Electronic Supplementary Material (ESI) for Nanoscale.

Rational design of MoS_2 supported Cu single atom catalysts by machine learning potential for enhanced peroxidase-like activity

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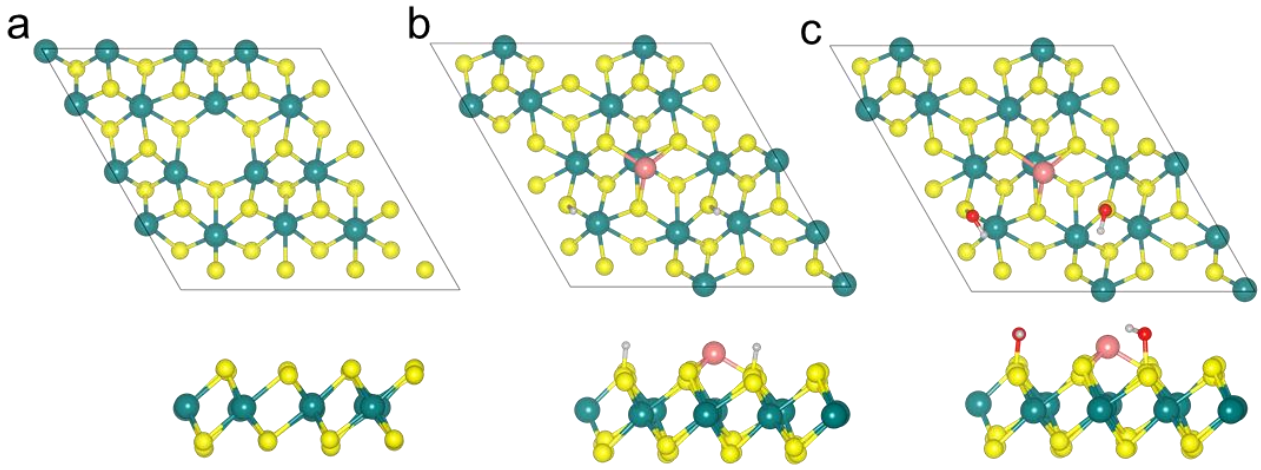

Figure S1 Top and side view of different optimized geometries associated with MoS_2. (a) MoS_2-Vs, (b) Cu@MoS_2 in acid and (c) Cu@MoS_2 in basic conditions.

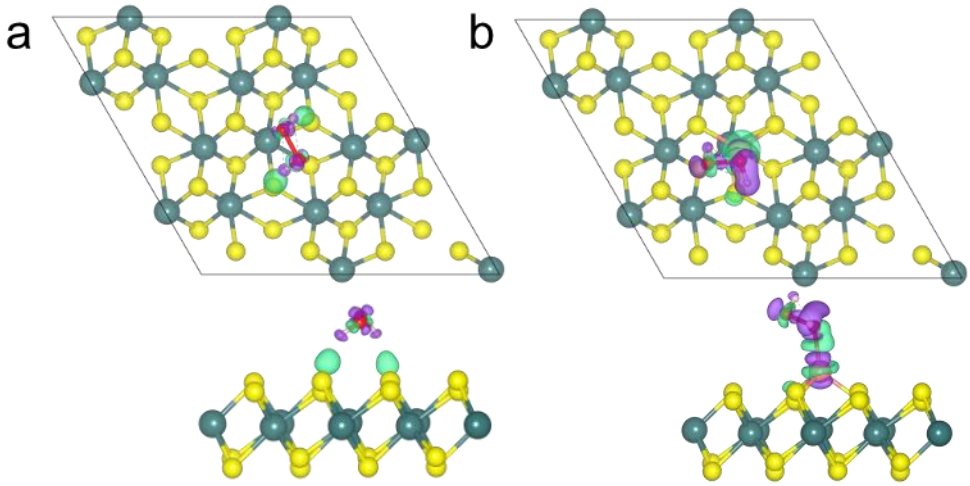

Figure S2 Charge density difference plots for H_2O_2 adsorbed surfaces of (a) pure MoS_2 and (b) Cu@MoS_2. The isosurface value of electron density is taken as 0.002 e/Å^3. The cyan and purple regions for the charge density difference represent the areas of electron accumulation and depletion, respectively.

