A computational evaluation of MoS_2-based materials for the electrocatalytic oxygen reduction reaction

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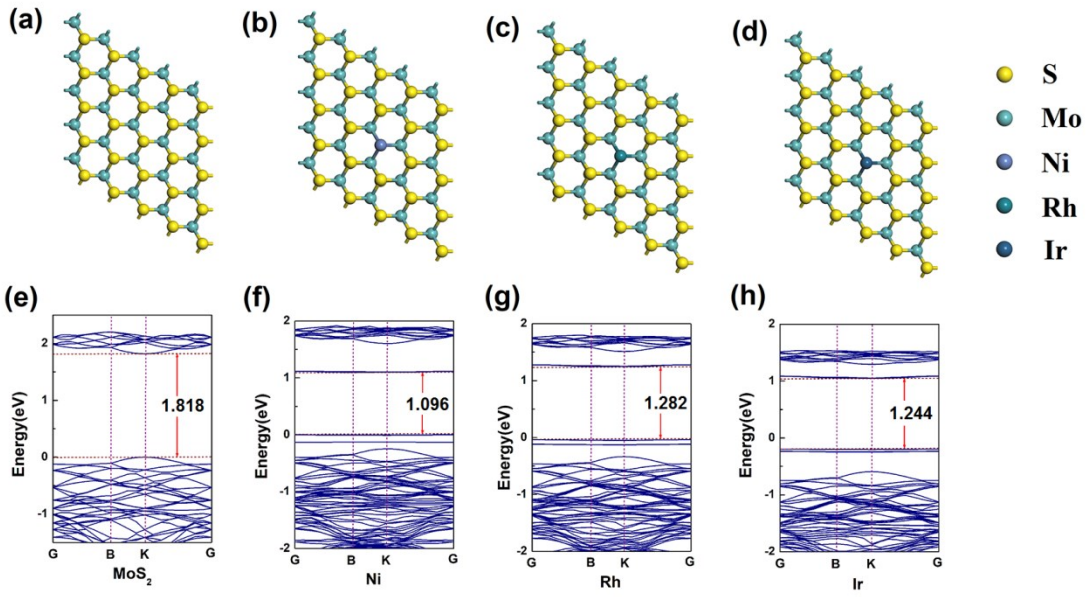

Fig.S1 Atomic structure of (a) pristine MoS_2 (b) Rh-doped MoS_2 (c) Ni-doped MoS_2 (d) Ir-doped MoS_2; and band structure of (e) pristine MoS_2 (f) Rh-doped MoS_2 (g) Ni-doped MoS_2 (h) Ir-doped MoS_2.

Figure S1 presents the geometry configurations and band structures of pristine MoS_2 and other doped MoS_2 that have not been demonstrated in Fig.1. The bond length between the dopant atom and Mo atoms varies from 2.52Å to 2.65Å for doped MoS_2, which were close to the S-Mo bond's 2.42Å. For the 4Pt-loaded MoS_2, the Pt-S bonds vary from 2.36Å to 2.41Å. All the dopant atoms bonded well with the atoms in the material. The band structure results show that the addition of dopant atoms could bring new states to the forbidden bands and improve the conductivity of MoS_2.

