Supporting Information

Dopant-driven electronic coupling and fast gas sensing in gold-boron co-doped Si/MoS_2 heterostructures: a first-principles study

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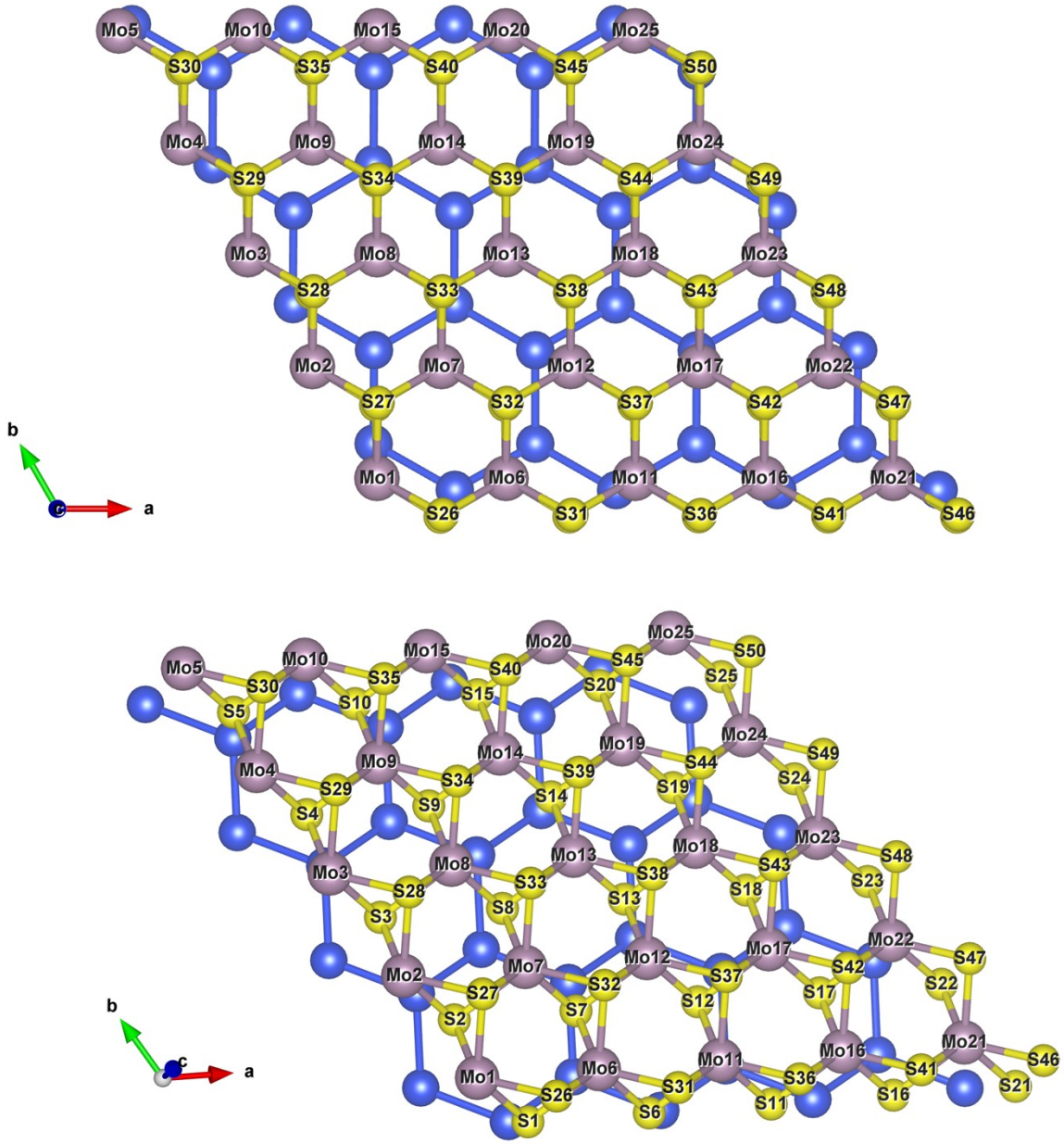

Figure S1. Possible doping sites in the Si/MoS_2 heterostructure

Table S1. Formation energy of Au-doped and B-doped Si/MoS_2 at different adsorption sites. These values are calculated by the M3GNet-UP-2022 potential implemented in the SCM package.

