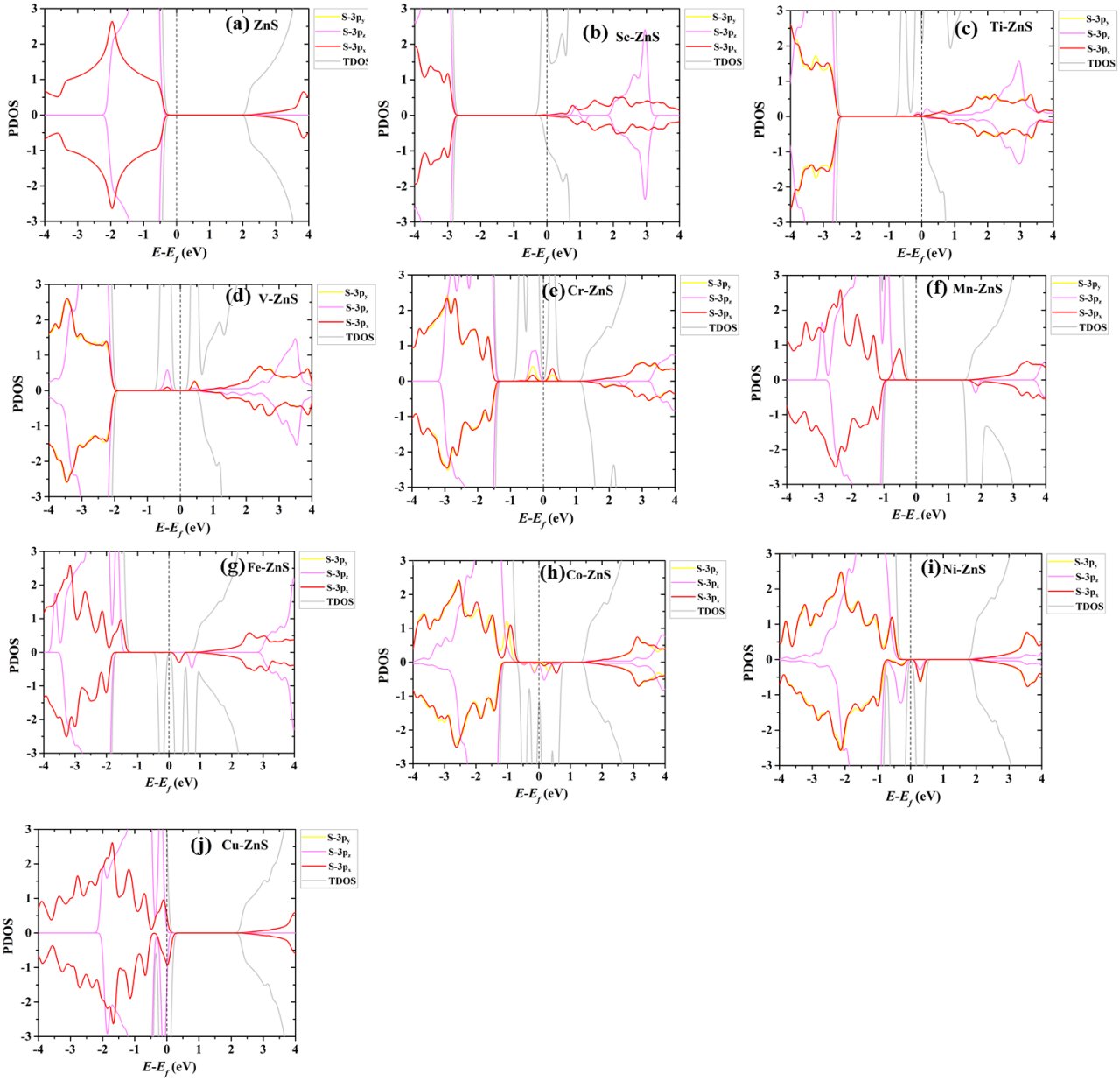


Figure S7 Projected DOS (PDOS) of sulfur for (a) ZnS, (b) Sc-ZnS, (c) Ti-ZnS, (d) V-ZnS, (e) Cr-ZnS, (f) Mn-ZnS, (g) Fe-ZnS, (h) Co-ZnS, (i) Ni-ZnS and (j) Ni-ZnS monolayers.

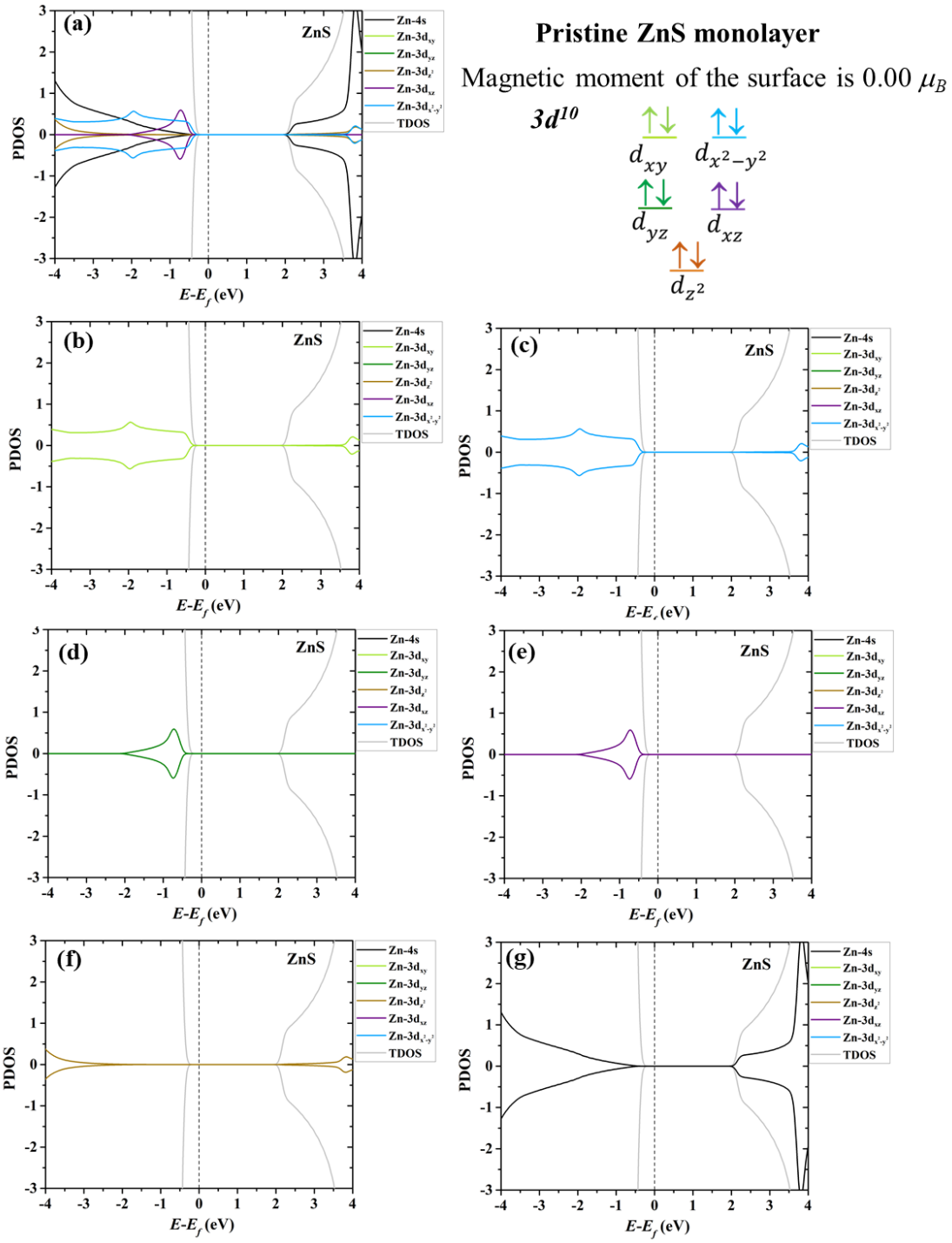


Figure S8 Projected DOS (PDOS) of Zn for the pristine ZnS monolayer.

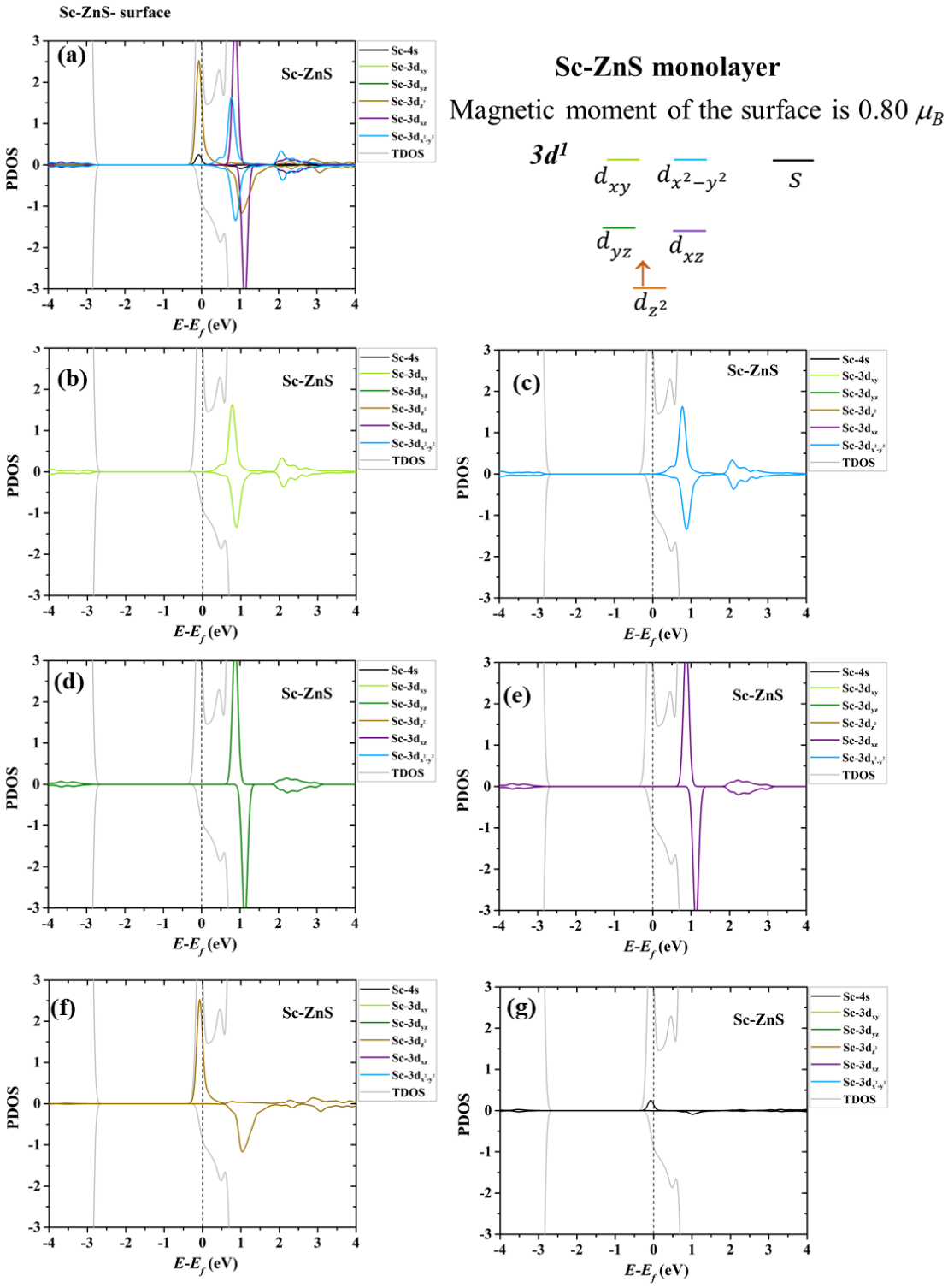


Figure S9 Projected DOS (PDOS) of Sc for the Sc-ZnS monolayer.

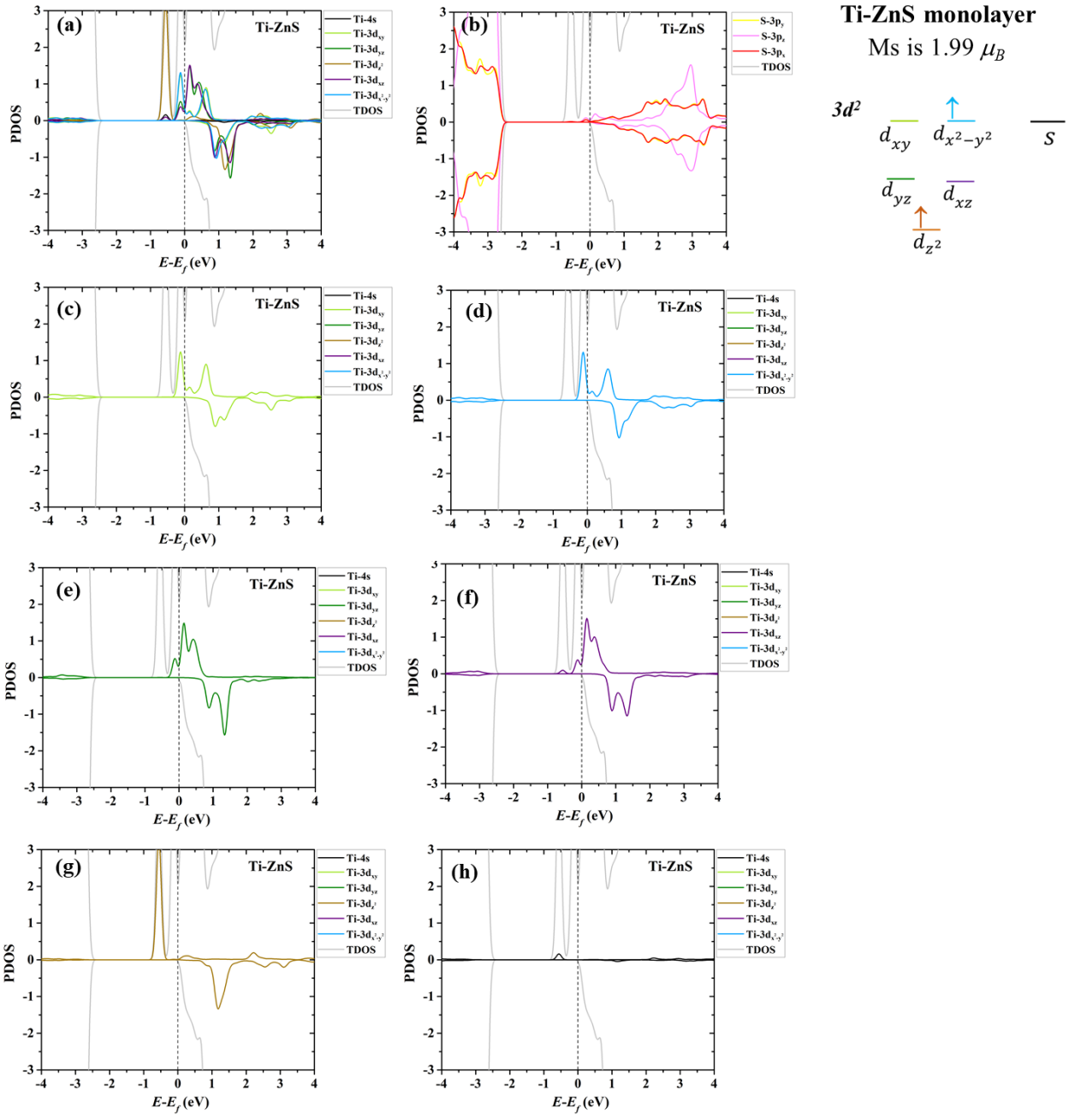


Figure S10 Projected DOS (PDOS) of Ti for the Ti-ZnS monolayer.