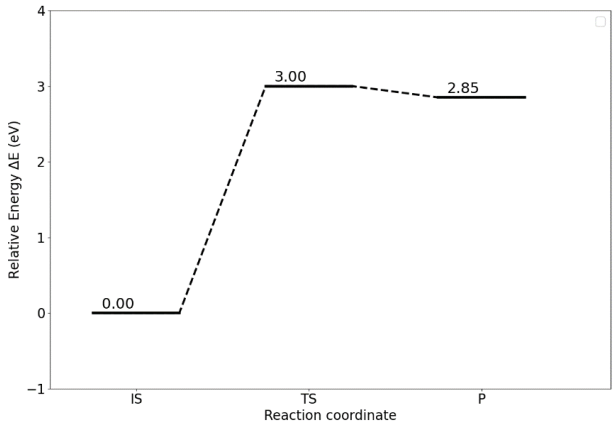

Figure S3 Energy profile for decomposition of H_2O_2 on pure MoS2. The path shows H_2O_2 decompose into HOO and H. The numbers represent the energy (eV) at each state. The abscissa IS, TS, and P represent reactants, transition states and products, respectively.

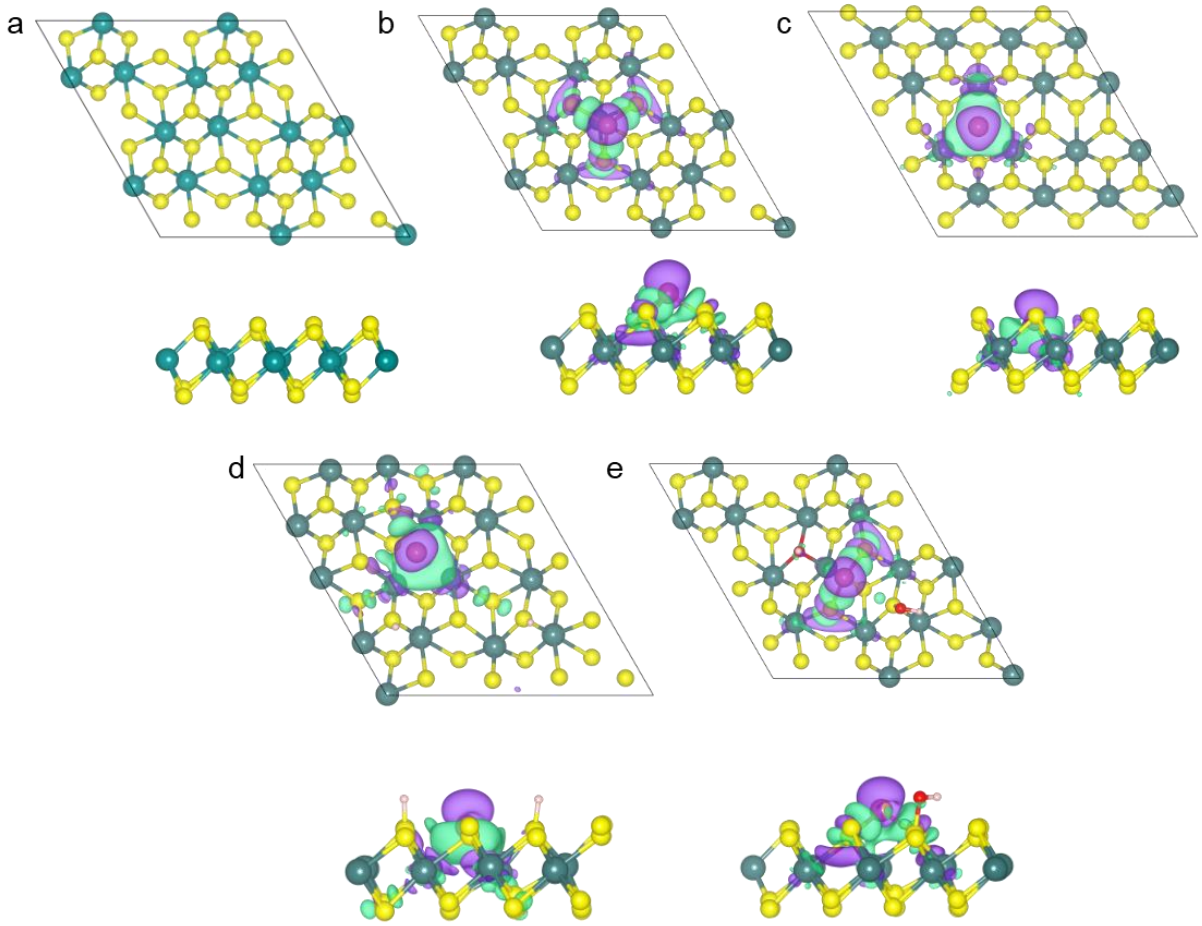

Figure S4 Charge density difference plots for Cu adsorbed different MoS_2 surfaces of (a) pure MoS_2, (b) Cu@MoS_2, (c) Cu@MoS_2-Vs, (d) Cu@MoS_2-Vs