Au-doped Si/MoS_2				**B-doped Si/MoS_2**			
Sites	**E_{form} (eV)**	**Sites**	**E_{form} (eV)**	**Sites**	**E_{form} (eV)**	**Sites**	**E_{form} (eV)**
Mo1	-0.51701006	S21	-0.52317329	Mo1	-0.53720263	S21	-0.52610457
Mo3	-0.52733741	S24	-0.52317329	Mo3	-0.51424632	S24	-0.52671149
Mo5	-0.52732257	S26	-0.52052030	Mo5	-0.53719464	S26	-0.52030517
Mo15	-0.52768764	S29	-0.52054996	Mo15	-0.51424632	S29	-0.52032114
Mo13	-0.52785991	S30	-0.52055053	Mo13	-0.51424632	S30	-0.52637038
Mo11	-0.52751823	S36	-0.52054996	Mo11	-0.53726766	S36	-0.52030517
Mo21	-0.52729348	S39	-0.52054882	Mo21	-0.53726766	S39	-0.52032114
Mo23	-0.52808579	S4	-0.52317329	Mo23	-0.51338614	S4	-0.52668125
Mo25	-0.52751823	S40	-0.52054882	Mo25	-0.53492497	S40	-0.52032114
S1	-0.52317329	S46	-0.52052030	S1	-0.52055044	S46	-0.52637038
S11	-0.52317329	S49	-0.52055053	S11	-0.52668183	S49	-0.52640460
S14	-0.52317329	S5	-0.52317329	S14	-0.52674856	S5	-0.52610400
S15	-0.52317329			S15	-0.52674856		

Table S2. Formation energy BAu- and AuB- co-doped Si/MoS_2 at different adsorption sites

BAu- co-doped Si/MoS_2				**AuB- co-doped Si/MoS_2**			
Sites	**E_{form} (eV)**	**Sites**	**E_{form} (eV)**	**Sites**	**E_{form} (eV)**	**Sites**	**E_{form} (eV)**
Mo1	-0.51725801	Mo24	-0.51877703	Mo1	-0.51377678	Mo24	-0.51533115
Mo2	-0.52191944	Mo25	-0.51718329	Mo2	-0.50908740	Mo25	-0.51957047
Mo3	-0.52188578	S49	-0.51966050	Mo3	-0.52334718	S49	-0.52240477
Mo4	-0.51877703	S24	-0.51500365	Mo4	-0.51689352	S24	-0.52577135
Mo5	-0.51722664	S48	-0.52508229	Mo5	-0.51783584	S48	-0.52227072
Mo6	-0.51726999	S23	-0.51843411	Mo6	-0.51779021	S23	-0.52518838
Mo7	-0.51909874	S43	-0.52508229	Mo7	-0.51735327	S43	-0.52258388
Mo8	-0.52103472	S18	-0.52001530	Mo8	-0.52100221	S18	-0.52590483
Mo9	-0.51678799	S1	-0.51897087	Mo9	-0.51638186	S1	-0.52339614
Mo10	-0.51720496	S26	-0.51328955	Mo10	-0.51819977	S26	-0.52191421
Mo11	-0.51746051	S21	-0.51904332	Mo12	-0.51617308	S21	-0.52523402
Mo12	-0.52189320	S46	-0.51326331	Mo13	-0.52152414	S46	-0.52223878
Mo13	-0.52103472	S30	-0.51349547	Mo14	-0.51850836	S30	-0.52173738
Mo14	-0.51992812	S5	-0.51958692	Mo15	-0.51819977	S5	-0.52292727
Mo15	-0.51728311	S34	-0.51281097	Mo16	-0.51778964	S34	-0.52204826
Mo16	-0.51368494	S9	-0.52536407	Mo17	-0.51617252	S9	-0.52334424
Mo17	-0.51562093	S36	-0.51274252	Mo18	-0.51851635	S36	-0.52459630
Mo18	-0.52188578	S11	-0.52145959	Mo19	-0.51886829	S11	-0.52314573
Mo19	-0.51678799	S31	-0.51326331	Mo20	-0.51784554	S31	-0.52459630
Mo20	-0.52154752	S6	-0.48458290	Mo21	-0.51377621	S6	-0.52314573
Mo21	-0.51746051	S37	-0.51323308	Mo22	-0.51735270	S37	-0.52312349
Mo22	-0.51530663	S12	-0.51546112	Mo23	-0.51949518	S12	-0.52473320