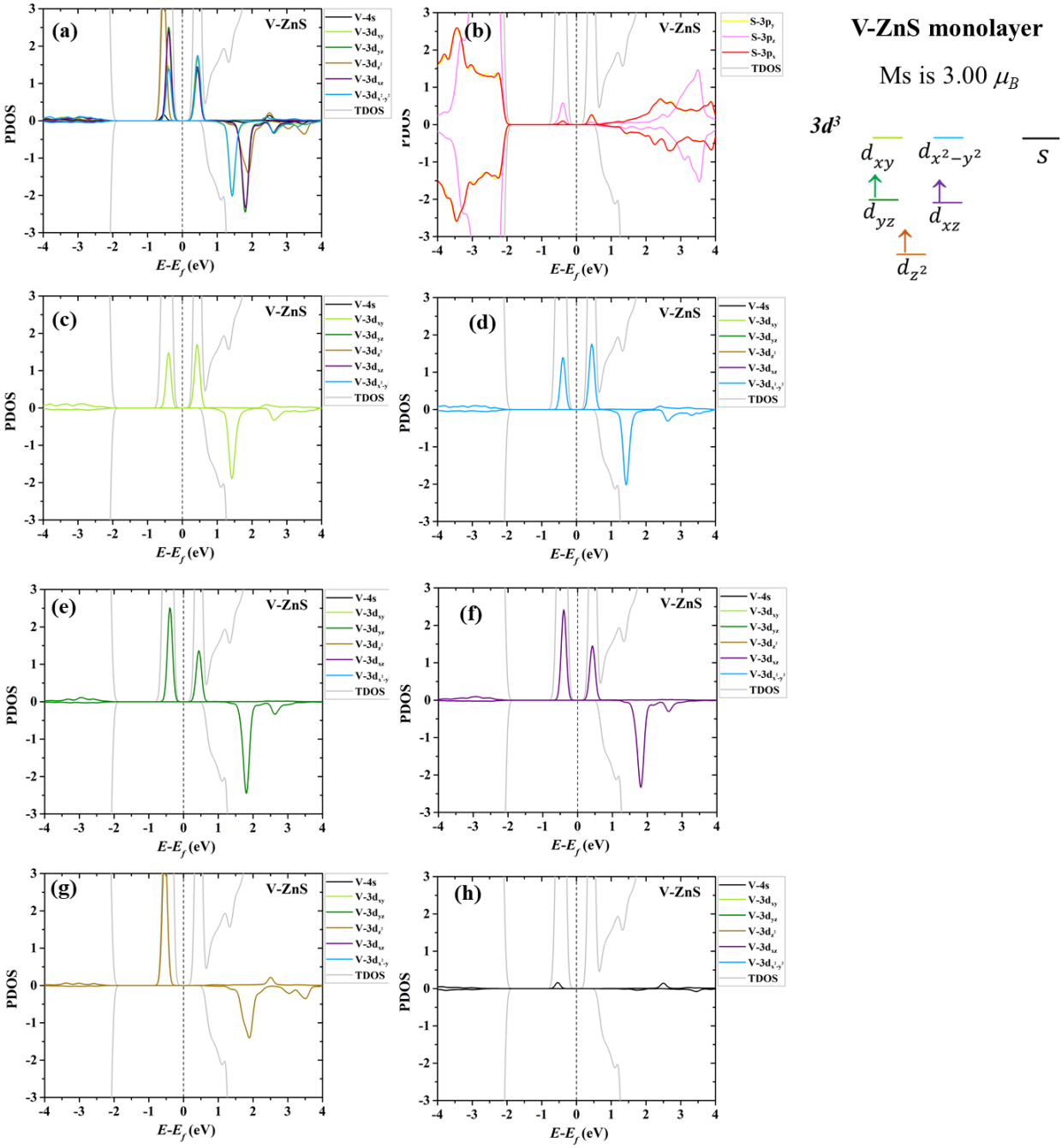


Figure S11 Projected DOS (PDOS) of V for the V-ZnS monolayer.

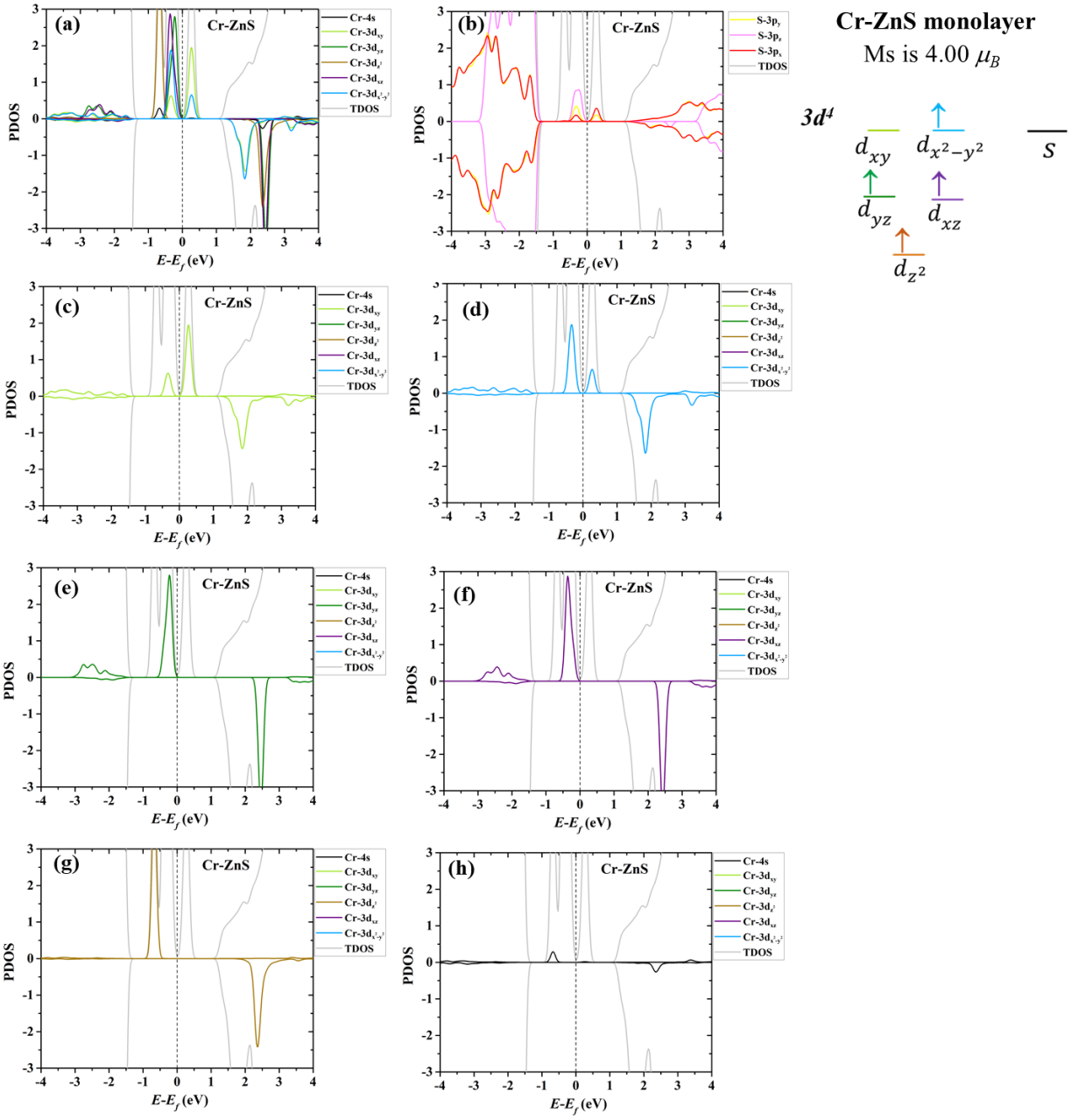


Figure S12 Projected DOS (PDOS) of Cr for the Cr-ZnS monolayer.

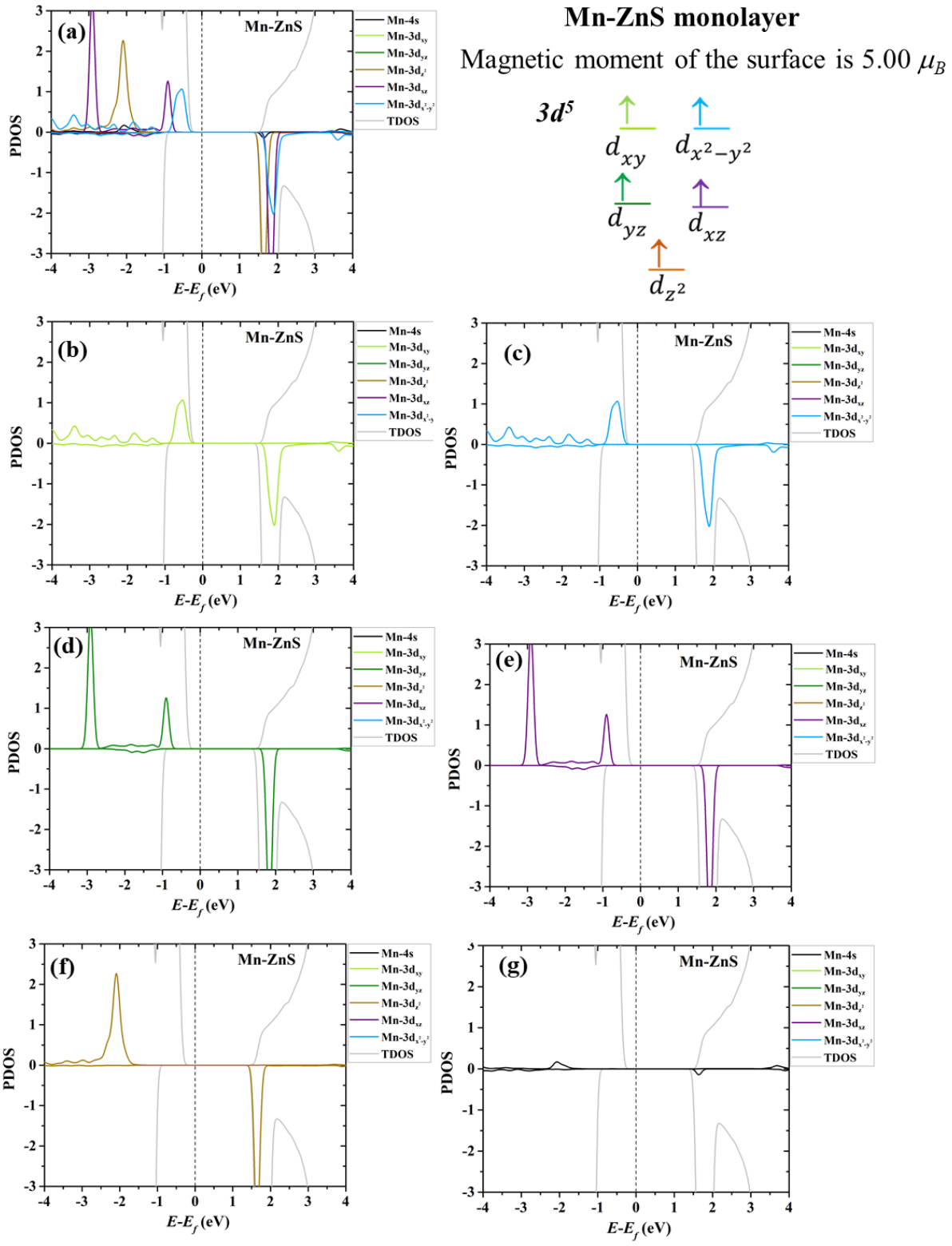


Figure S13 Projected DOS (PDOS) of Mn for the Mn-ZnS monolayer.

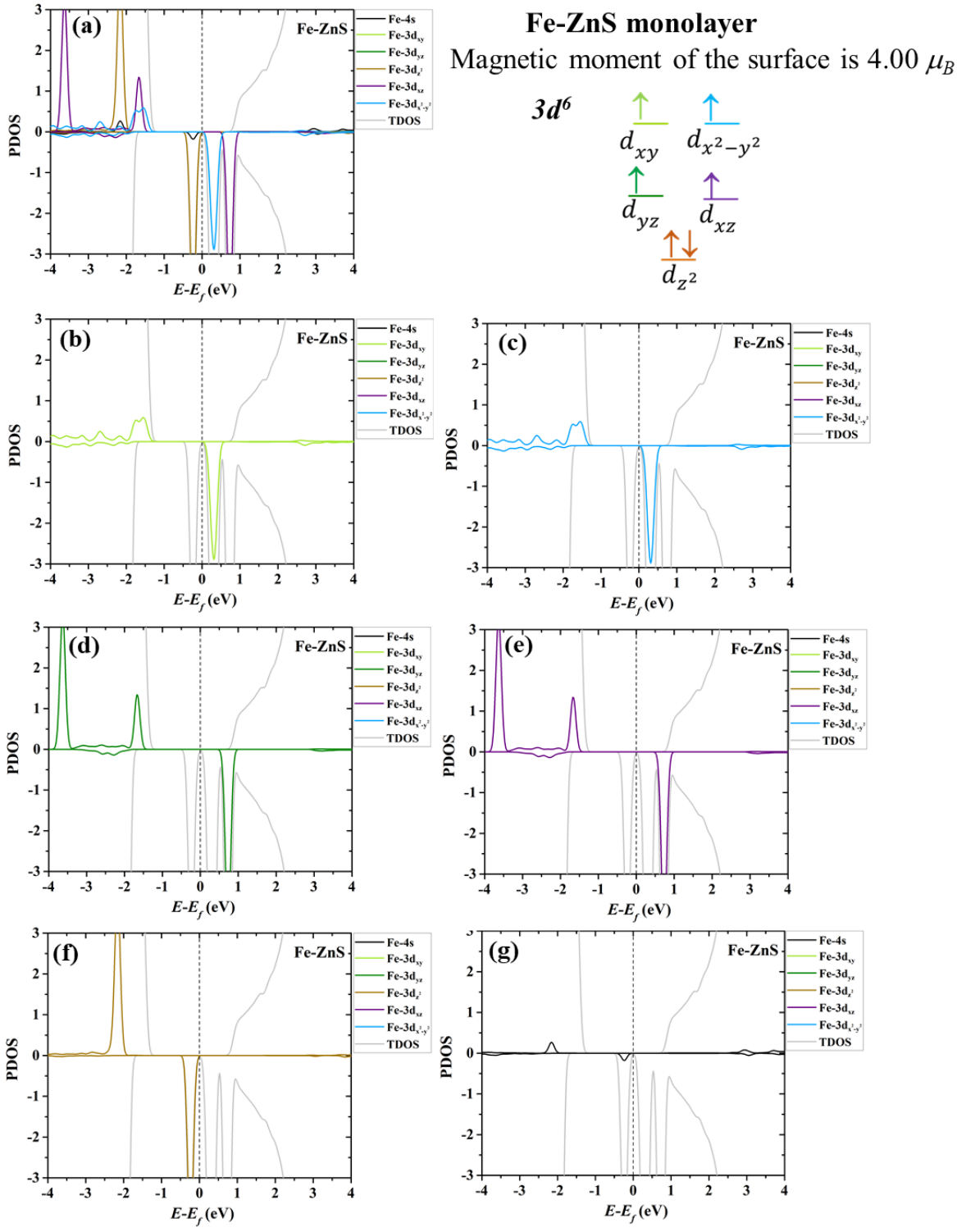


Figure S14 Projected DOS (PDOS) of Fe for the Fe-ZnS monolayer.