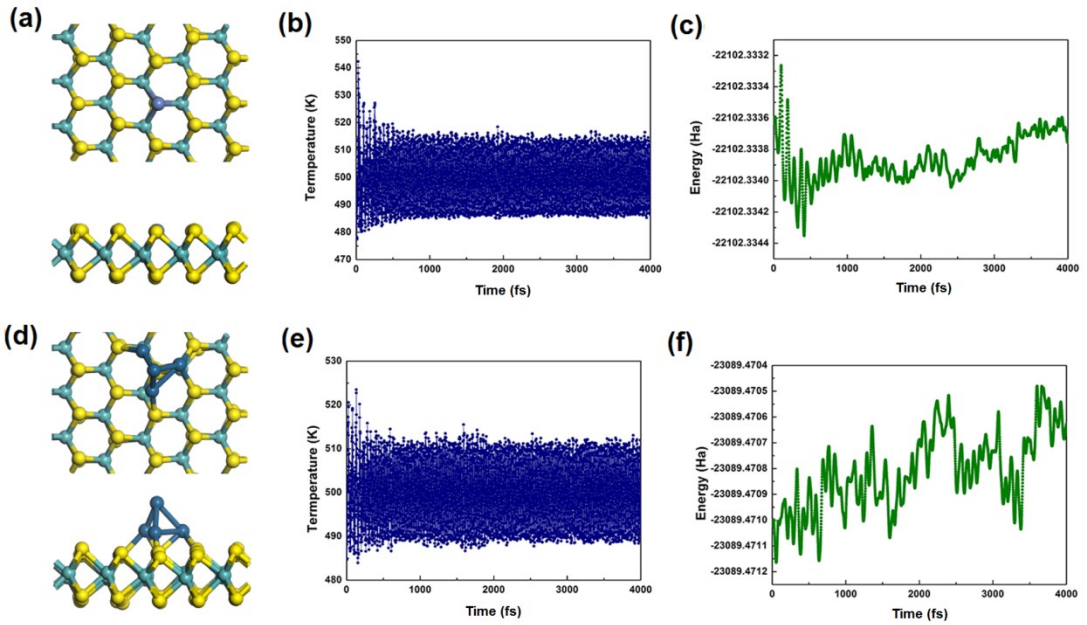

Fig.S2 Geometry configuration after 4000 steps of (a) Ni-doped MoS_2 (d) 4Pt-deposited MoS_2; Temperature fluctuation of (b) Ni-doped MoS_2 (e) 4Pt-deposited MoS_2; Total energy change of (c) Ni-doped MoS_2 (f) 4Pt-deposited MoS_2.

Figure S2 demonstrated the molecular dynamics (MD) simulation results of Ni-doped MoS_2 and 4Pt-deposited MoS_2. From the geometry results, it could be found that after 4000fs at 500K, the Ni-doped MoS_2 has no evident structural change. For the 4Pt-deposited one, the Pt atoms have some displacement, while they still closely adsorbed on the surface of MoS_2. From the energy results, there is no significant energy charge for these two structures during the process. Thus, the two structures could be considered to be stable thermodynamically.

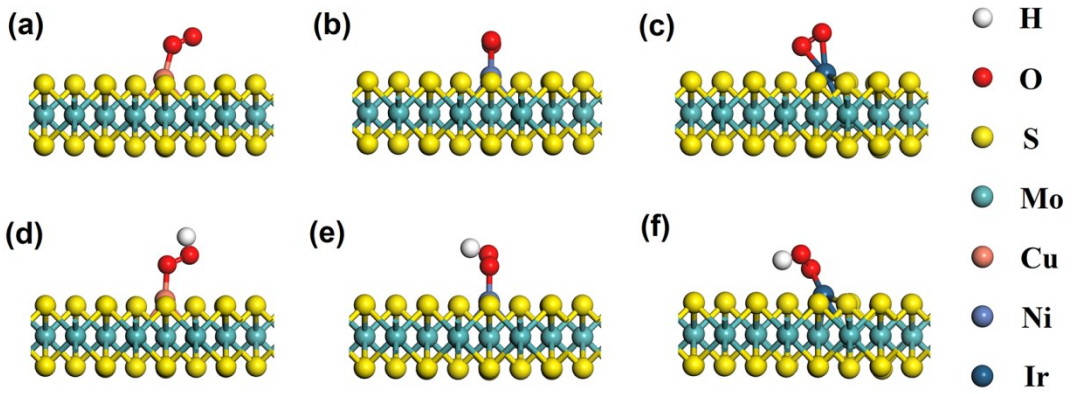

Fig.S3 Lowest energy configurations of O_2 on (a) Cu-doped MoS_2 (b) Ni-doped MoS_2 and (c) Ir-doped MoS_2; OOH* on (d) Cu-doped MoS_2 (e) Ni-doped MoS_2 and (f) Ir-doped MoS_2