In the BAu co-doped system, the B atom is first fixed at its most stable site on Si/MoS_2 (as listed in **Table S1**). The Au atom is then placed at each of the alternative sites shown in **Fig. S1**. The same procedure applies to the Au-B configuration: the Au atom remains at its most stable position, while the B atom is moved to the other sites. The formation energies of all resulting BAu- and AuB-codoped structures are compared, showing that the AuB co-doped Si/MoS_2 has a lower formation energy and is therefore thermodynamically more stable. As a result, the AuB co-doped configuration is selected for all subsequent calculations.

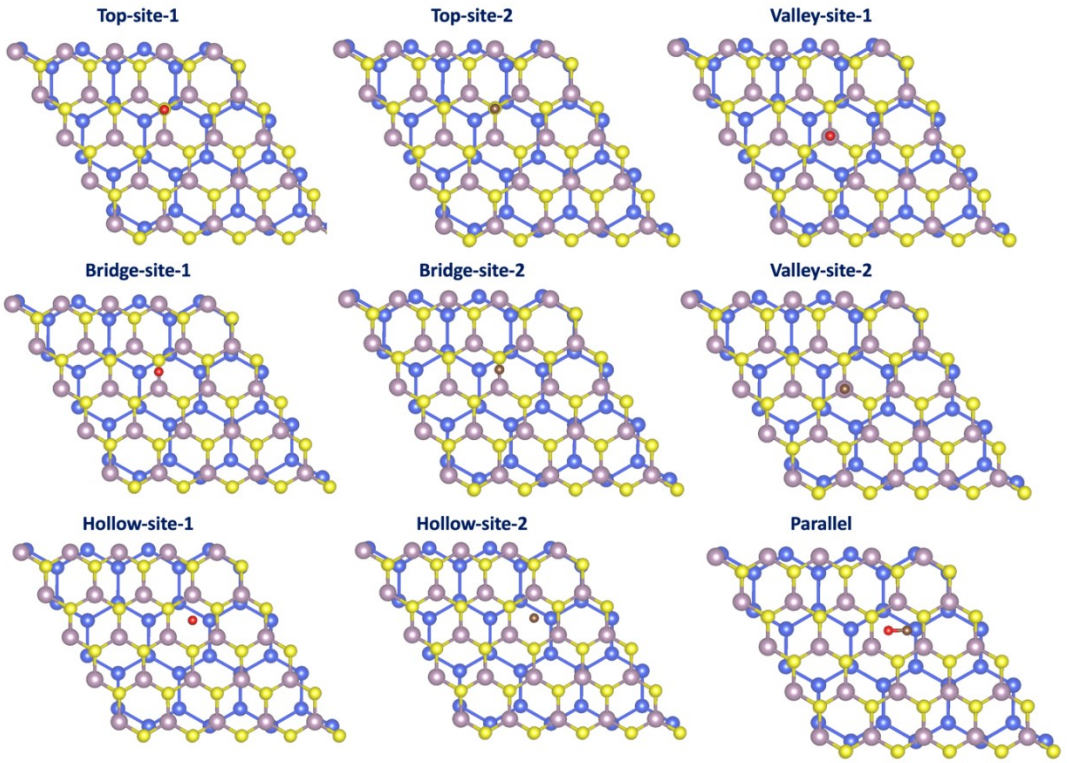

Figure S2. Top-view of all possible adsorption sites of a CO gas molecule on the Si/MoS_2 heterostructure.