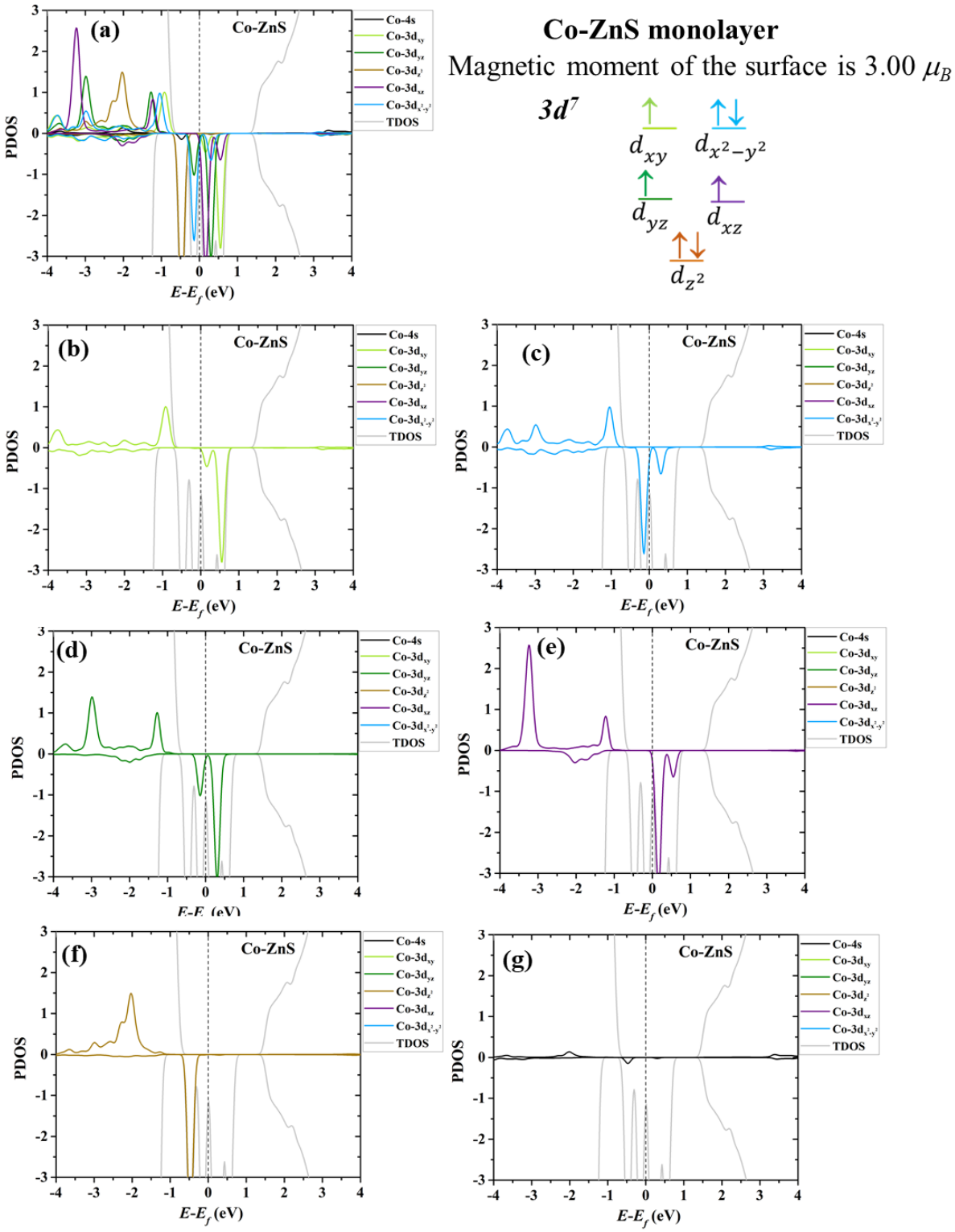


Figure S15 Projected DOS (PDOS) of Co for the Co-ZnS monolayer.

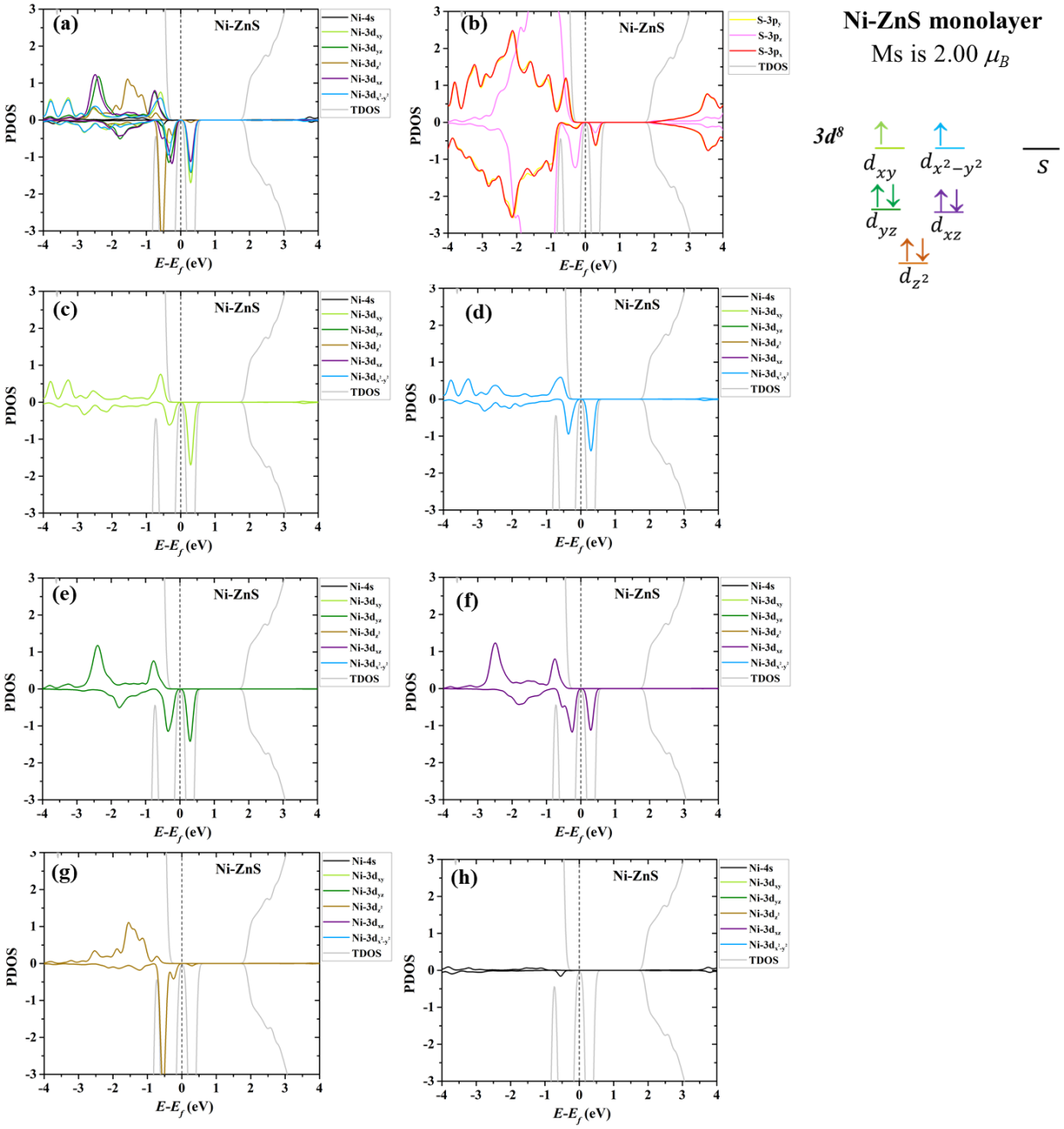


Figure S16 Projected DOS (PDOS) of Ni for the Ni-ZnS monolayer.

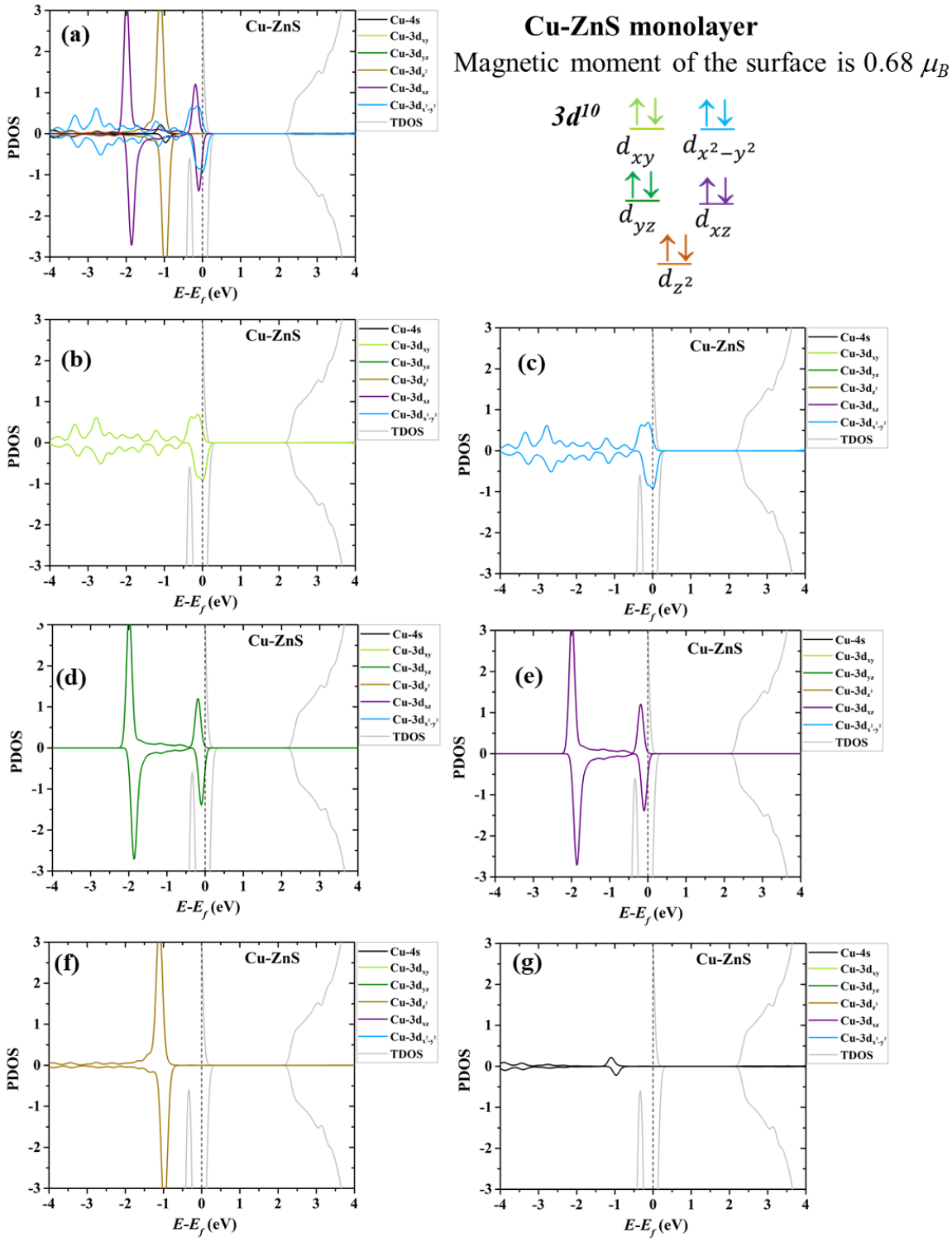


Figure S17 Projected DOS (PDOS) of Cu for the Cu-ZnS monolayer.

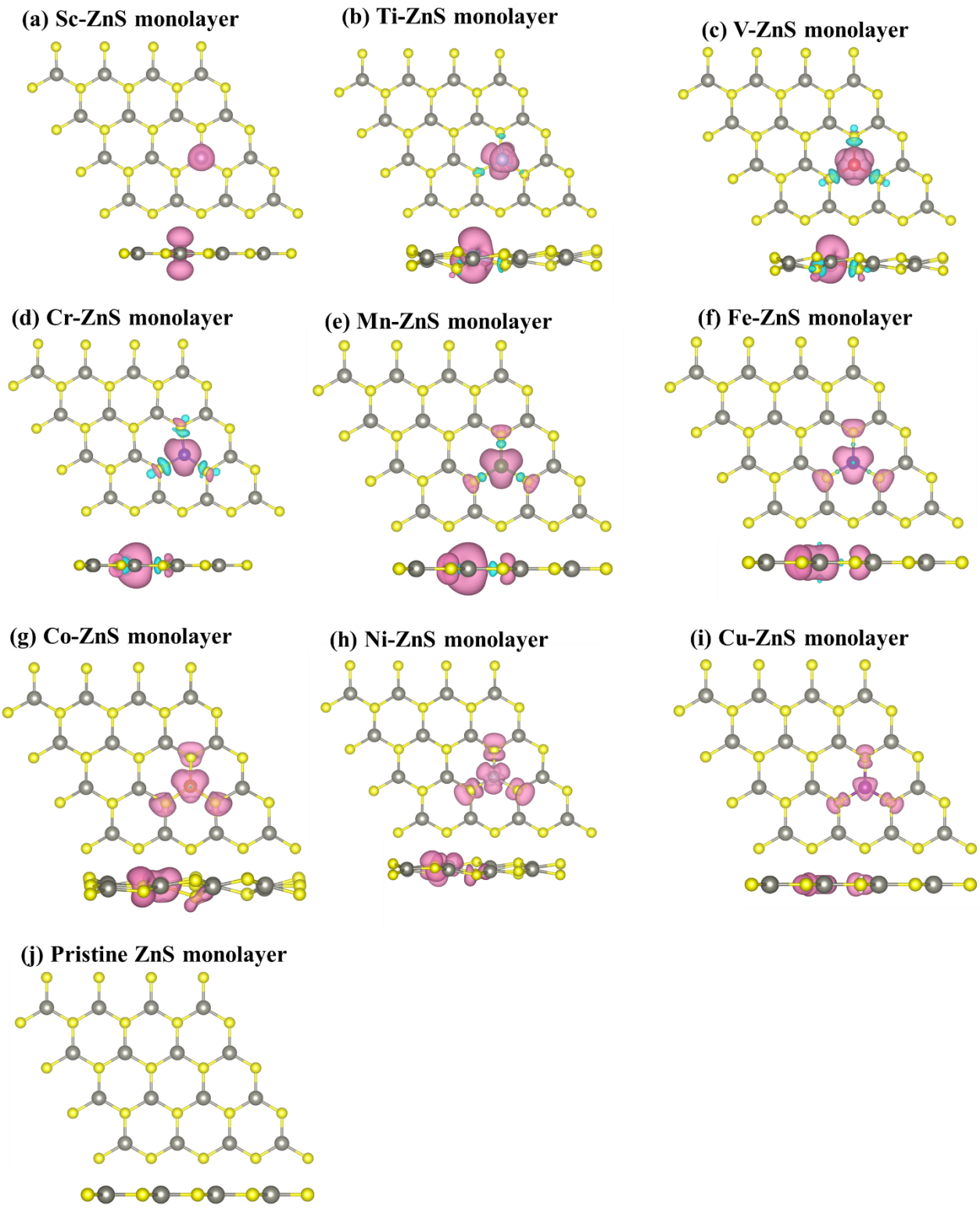


Figure S18 Spin density of a) Sc-ZnS, (b) Ti-ZnS, (c) V-ZnS, (d) Cr-ZnS, (e) Mn-ZnS, (f) Fe-ZnS, (g) Co-ZnS, (h) Ni-ZnS, (i) Ni-ZnS and (j) pristine ZnS monolayers with isosurface level of 0.002 e/bohr^3. Blue and pink colors are represented spin down and spin up electrons, respectively.