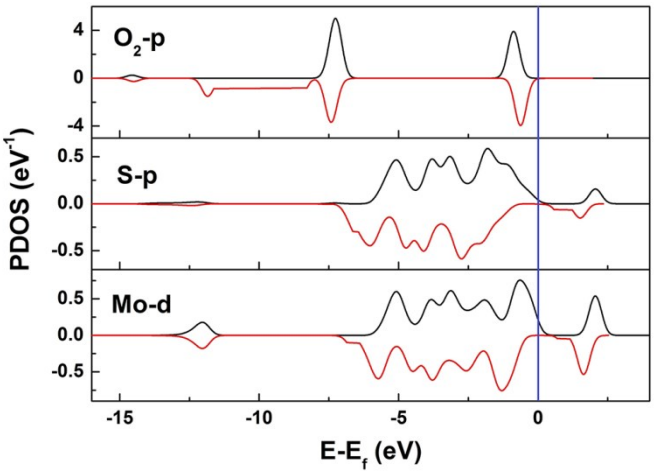

Fig.S4 Computed projected density of states (PDOS) of O_2 adsorbed on pristine MoS_2 surface.

The charge transfer mechanism between an adsorbate and materials could be determined by mixing the molecular HOMO and LUMO with the orbitals of the atoms in materials [1]. It could be judged by the relationship between the Fermi level of the materials and the HOMO and LUMO levels of adsorbates. Form the DFT calculation results, the HOMO level and LUMO level of a single O_2 molecule is -6.879eV and -4.594eV, respectively. It is comparing with the Fermi Levels E_f of these catalytic materials (Table 1). It could be found that all the E_f values were between the HOMO level and the LUMO level of an O_2 molecule. That indicates the charge transfer between an O_2 molecule, and these materials mainly depend on the orbital mixing theory [2].

Figure S4 presented the PDOS of the pristine MoS_2 surface when O_2 molecule adsorbed. It could be found that there are no evident peak overlaps between the PDOS of O_2 and MoS_2. Indicating the orbital mixing between O_2 molecule and pristine MoS_2 is weak.

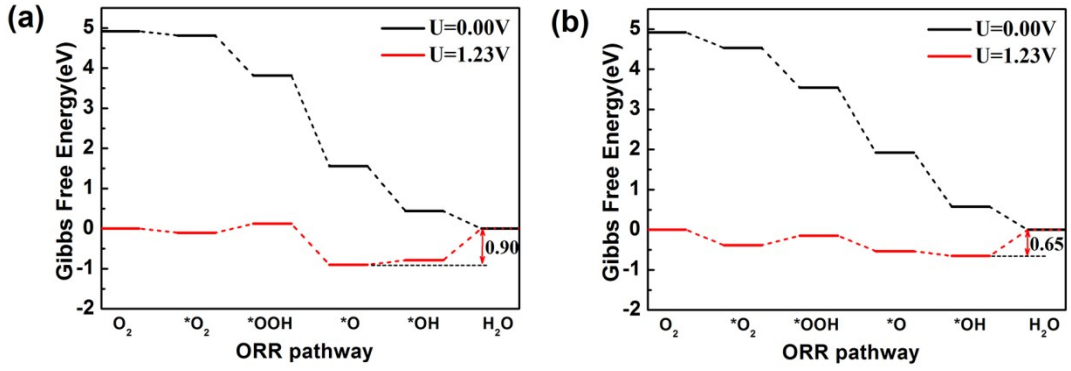

Fig.S5 Schematic Gibbs, free energy diagrams of ORR on the (a), 2Pt-deposited MoS_2 (b) 7Pt-deposited MoS_2