The number of possible adsorption sites is determined by the molecular structure and symmetry of the adsorbate, as these factors define the complete set of symmetry-inequivalent adsorption orientations and binding configurations that must be systematically sampled to ensure a comprehensive and unbiased identification of the lowest-energy adsorption state.

For CO, the molecule has two chemically distinct ends (C and O), allowing adsorption at a given site via either end. Consequently, for each surface position, multiple orientations must be examined. By considering the four principal adsorption sites on the substrate: top, bridge, hollow, and valley, and accounting for both vertical and parallel molecular orientations, a total of nine distinct CO adsorption configurations were evaluated. These include C-end and O-end approaches at the respective sites, enabling a comprehensive assessment of orientation-dependent interaction mechanisms between CO and the surface.

In contrast, CO_2, NH_3, NO_2, and H_2O do not exhibit a clear two-end asymmetry comparable to CO, despite their asymmetric charge distributions. For these molecules, adsorption was examined at eight representative configurations, comprising: (i) four vertical orientations (top-1, bridge-1, hollow-1, and valley-1), where the molecular axis is perpendicular to the surface, and (ii) four corresponding parallel orientations (top-2, bridge-2, hollow-2, and valley-2), where the molecule lies approximately parallel to the substrate. This systematic sampling captures the combined effects of adsorption site and molecular orientation on adsorption energy, structural stability, and gas selectivity of the sensing material.

Table S3. Adsorption Energies (meV) of CO, CO_2, H_2O, NO_2, and NH_3 on pristine and doped Si/MoS_2. These values are calculated by the M3GNet-UP-2022 potential implemented in the SCM package.

Gases	Sites	Adsorption Energies (meV)			
		Si/MoS_2	**Au-doped Si/MoS_2**	**B-doped Si/MoS_2**	**AuB co-doped Si/MoS_2**
CO	Top-1	-0.05333	0.00762	0.00762	0.00762
	Bridge-1	-0.05333	0.00762	-0.05333	0.00762
	Hollow-1	0.00762	-5.72955	-7.01119	-7.31649
	Valley-1	-5.66860	**-7.25527**	-6.95023	-7.31649
	Top-2	-1.94531	-0.05333	0.00762	0.00762
	Bridge-2	**-5.72955**	0.00762	0.00762	-0.05333
	Hollow-2	0.00762	-4.53417	-7.01119	-2.55593
	Valley-2	-1.94531	-5.72955	**-8.72004**	**-8.59813**
	Parallel	-0.05333	-5.72955	-8.66562	-7.31649
CO_2	Top-1	-59.68189	-64.07646	-67.25008	-69.75268
	Bridge-1	-59.68189	-64.13742	-66.39566	-65.72436
	Hollow-1	-48.45163	-69.75268	**-92.70162**	-73.10970
	Valley-1	-66.09062	-73.28439	-71.70561	-73.90317
	Top-2	-66.09062	-62.55074	-90.74841	-65.48028
	Bridge-2	-66.09062	**-73.29256**	-72.98752	-72.74344
	Hollow-2	**-66.15157**	-72.80439	-92.69618	**-99.96478**
	Valley-2	-59.37685	-71.94997	-55.28758	-72.74344
H_2O	Top-1	**-70.08166**	-66.08409	-72.12629	-72.46180
	Bridge-1	-69.80411	-66.99947	-72.09582	-67.42668
	Hollow-1	-69.92900	-63.76462	-80.70157	-72.46180
	Valley-1	-66.93852	-73.37773	**-134.10669**	**-122.84569**
	Top-2	-54.24322	-53.99914	-54.94527	-65.04626
	Bridge-2	-69.92900	-57.75290	-60.40788	-52.41220
	Hollow-2	-54.39588	-55.52513	-134.09853	-77.13094
	Valley-2	-69.95948	**-81.67817**	-134.09744	-86.86595
NO_2	Top-1	-40.96153	-39.25268	-42.27392	-37.48261
	Bridge-1	-40.93106	-39.25268	-42.24344	-37.45213
	Hollow-1	**-41.05324**	-39.89350	-39.52751	-39.00833
	Valley-1	-41.02276	**-41.57215**	**-105.38331**	**-91.25372**
	Top-2	-30.58571	-28.72448	-31.56231	-25.12310
	Bridge-2	-30.67741	-30.09754	-31.65401	-24.69589
	Hollow-2	-30.46380	-30.00611	-71.72303	-25.12310
	Valley-2	-30.61618	-30.00611	-71.75350	-59.08869
	Top-1	185.23154	185.26201	185.56705	192.86096
	Bridge-1	184.10255	185.01793	185.56705	191.54857
	Hollow-1	**184.07180**	184.04133	**184.13276**	191.57932