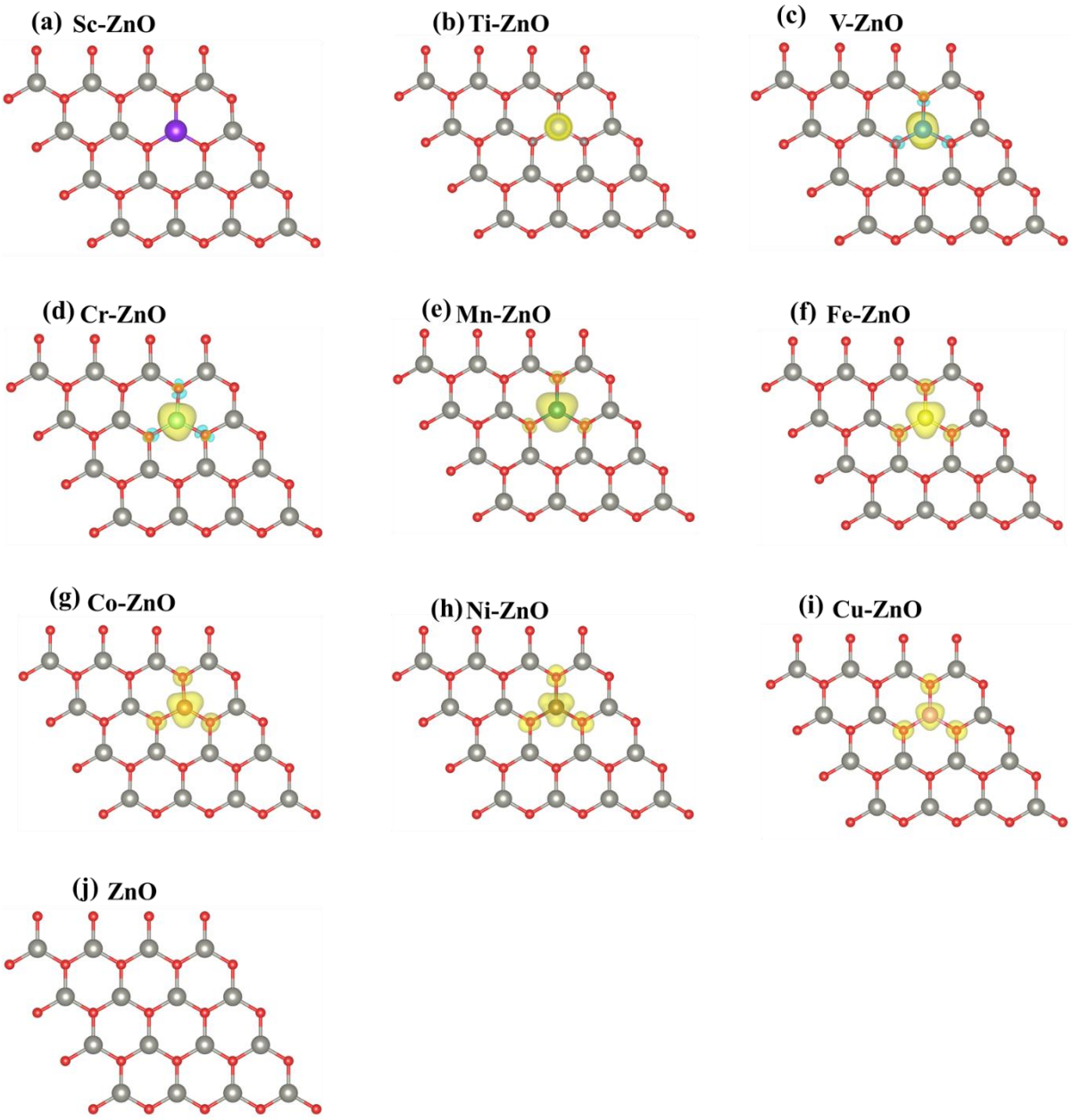


Figure S19 Spin density of (a) Sc-ZnO, (b) Ti-ZnO, (c) V-ZnO, (d) Cr-ZnO, (e) Mn-ZnO, (f) Fe-ZnO, (g) Co-ZnO, (h) Ni-ZnO, (i) Ni-ZnO and (j) pristine ZnO monolayers. The yellow and cyan regions stand for the spin up and spin down electron densities, respectively. The isosurface value is taken as 0.005 e/bohr^{3}[7].

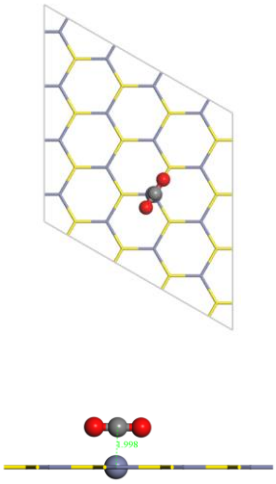
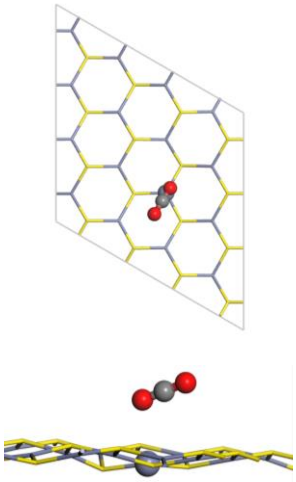
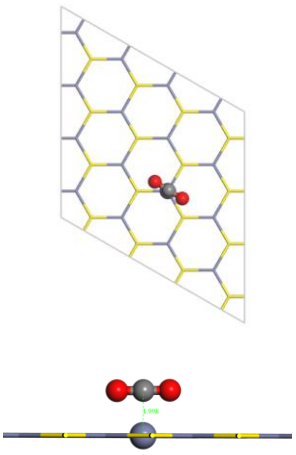
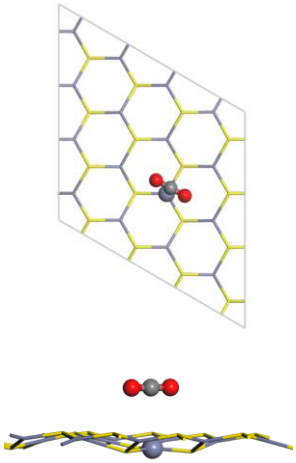
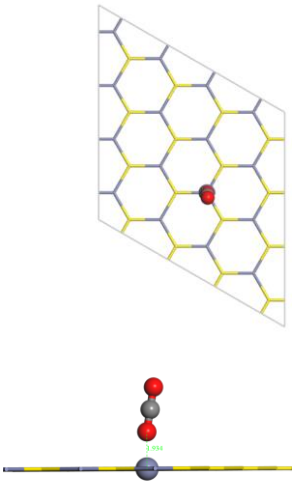
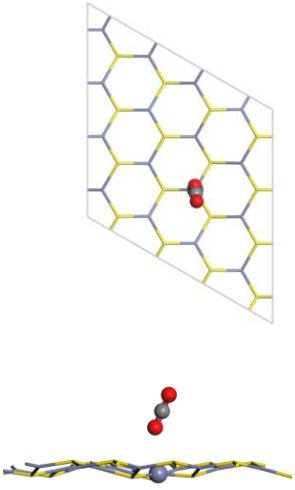
Type	Initial structure	Optimized structure	E_{total} (eV)
1			-128.68
2			-128.65
3			-128.64

Figure S20 CO_2 adsorption on the pristine ZnS monolayer with total energy of each structure (E_{total}). The most stable structures are labeled by E_{min}.

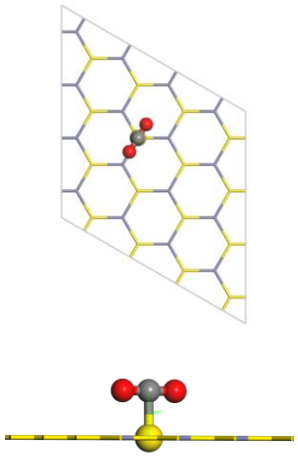
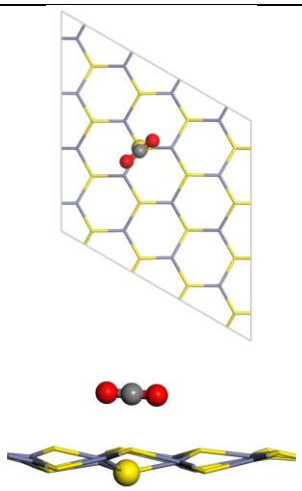
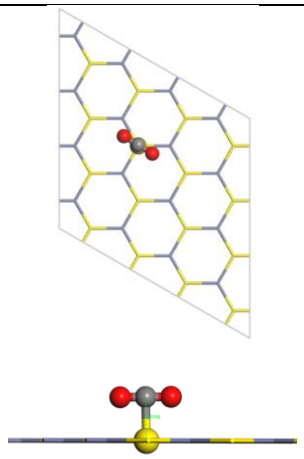
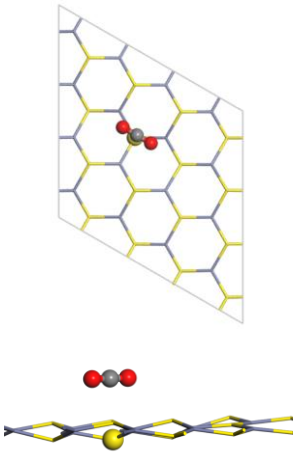
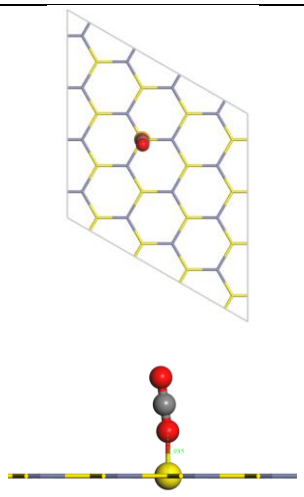
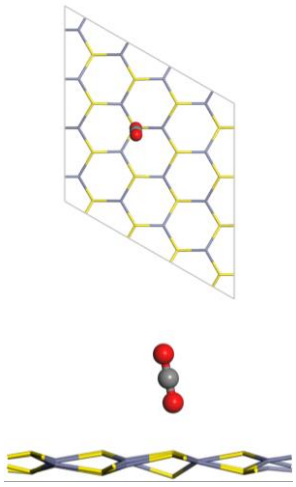
Type	Initial structure	Optimized structure	E_{total} (eV)
4			-128.70 (E_{min})
5			-128.69
6			-128.63

Figure S20 CO_2 adsorption on the pristine ZnS monolayer with total energy of each structure (E_{total}). The most stable structures are labeled by E_{min}. (Cont.)

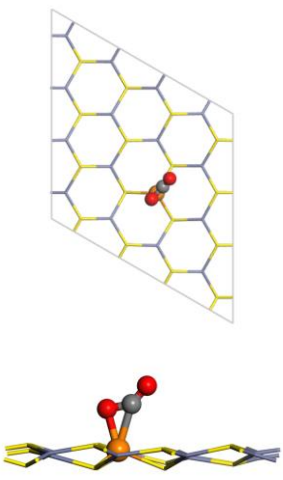
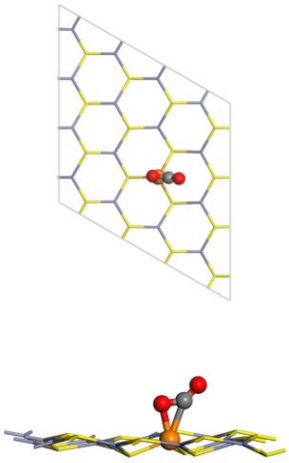
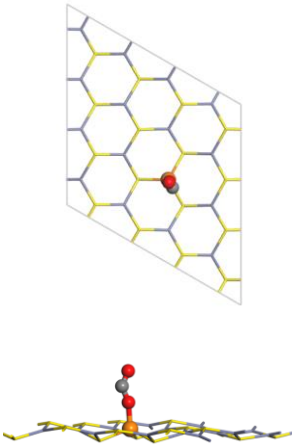
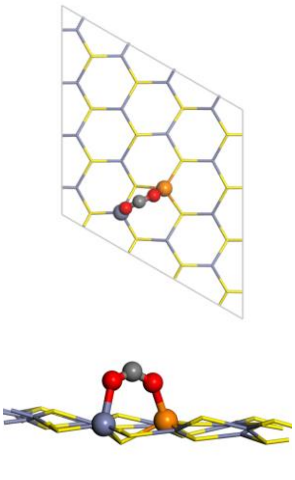
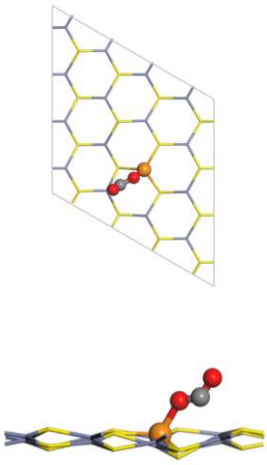
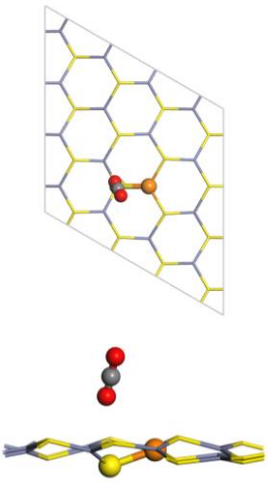
	1	2	3
			
E_{tot} (eV)	-135.14	-135.17	-134.95
	4	**5**	**6**
			
E_{tot} (eV)	-135.23	-135.24 (E_{min})	-134.30

Figure S21 The optimized structures of CO_2 adsorbed on Sc-ZnS monolayer with total energy (E_{tot}). Orange, flint, yellow, dark grey and red balls represent Sc, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

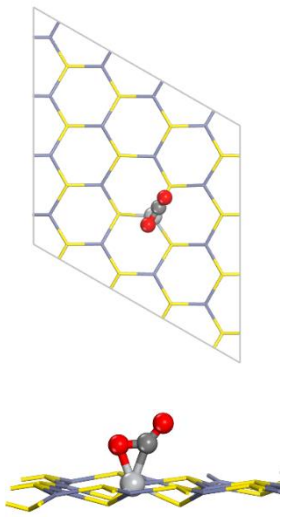
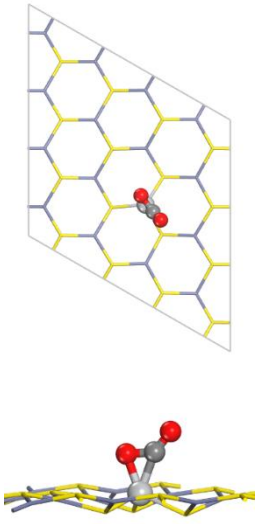
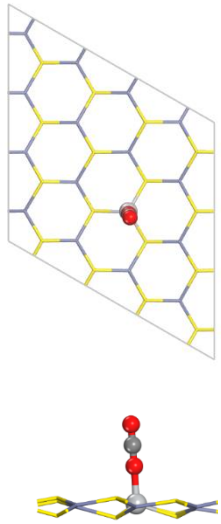
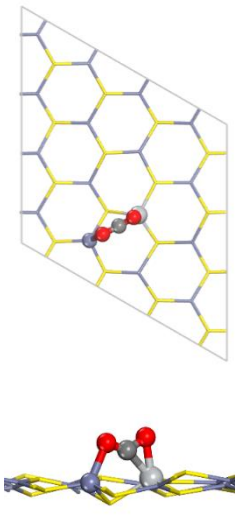
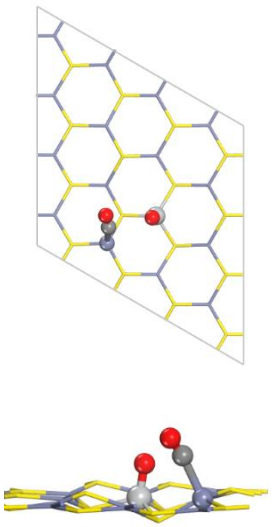
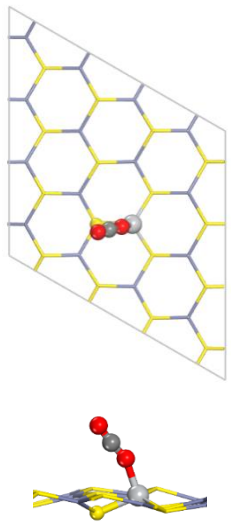
	1	**2**	**3**
			
E_{tot} (eV)	-135.83	-135.83	-134.81
	4	**5**	**6**
			
E_{tot} (eV)	-135.98 (E_{min})	Broken	-134.81

Figure S22 The optimized structures of CO_2 adsorbed on Ti-ZnS monolayer with total energy (E_{tot}). Light grey, flint, yellow, dark grey and red balls represent Ti, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