Figure S5 shows the Gibbs free energy diagrams of the ORR process on 2Pt- and 7Pt-deposited MoS_2. The results reveal that the total overpotential of 2Pt-deposited MoS_2 is 0.90eV, which is inferior to that of the 4Pt-deposited one. While that of 7Pt-deposited MoS_2 is 0.65eV, even better than pure Pt (0.68eV). These results indicate that the depositing content of Pt easily influences the catalytic activity of Pt-deposited MoS_2. But it is mentionable that Pt-deposited MoS_2 has the potential to have better ORR catalytic activity than pure Pt. Further studies are expected to optimize this Pt-deposited MoS_2 for ORR applications.

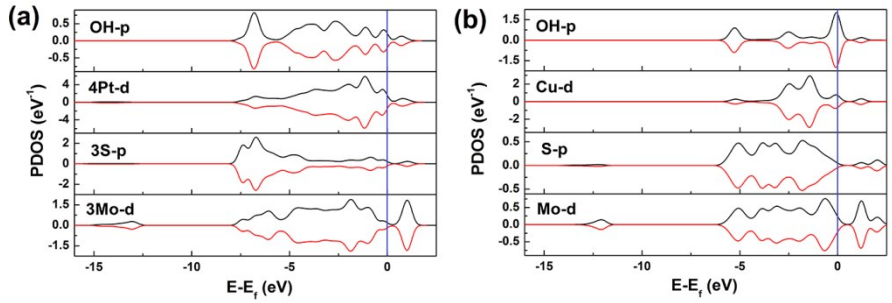

Fig.S6 Computed projected density of states (PDOS) of OH adsorbed on (a) 4Pt-loaded MoS_2 (b) Cu-doped MoS_2

Figure S6 showed the whole PDOS when OH adsorbed on 4Pt-loaded MoS_2 and Cu-doped MoS_2. It could be found there are several overlaps of DOS between OH and the dopant atoms, such as the 4Pt-loaded one at -6.9eV and -1.3eV, the Cu-doped one at -2.5eV and 0eV. The OH species bonded well with the materials.

Table S1 Primitive values of intermediate quantity of E_{form}

Materials	$E_{X\text{-}MoS2}$ (Ha)	E_{MoS2} (Ha)	E_X (Ha)	E_{host} (Ha)
Cu-MoS_2	-22119.7277006	-22295.3548080	-444.9117939	-398.0380858
Rh-MoS_2	-22040.9639438		-287.2875427	
Ni-MoS_2	-22090.7540116		-386.8678644	
Ir-MoS_2	-22075.1500543		-355.6566241	
Co-MoS_2	-22064.0584944		-333.5050130	
N-MoS_2	-21951.9447713		-109.4491128	

Table S2 Primitive values of adsorption energy to reaction intermediates E_{ads}

Materials	$E_{substrate}$ (Ha)	E_{system} (Ha)			
		O_2	OOH	O	OH
MoS_2	-22295.354809	-22445.579299	-22446.186468	-22370.497497	-22371.071891
Cu-MoS_2	-22119.727701	-22270.005047	-22270.633420	-22194.849648	-22195.531593
Rh-MoS_2	-22040.963944	-22225.448150	-22226.051221	-22150.325831	-22150.945799
Ni-MoS_2	-22090.754012	-22191.258373	-22191.865542	-22116.114452	-22116.754942
Ir-MoS_2	-22075.150054	-22225.448149	-22226.051221	-22150.325831	-22150.945799
4Pt-MoS_2	-21951.944771	-23227.014528	-23227.637619	-23151.893410	-23152.534069
Pure Pt	-7034.430010	-7184.704819	-7185.317651	-7109.548687	-7110.206089
Pt-MoS_2	-22092.605065	-22242.869005	/	/	/
Co-MoS_2	-22064.053771	-22214.364744	/	/	/
Pd-MoS_2	-22060.611499	-22210.873939	/	/	/

$E_{adsorbate}$ values are -150.246707 Ha for O_2, -150.828929 Ha for OOH, -75.007936 Ha for O and -75.682944 Ha for OH.