	Valley-1	184.07316	184.13276	187.30665	187.09331
	Top-2	186.94039	186.94039	187.30665	194.75294
	Bridge-2	186.94039	196.79757	187.33712	194.78341
	Hollow-2	203.29773	169.91174	185.56705	191.24353
	Valley-2	199.63568	**160.32939**	184.25493	**182.79016**

Table S4. Comparison of adsorption energies for target (CO, CO_2) and interfering gases (H_2O, NH_3, NO_2) on various Si/MoS_2-based systems computed with different dispersion corrections (DFT-D2, DFT-D3, and TS).

Substrate	**Gases**	**Adsorption Energies (meV)**		
		DFT-D2	**DFT-D3**	**TS**
Si/MoS_2	CO	-45.6	-72.3	-69.6
	CO_2	-79.7	-111.9	-115.9
	H_2O	-95.3	-118.3	-129.1
	NH_3	-65.4	-89.0	-92.0
	NO_2	-234.5	-273.4	-276.1
Au-doped Si/MoS_2	CO	-45.5	-70.6	-68.7
	CO_2	-90.6	-120.5	-126.5
	H_2O	-130.4	-143.9	-145.5
	NH_3	-128.6	-153.0	-132.9
	NO_2	-286.2	-323.2	-321.4
B-doped Si/MoS_2	CO	-47.0	-73.7	-74.8
	CO_2	-91.5	-124.5	-130.9
	H_2O	-150.2	-166.0	-175.0
	NH_3	-61.3	-76.7	-76.4
	NO_2	-248.4	-279.4	-279.0
AuB co-doped Si/MoS_2	CO	-45.1	-71.2	-69.1
	CO_2	-71.5	-101.1	-105.3
	H_2O	-144.1	-158.4	-166.0
	NH_3	-21.3	-12.3	-10.5
	NO_2	-222.4	-253.8	-253.5