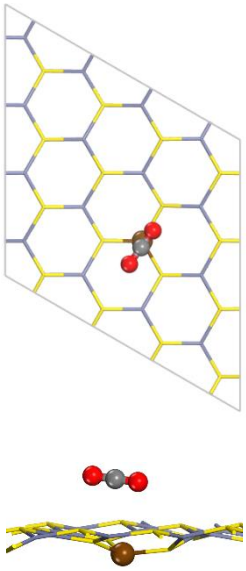
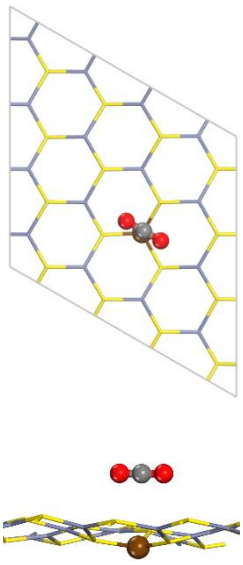
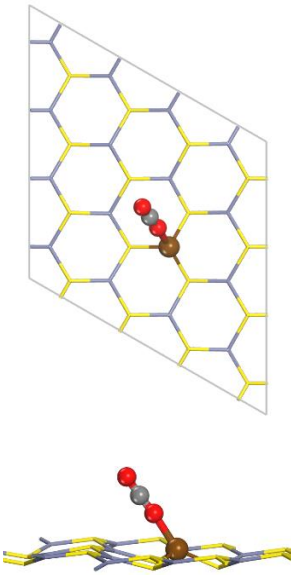
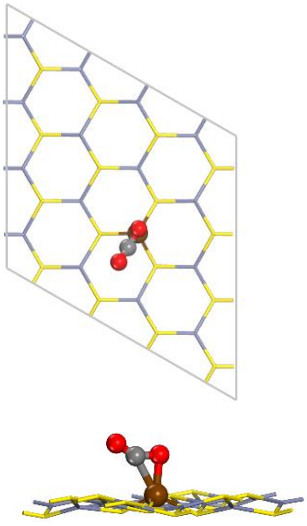
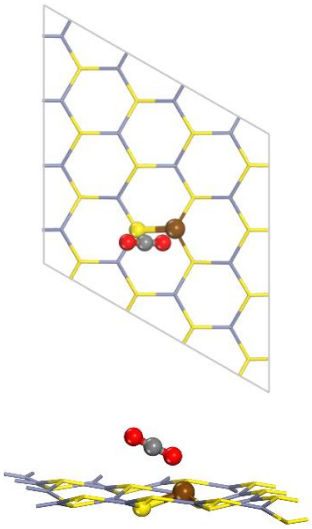
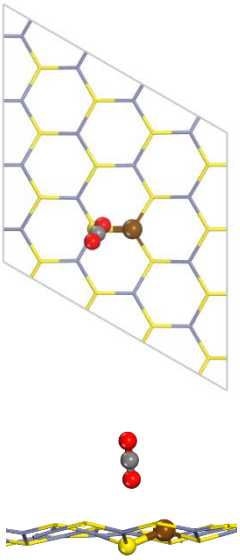
	1	2	3
			
E_{tot} (eV)	-134.96	-134.98	-135.15
	4	**5**	**6**
			
E_{tot} (eV)	-135.21 (E_{min})	-135.14	-134.99

Figure S23 The optimized structures of CO_2 adsorbed on V-ZnS monolayer with total energy (E_{tot}). Brown, flint, yellow, grey and red balls represent V, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

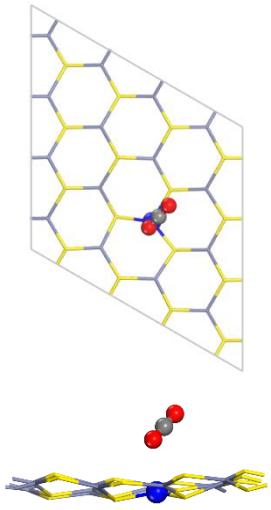
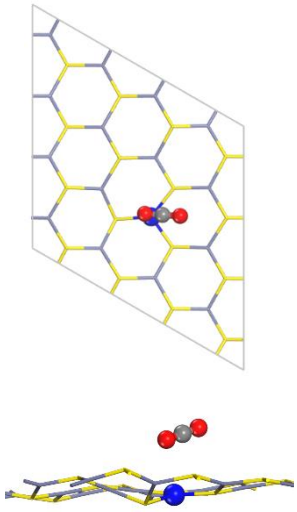
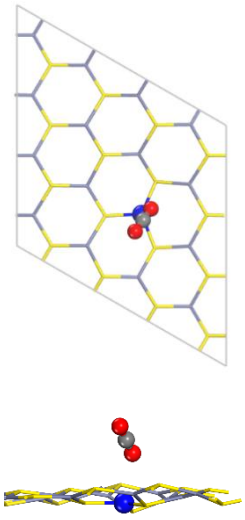
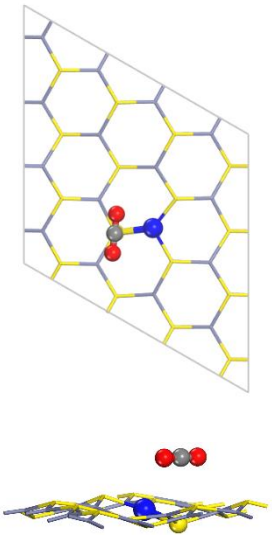
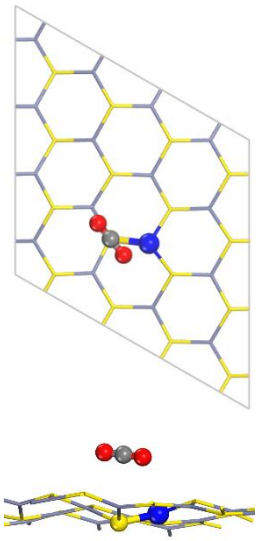
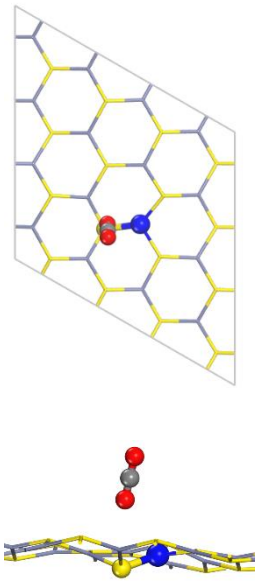
	1	2	3
			
E_{tot} (eV)	-135.71	-135.71	-135.70
	4	**5**	**6**
			
E_{tot} (eV)	-135.81 (E_{min})	-135.71	-135.71

Figure S24 The optimized structures of CO_2 adsorbed on Cr-ZnS monolayer with total energy (E_{tot}). Blue, flint, yellow, grey and red balls represent Cr, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

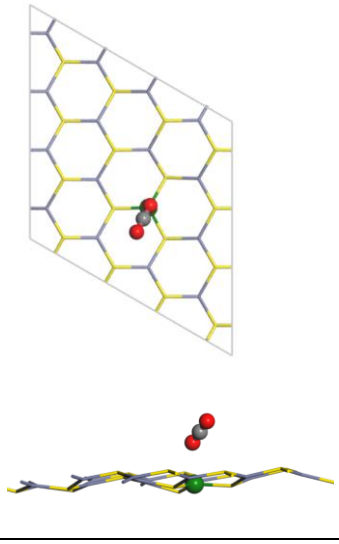
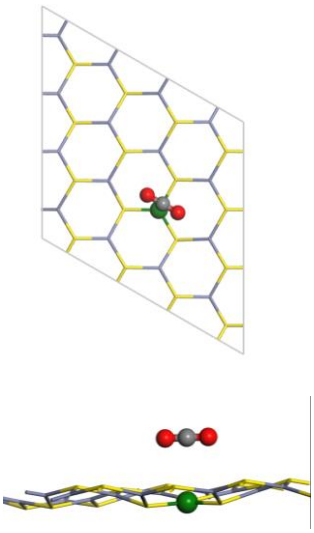
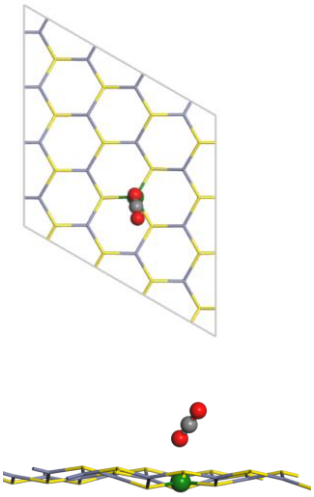
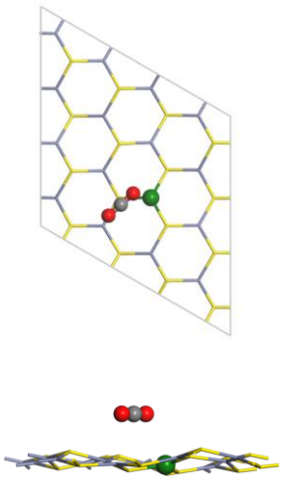
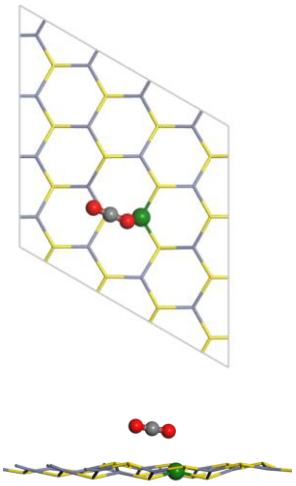
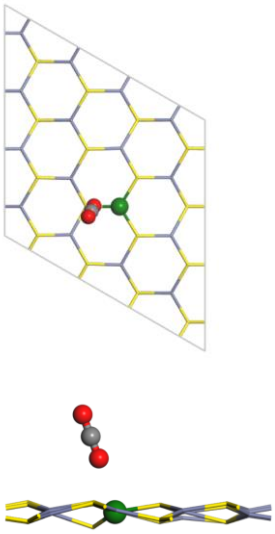
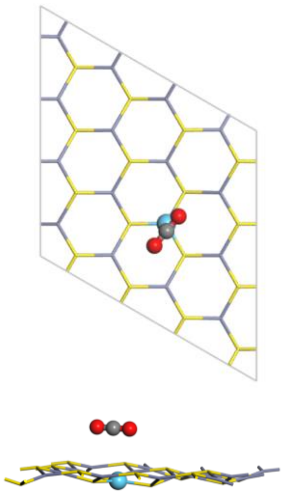
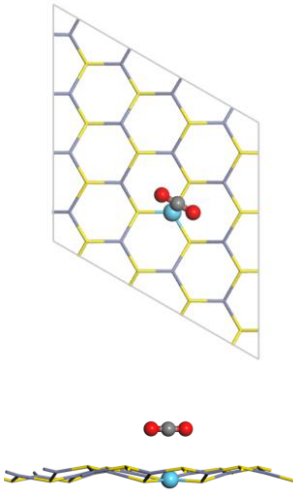
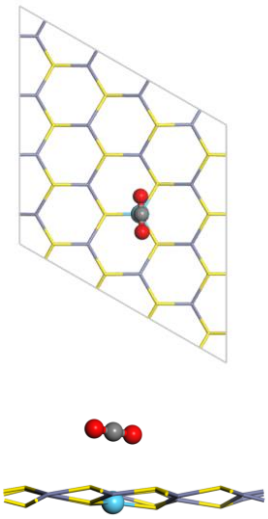
	1	2	3
			
E_{tot} (eV)	-135.98 (E_{min})	-135.90	-135.98
	4	**5**	**6**
			
E_{tot} (eV)	-135.97	-135.97	-135.90

Figure S25 The optimized structures of CO_2 adsorbed on Mn-ZnS monolayer with total energy (E_{tot}). Green, flint, yellow, grey and red balls represent Mn, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

	1	2	3
			
E_{tot} (eV)	-134.28	-134.29	-134.26

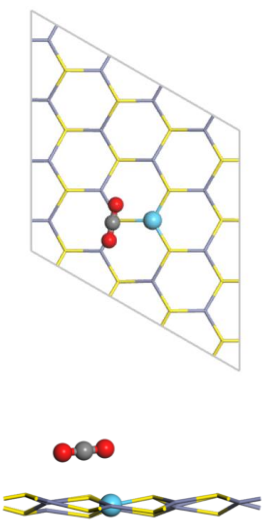
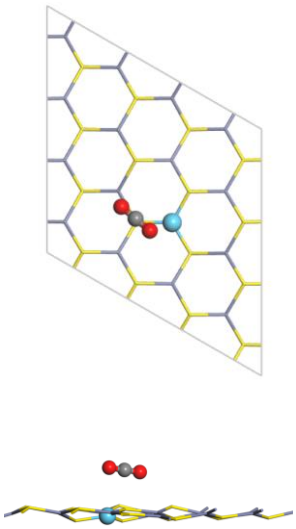
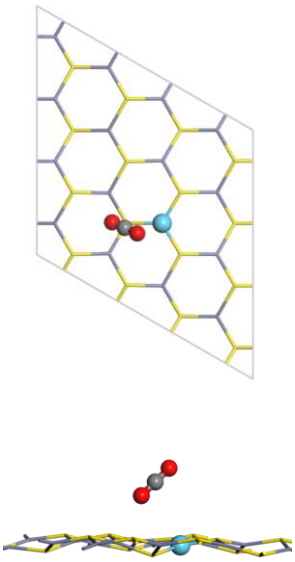
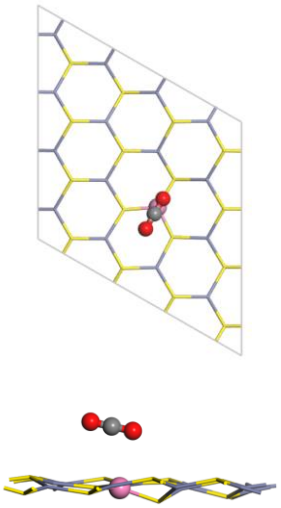
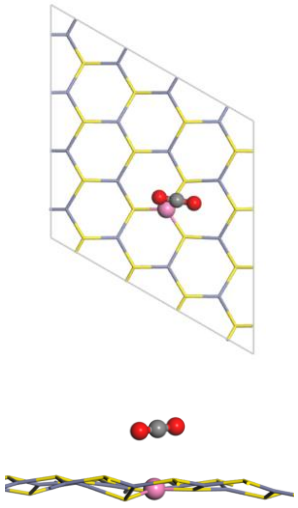
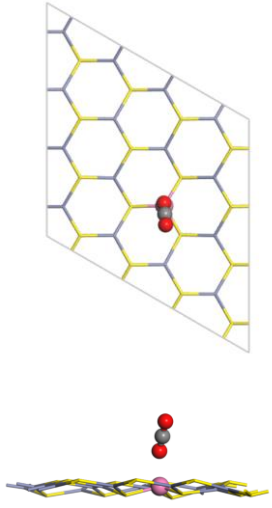
	4	5	6
			
E_{tot} (eV)	-134.34 (E_{min})	-134.29	-134.25

Figure S26 The optimized structures of CO_2 adsorbed on Fe-ZnS monolayer with total energy (E_{tot}). Blue, flint, yellow, grey and red balls represent Fe, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