The calculated E_{ads} value for Pt-doped MoS_2 is -0.47eV; for Co-doped MoS2 is -1.75eV; for Pd-doped MoS_2 is -0.43eV. All the three are not in the range of -1.4eV to -0.5eV. Indicating doping Pt, Co, or Pd atoms is not favorable for the ORR process.

Table S3 Hirshfeld charge results of ORR species when adsorbed on catalytic materials

Materials	O_2	OOH	O	OH
MoS_2	0.0507	0.1137	0.2525	0.0763
Cu-MoS_2	0.2146	0.1916	0.3423	0.265
Rh-MoS_2	0.1667	0.0528	0.2549	0.1463
Ni-MoS_2	0.0942	0.0682	0.2465	0.1482
Ir-MoS_2	0.1785	0.0507	0.2044	-0.1275
4Pt-MoS_2	0.1827	0.1279	0.2756	0.1629
Pure Pt	0.2202	0.0648	0.3049	0.1776

Table S4 Primitive values of zero-point energy and entropy.

Materials	pristine		O_2		OOH		O		OH	
	S (cal/mol/K)	ZPVE (kcal/mol)	S (cal/mol/K)	ZPVE (kcal/mol)	S (cal/mol/K)	ZPVE (kcal/mol)	S (cal/mol/K)	ZPVE (kcal/mol)	S (cal/mol/K)	ZPVE (kcal/mol)
MoS_2	356.01	92.98	370.29	95.13	390.35	102.19	369.47	95.24	374.24	100.22
Cu-MoS_2	374.13	91.40	398.61	94.45	391.41	101.81	378.36	93.06	382.19	99.55
Rh-MoS_2	374.53	91.42	380.38	95.66	389.58	101.96	379.25	93.08	382.50	99.44
Ni-MoS_2	372.13	91.71	390.30	94.43	389.15	101.32	379.65	93.03	383.64	99.33
Ir-MoS_2	375.91	91.27	386.09	94.70	387.41	101.94	379.49	91.09	381.24	99.74
4Pt-MoS_2	409.41	94.81	423.39	97.58	428.64	101.65	419.02	96.03	420.27	102.66
Pure Pt	349.34	17.55	352.42	20.80	360.43	27.86	347.76	18.62	358.82	25.36

Table S5 Δ*G* values for each step of ORR occurred on the six kinds of materials

Materials	ΔG (eV)				
	Step (1)	Step (2)	Step (3)	Step (4)	Step (5)
Cu-MoS_2	-0.4634036	-0.7689922	-0.8021236	-2.4067515	-0.4787291
Rh-MoS_2	-0.5974830	-0.4500454	-1.7325706	-1.2770819	-0.8628191
Ni-MoS_2	-0.7290691	-0.4518576	-1.4313767	-1.8159060	-0.4917906
Ir-MoS_2	-1.0119312	-0.1959040	-2.5479899	-0.6001511	-0.5640238
4Pt-MoS_2	-0.4330286	-0.7991790	-1.9173312	-1.243957	-0.5256038
Pure Pt	-0.2816292	-0.5550804	-1.2381629	-1.8211867	-1.0239407

Reference

[1] O. Leenaerts, B. Partoens, and F. M. Peeters, Adsorption of H_2O, NH_3, CO, NO_2, and NO on graphene: A first-principles study *Phys. Rev. B* **2008**, *77, 125416*

[2] Zhou, C. J.; Yang, W. H.; Zhu, H. L., Mechanism of Charge Transfer and Its Impacts on Fermi-Level Pinning for Gas Molecules Adsorbed on Monolayer WS_2. *Journal of Chemical Physics* **2015**, *142*.