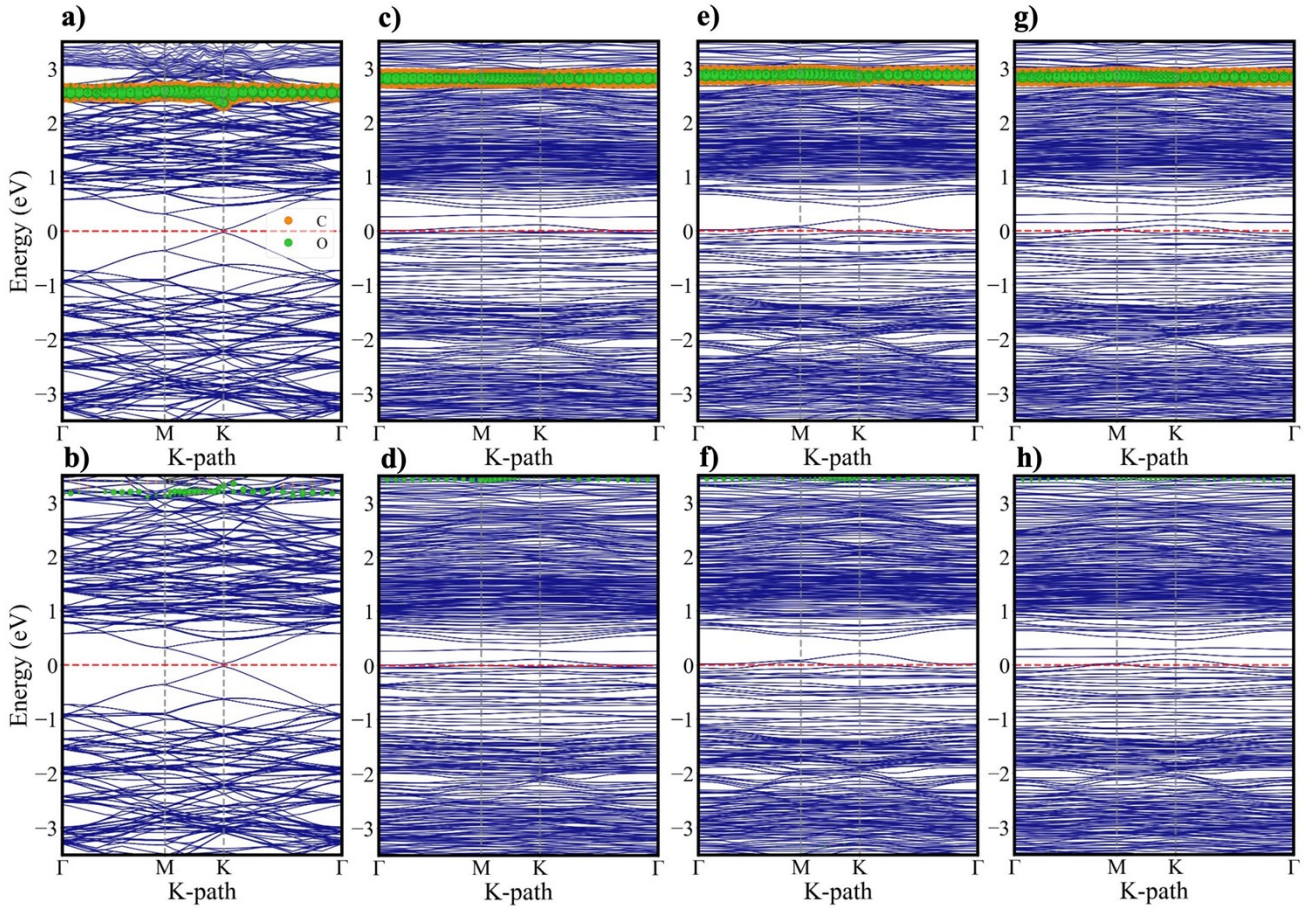

Figure S3. Electronic band structure of CO and CO_2 adsorbed on pristine (a,b), Au-doped (c,d), B-doped (e,f), and AuB co-doped silicene/MoS_2 (g,h), respectively. The red-dashed line indicates the Fermi level. These band structures are calculated by the DFT-D3 potential implemented in the VASP package.