	1	2	3
			
E_{tot} (eV)	-132.48	-132.48	-132.54

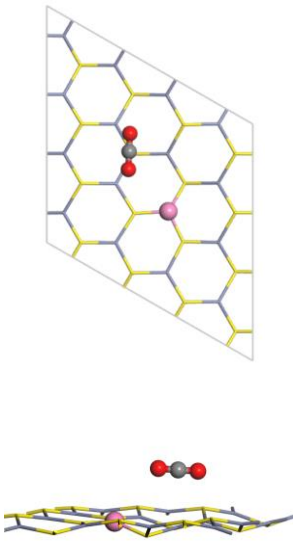
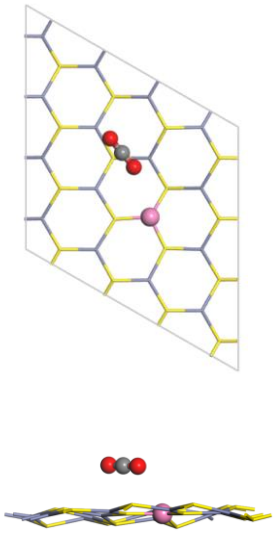
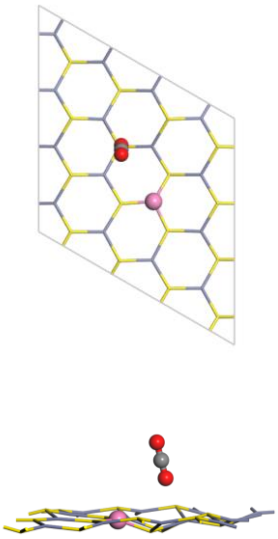
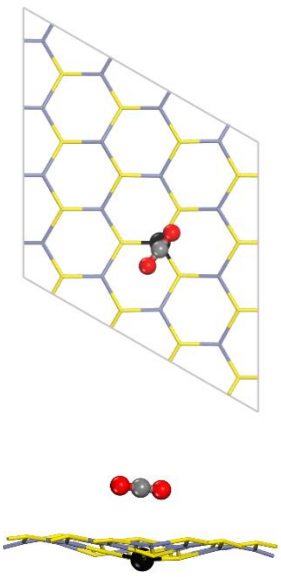
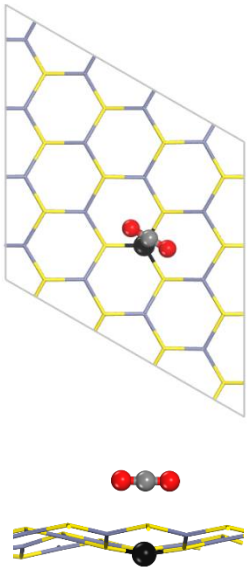
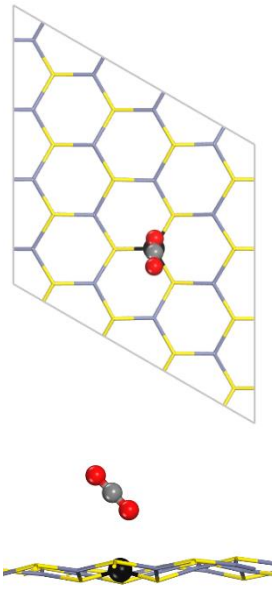
	4	5	6
			
E_{tot} (eV)	-132.53	-132.57 (E_{min})	-132.42

Figure S27 The optimized structures of CO_2 adsorbed on Co-ZnS monolayer with total energy (E_{tot}). Pink, flint, yellow, grey and red balls represent Co, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

	1	2	3
			
E_{tot} (eV)	-131.02	-131.02	-130.94

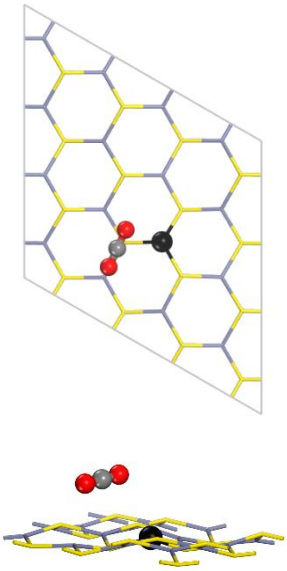
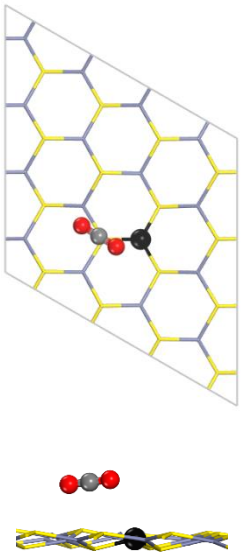
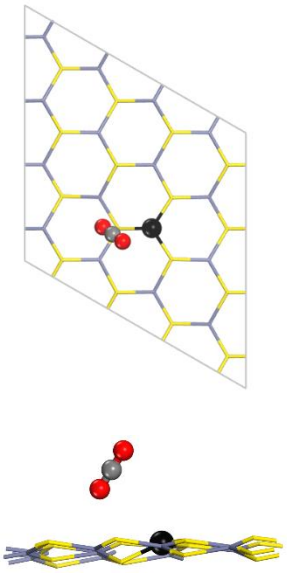
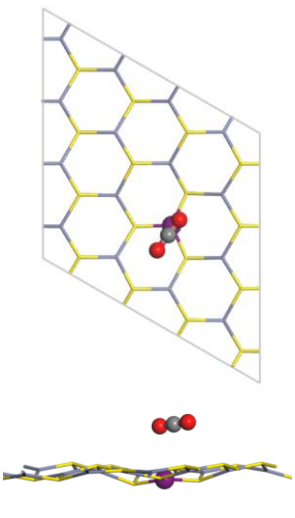
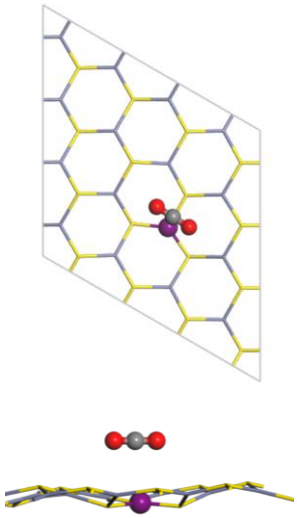
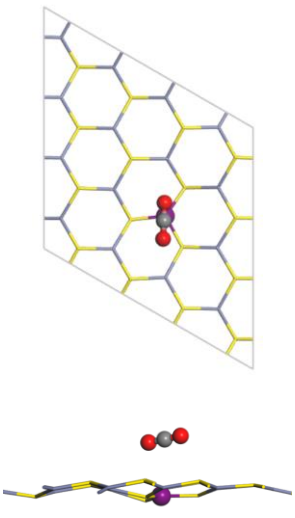
	4	5	6
			
E_{tot} (eV)	-131.04 (E_{min})	-131.02	-130.97

Figure S28 The optimized structures of CO_2 adsorbed on Ni-ZnS monolayer with total energy (E_{tot}). Black, flint, yellow, grey and red balls represent Ni, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

	1	2	3
			
E_{tot} (eV)	-129.46	-129.46	-129.45

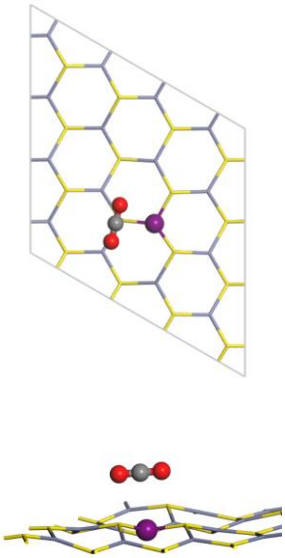
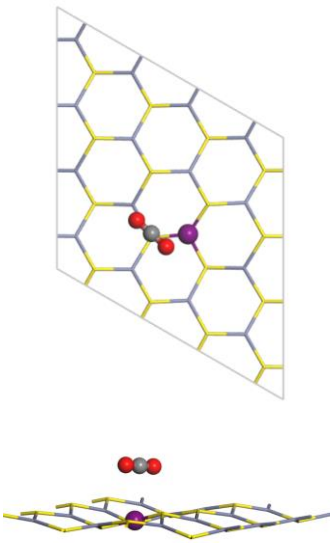
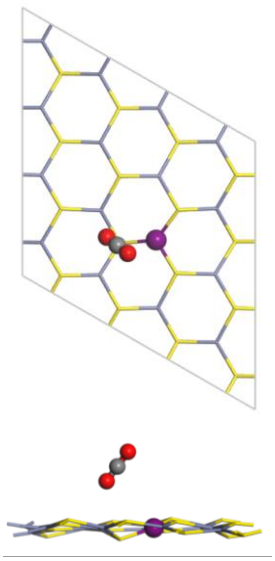
	4	5	6
			
E_{tot} (eV)	-129.50 (E_{min})	-129.49	-129.39

Figure S29 The optimized structures of CO_2 adsorbed on Cu-ZnS monolayer with total energy (E_{tot}). Purple, flint, yellow, grey and red balls represent Cu, Zn, S, C and O atoms, respectively. The most stable structures are labeled by E_{min}.

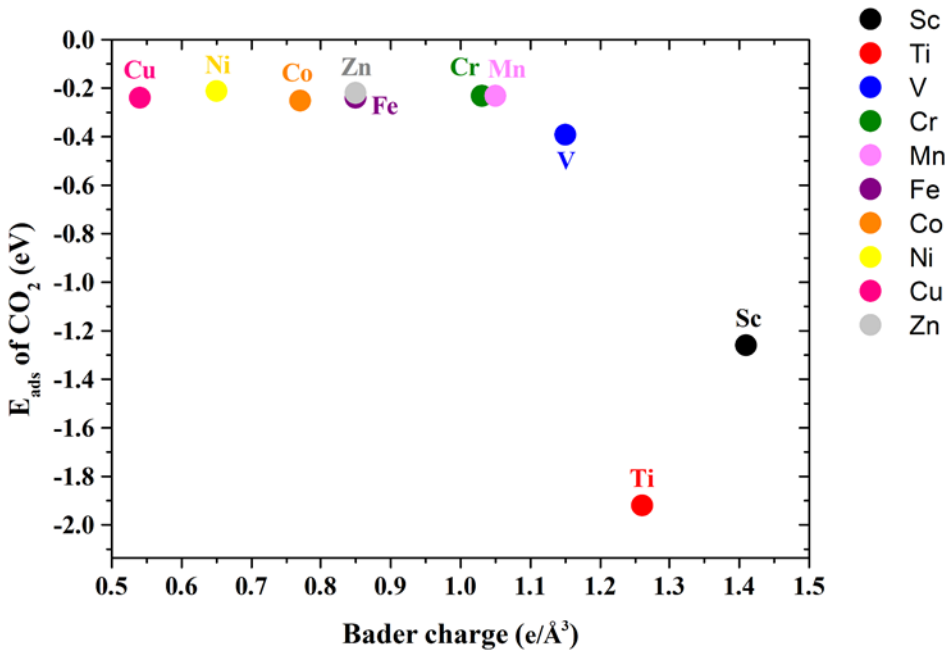


Figure S30 The relationship between Bader charge of the transition metals and the adsorption energy of CO_2 on TM-ZnS.

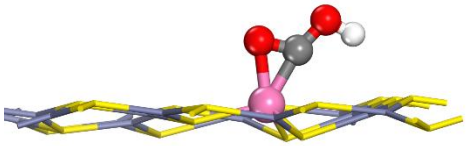
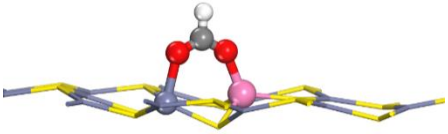
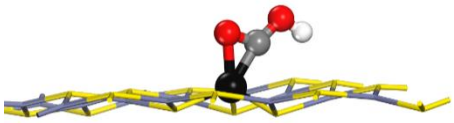
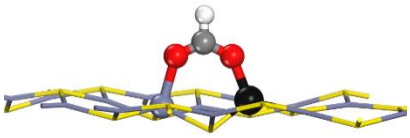
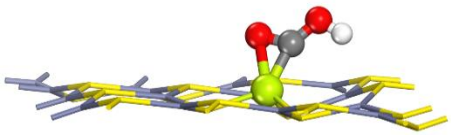
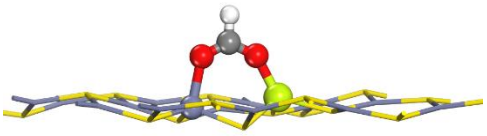
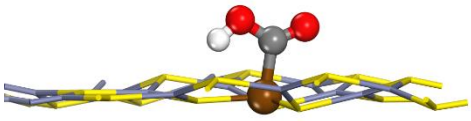
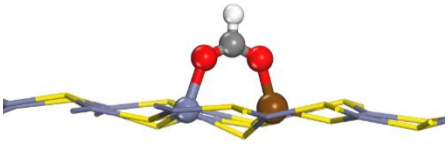
Surfaces	*COOH	*OCHO
Ti-ZnS		
ΔG (eV)	-0.85	**-1.88**
V-ZnS		
ΔG (eV)	-0.29	**-1.31**
Cr-ZnS		
ΔG (eV)	-0.10	**-0.90**
Ni-ZnS		
ΔG (eV)	**0.08**	0.67

Figure S31 The most stable structures for 1st protonation for CRR of Ti-ZnS, V-ZnS, Cr-ZnS and Ni-ZnS. Bold letters show the preferred pathways. Pink, black, green, brown, white, flint, yellow, dark grey and red balls represent Ti, V, Cr, Ni, H, Zn, S, C and O atoms, respectively.

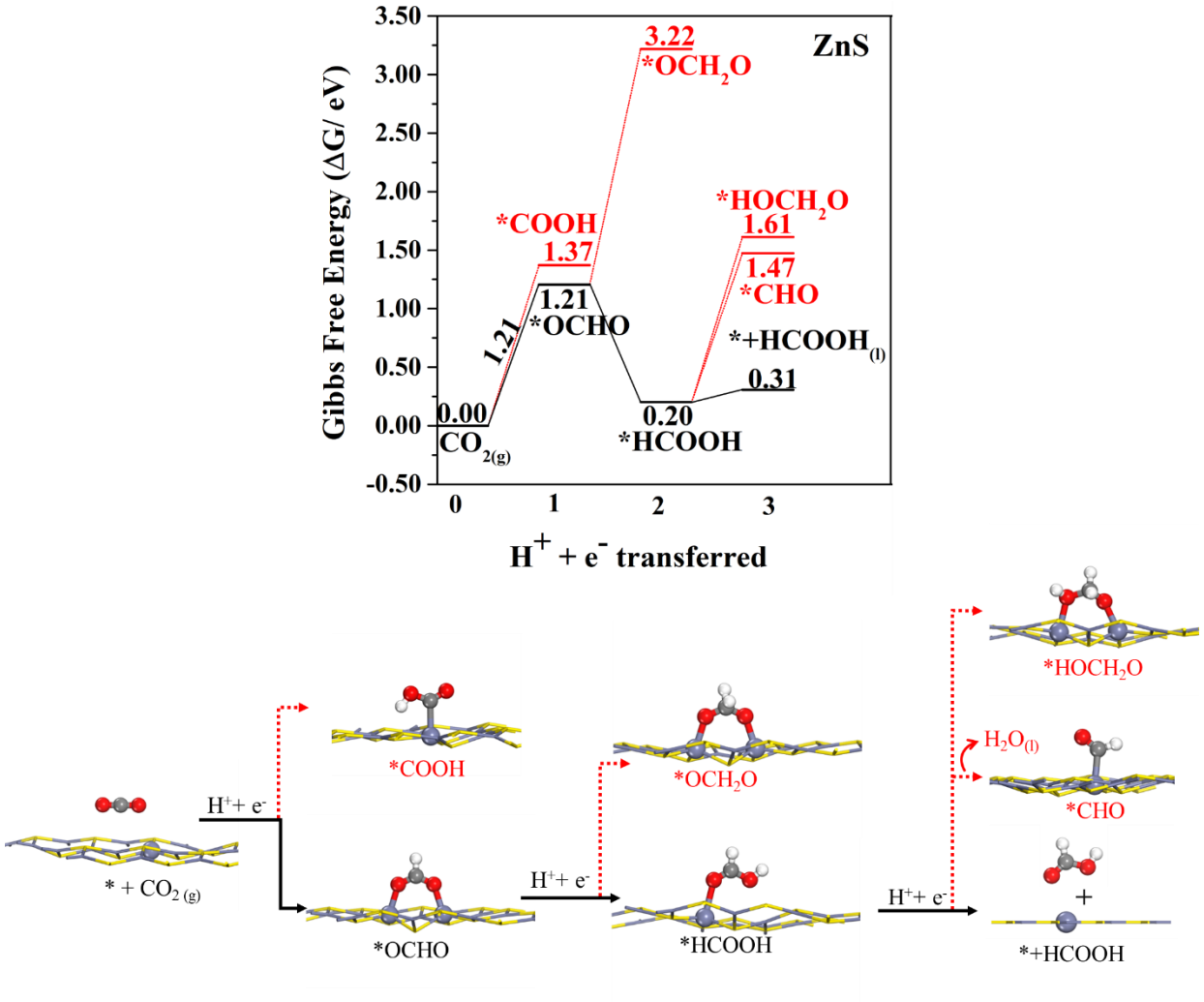


Figure S32 CO_2 pathway with the most stable structures of the ZnS monolayer. Flint, yellow, red, grey, and white balls are Zn, S, O, C, and H atoms, respectively.