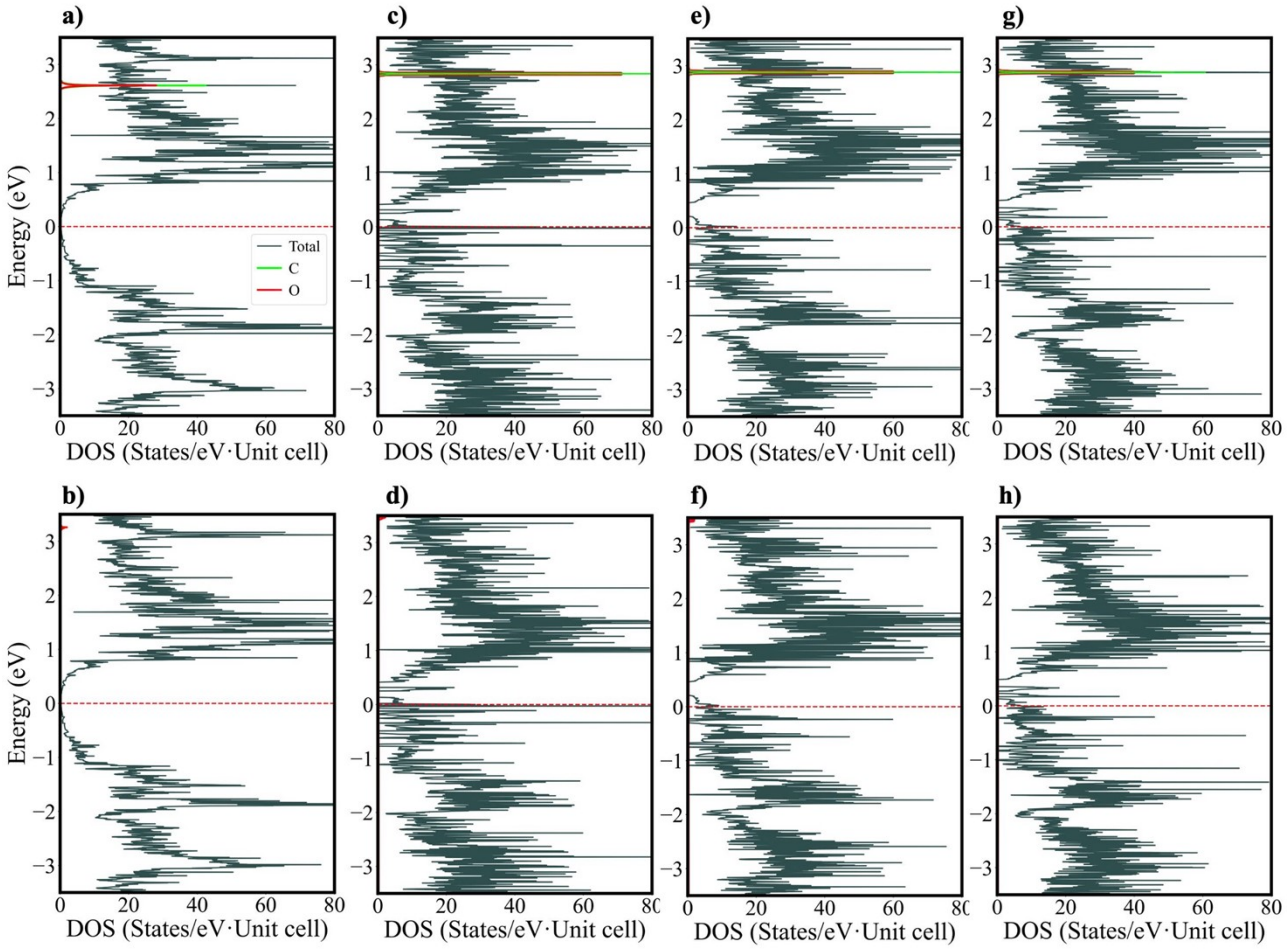

Figure S4. Project density of states of CO and CO_2 adsorbed on pristine (a,b), Au-doped (c,d), B-doped (e,f), and AuB co-doped Si/MoS_2 co-doped Si/MoS_2 (g,h), respectively. The dashed line demonstrates the Fermi level. These pDOS are calculated by the DFT-D3 potential implemented in the VASP package.