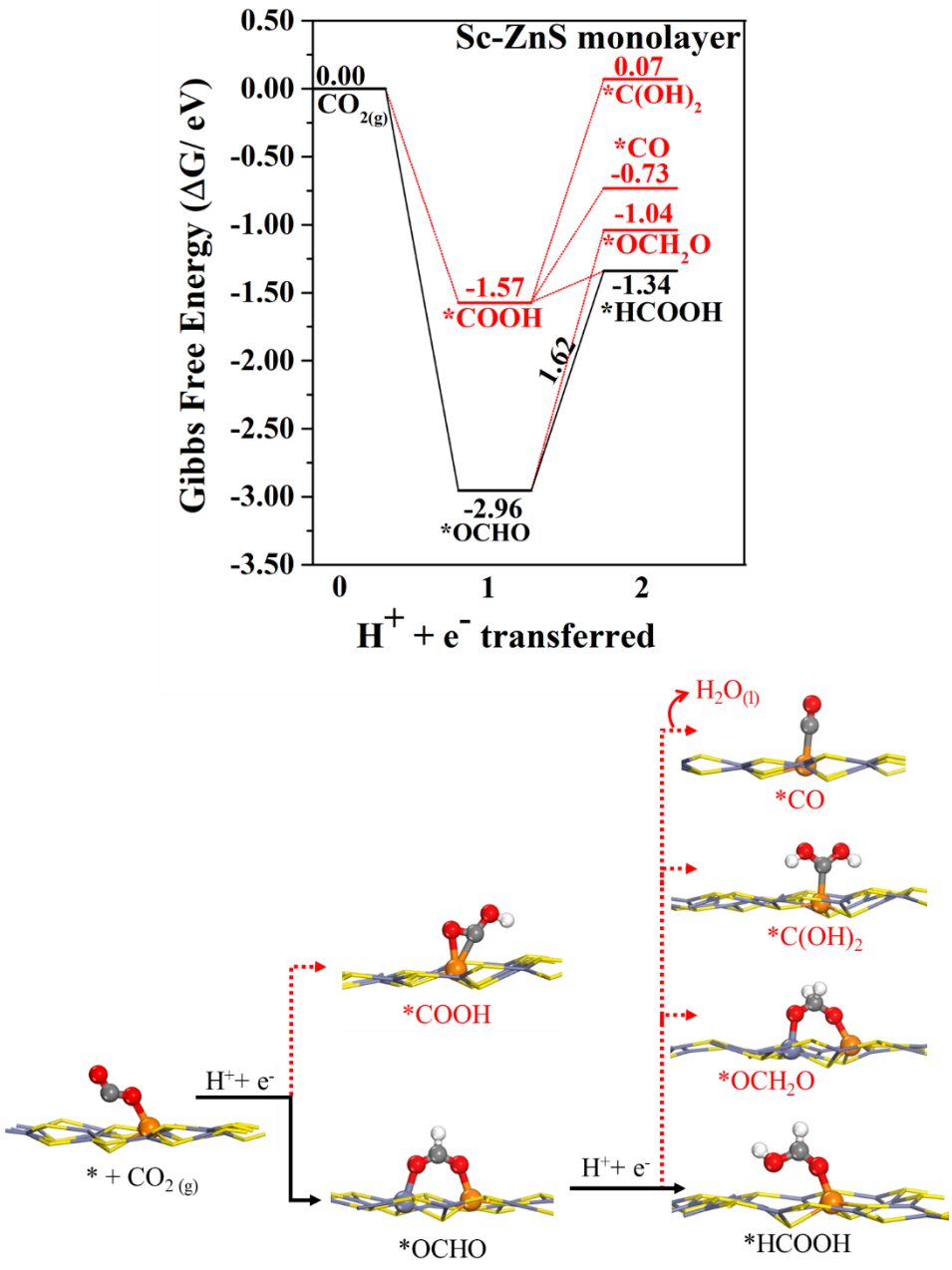


Figure S33 CO_2 pathway with the most stable structures of the Sc-ZnS monolayer. Flint, yellow, orange, red, grey, and white balls are Zn, S, Sc, O, C, and H atoms, respectively.

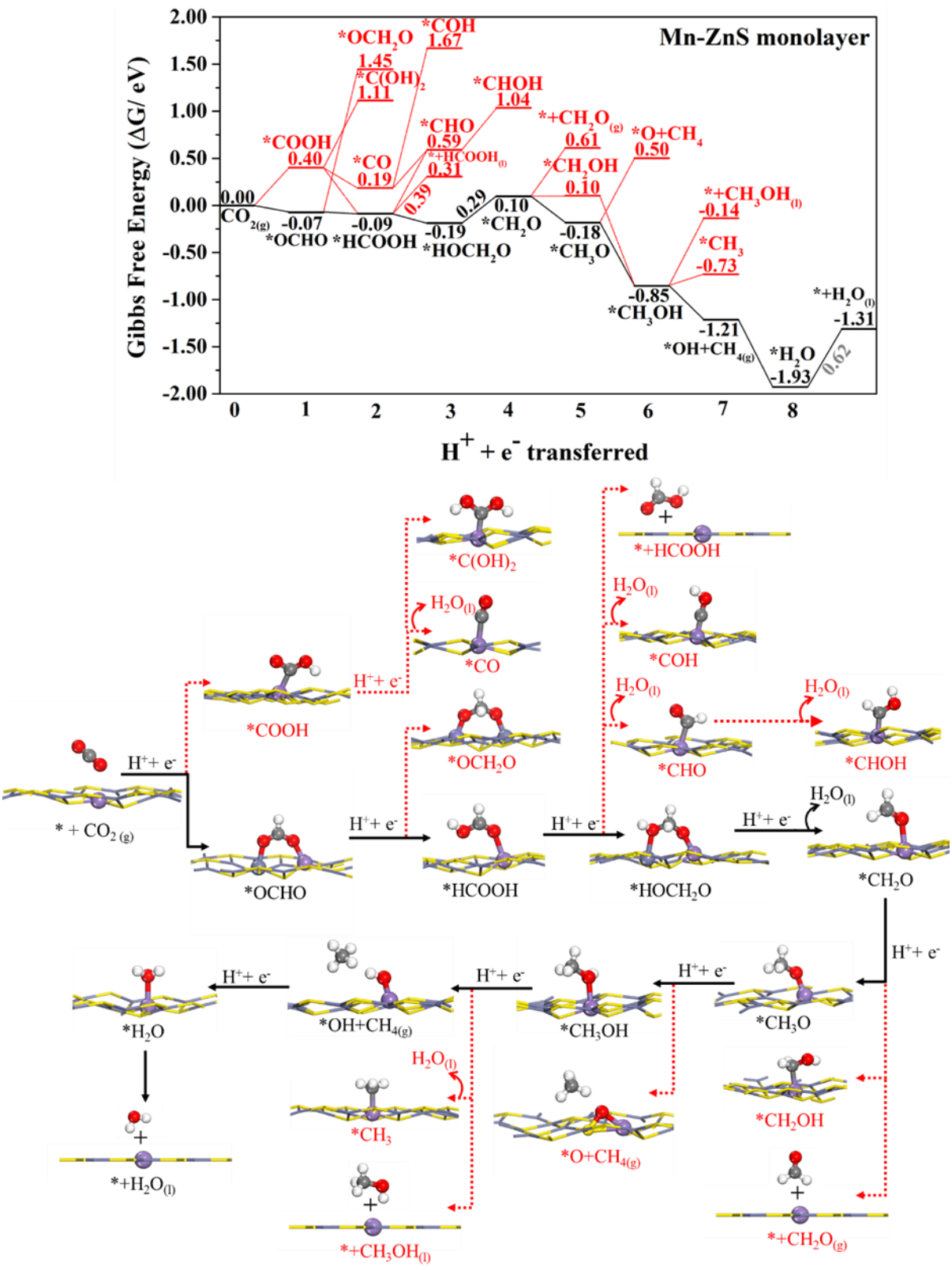


Figure S34 CO_2 pathway with the most stable structures of the Mn-ZnS monolayer. Flint, yellow, purple, red, grey, and white balls are Zn, S, Mn, O, C, and H atoms, respectively.

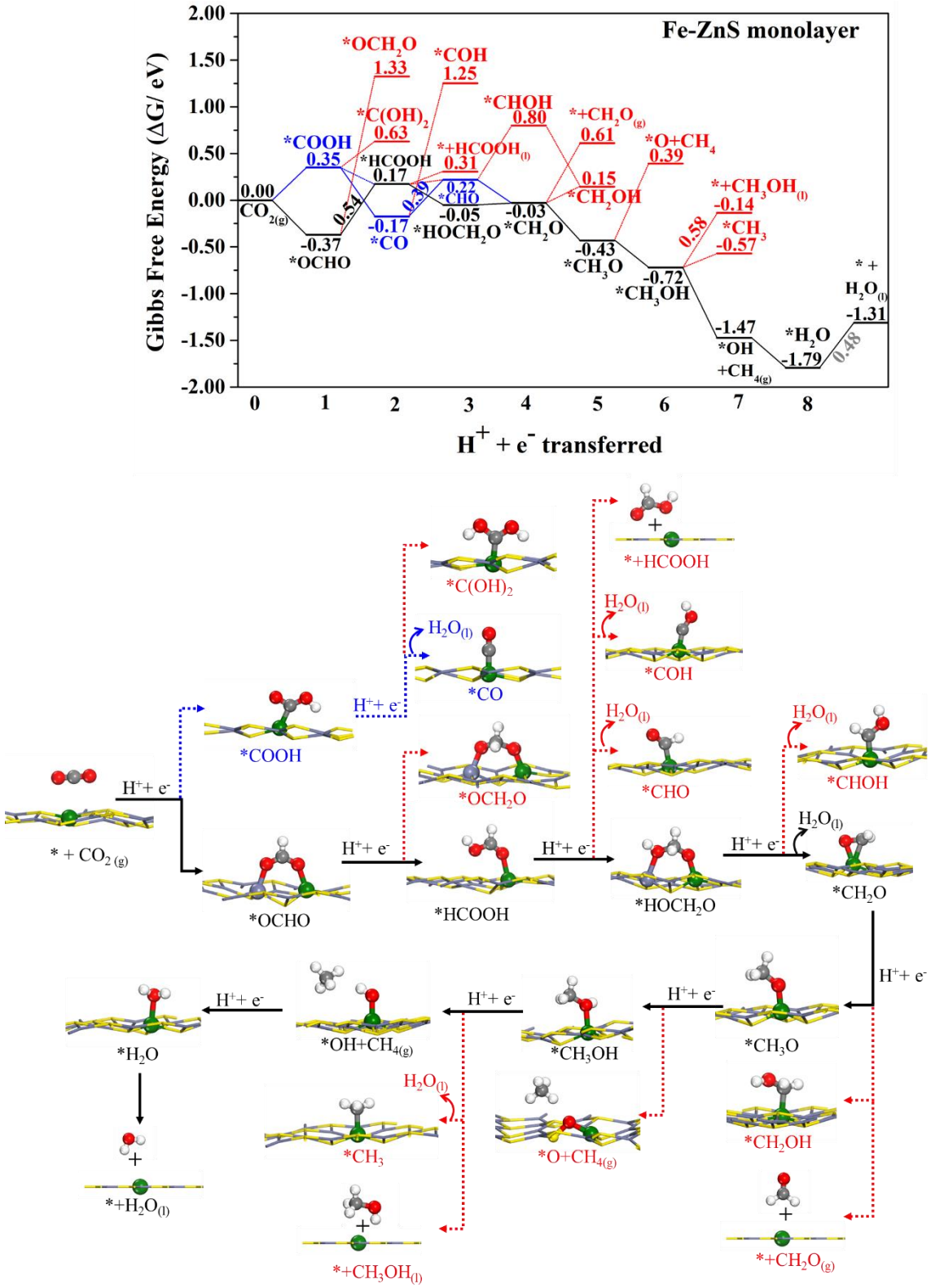


Figure S35 CO_2 pathway with the most stable structures of the Fe-ZnS monolayer. Flint, yellow, green, red, grey, and white balls are Zn, S, Fe, O, C, and H atoms, respectively.

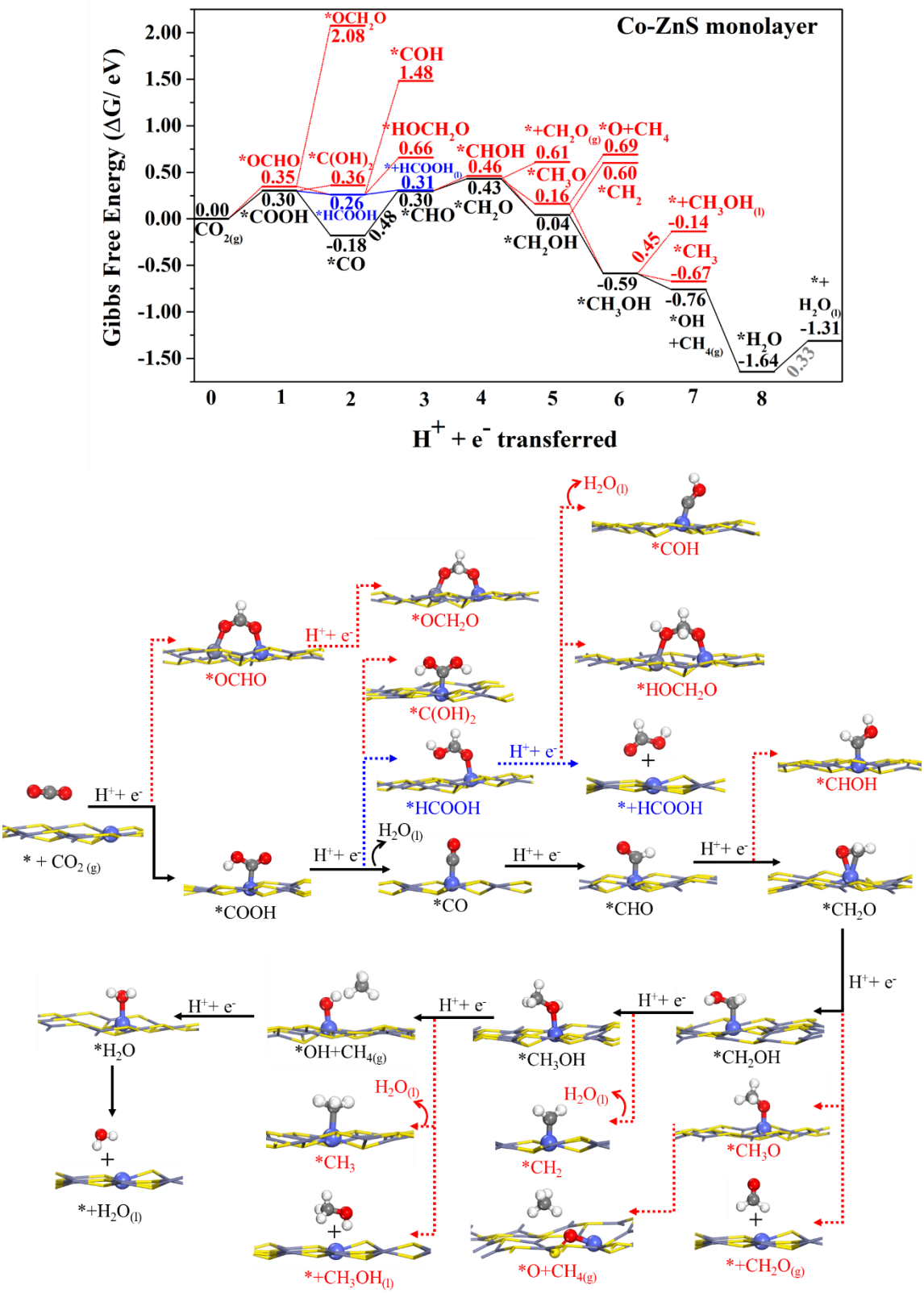


Figure S36 CO_2 pathway as well as the most stable structures of the Co-ZnS monolayer. Flint, yellow, blue, red, grey, and white balls are Zn, S, Co, O, C, and H atoms, respectively.

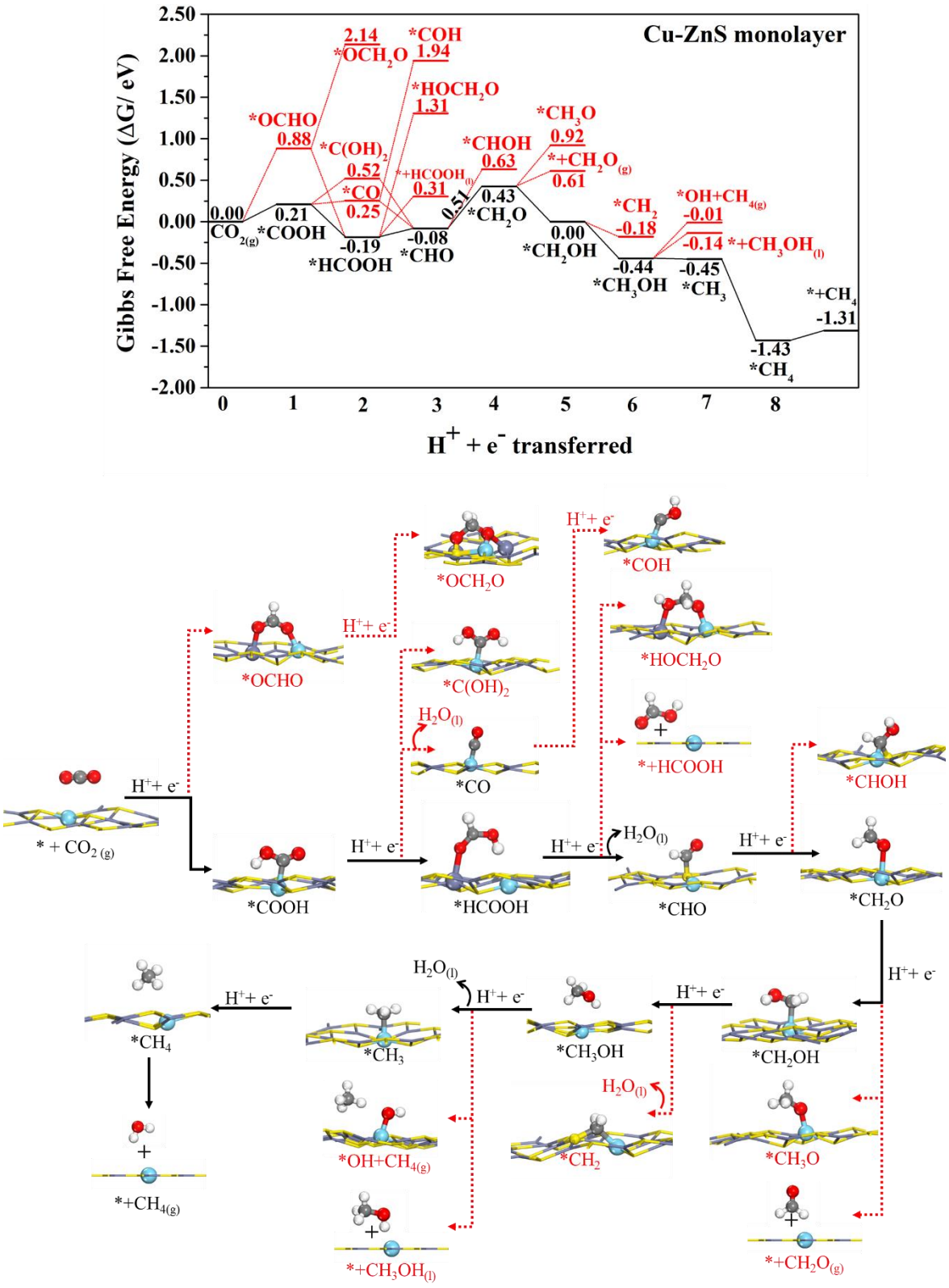


Figure S37 CRR pathway with the most stable structures of Cu-ZnS monolayer. Flint, yellow, red, light blue, grey, and white balls are Zn, S, Cu, O, C, and H atoms, respectively.

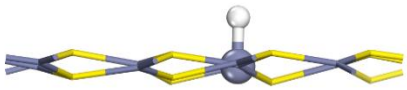
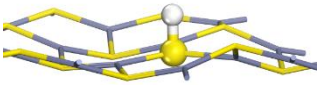
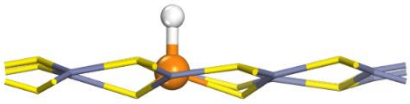
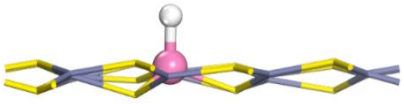
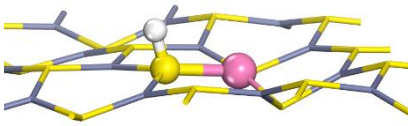
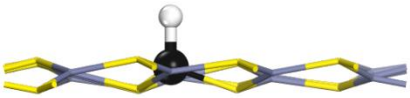
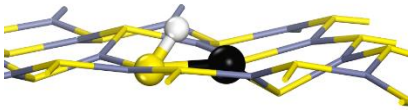
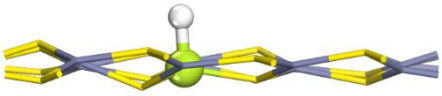
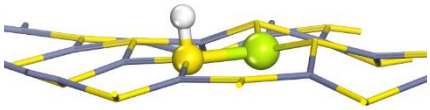
Surfaces	Active sites	
	TM	**S**
ZnS		
E_{tot} (eV)	-107.14 (E_{min})	-107.11
Sc-ZnS		-
E_{tot} (eV)	-115.29 (E_{min})	
Ti-ZnS		
E_{tot} (eV)	-115.26 (E_{min})	-113.25
V-ZnS		
E_{tot} (eV)	-115.56 (E_{min})	-113.96
Cr-ZnS		
E_{tot} (eV)	-115.73 (E_{min})	-115.12

Figure S38 *H on the pristine ZnS, Sc-ZnS, Ti-ZnS, V-ZnS and Cr-ZnS monolayers at difference active sites with total energy of each structure (E_{total}), and the most stable structures are labeled by E_{min}.

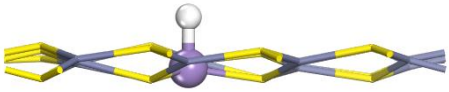
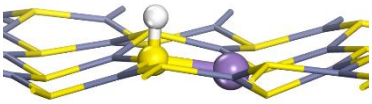
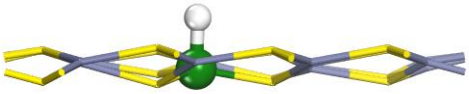
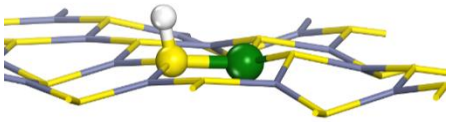
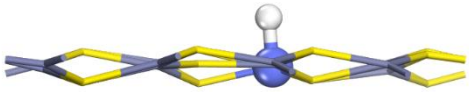
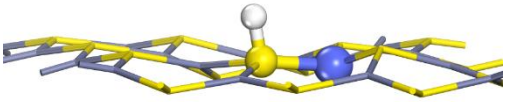
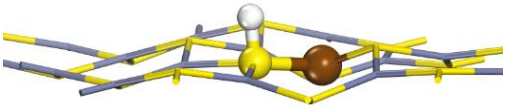
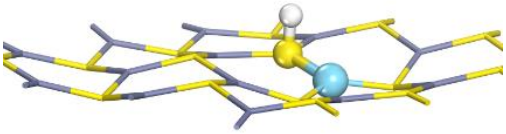
Surfaces	Active sites	
	TM	**S**
Mn-ZnS		
E_{tot} (eV)	-115.59 (E_{min})	-114.52
Fe-ZnS		
E_{tot} (eV)	-113.92 (E_{min})	-113.37
Co-ZnS		
E_{tot} (eV)	-112.53 (E_{min})	-112.31
Ni-ZnS		
E_{tot} (eV)	-111.12	-111.22 (E_{min})
Cu-ZnS	-	
E_{tot} (eV)		-110.34 (E_{min})

Figure S39 *H on the pristine ZnS, Sc-ZnS, Ti-ZnS, V-ZnS and Cr-ZnS monolayers at difference active sites with total energy of each structure (E_{total}), and the most stable structures are labeled by E_{min}.

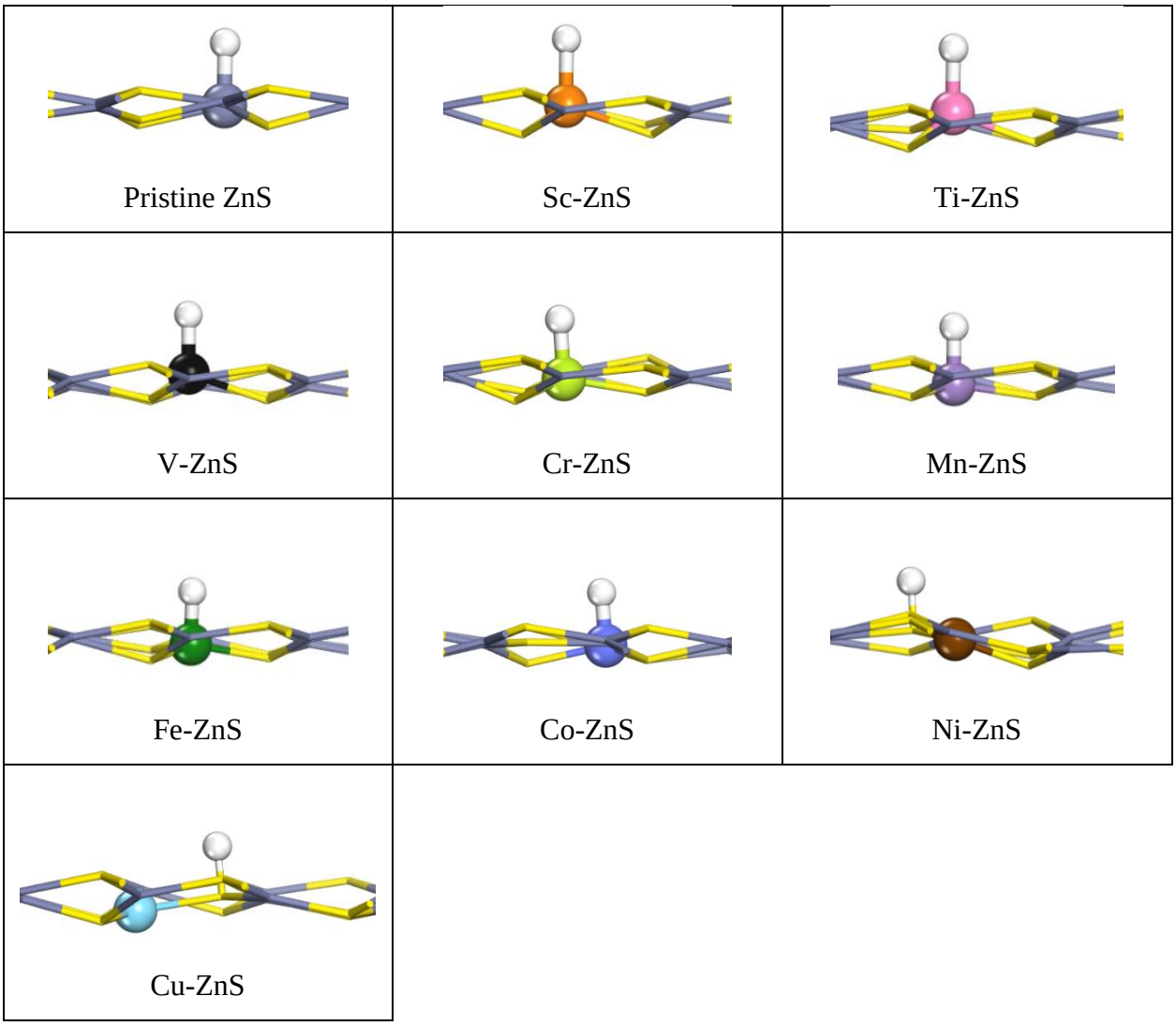


Figure S40 The most stable structures of *H adsorbed on pristine ZnS and TM-ZnS monolayers. Flint, yellow, white, orange, pink, black, light green, purple, dark green, blue, brown and light blue balls represent Zn, S, H, Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu atoms, respectively.

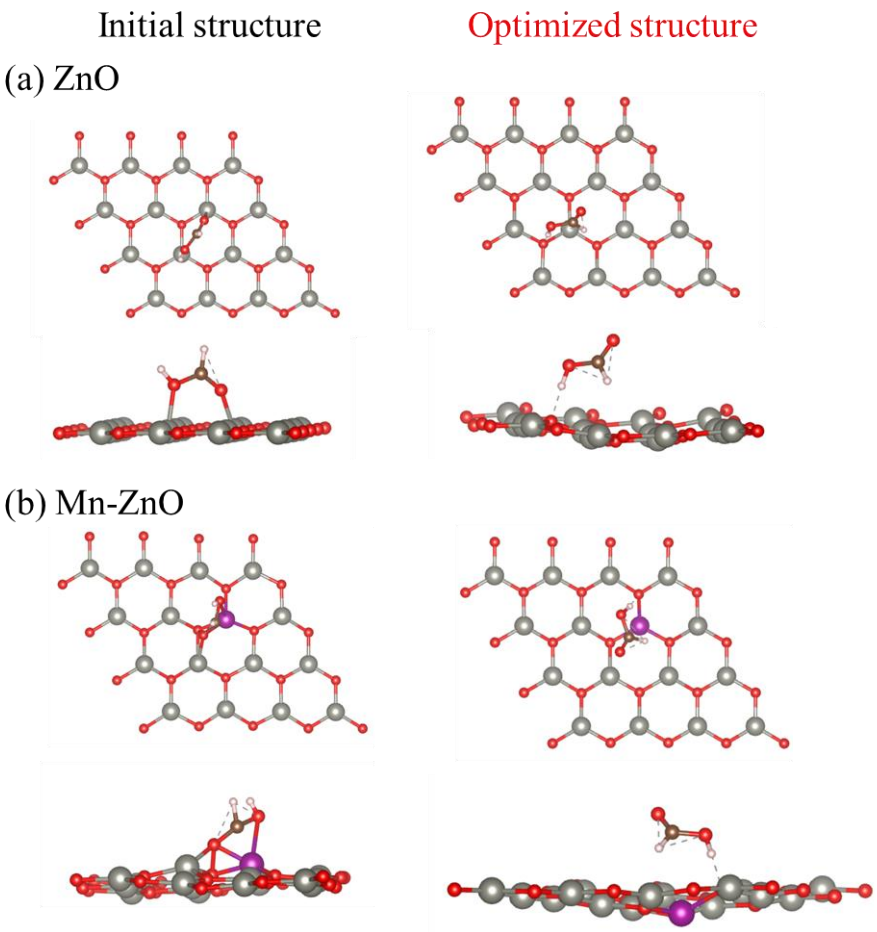


Figure S41 The initial and optimized structure for *HCOOH on (a) ZnO and (b) Mn-ZnO. Flint, red, white, purple, and brown balls represent Zn, O, H, Mn, and C atoms, respectively.

References

1. J.-H. Liu, L.-M. Yang and E. Ganz, *Journal of Materials Chemistry A*, 2019, **7**, 11944-11952.
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6. X. Cui, W. An, X. Liu, H. Wang, Y. Men and J. Wang, *Nanoscale*, 2018, **10**, 15262-15272.