in acid and (e) Cu@MoS_2-Vs in basic. The isosurface value of electron density is taken as 0.002 e/Å^3. The cyan and purple regions for the charge density difference represent the areas of electron accumulation and depletion, respectively.

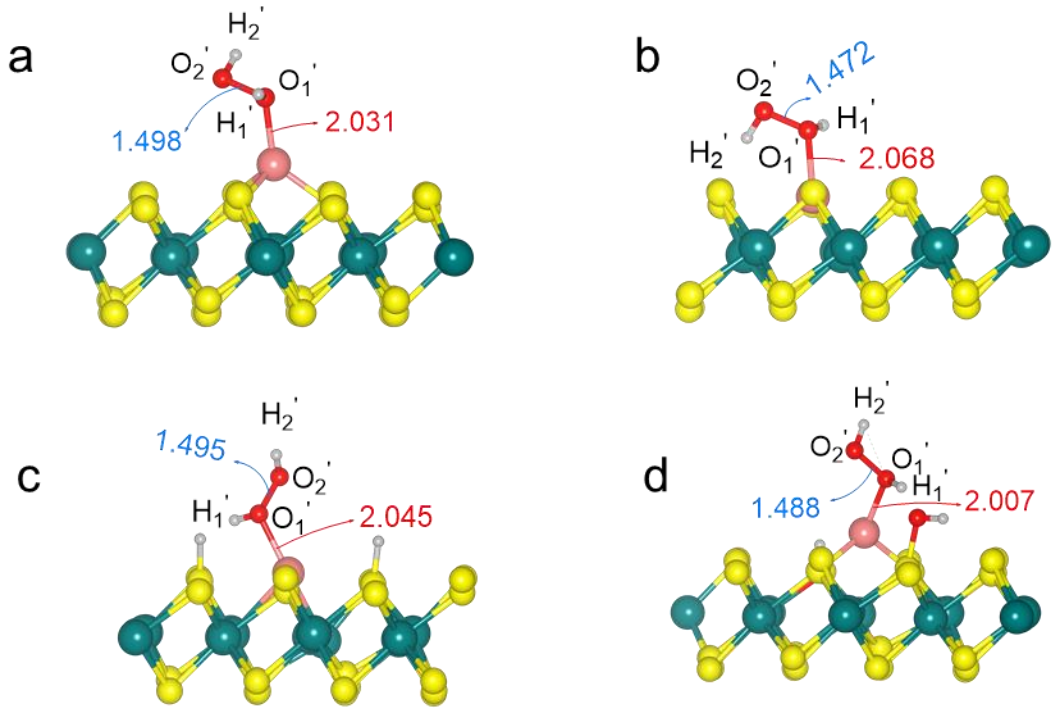

Figure S5 The optimized geometrical structures of H_2O_2 adsorption on (a) Cu@MoS_2, (b) Cu@MoS_2-Vs, (c) Cu@MoS_2-Vs in acid and (d) Cu@MoS_2-Vs in basic conditions. The bond length is in Å.

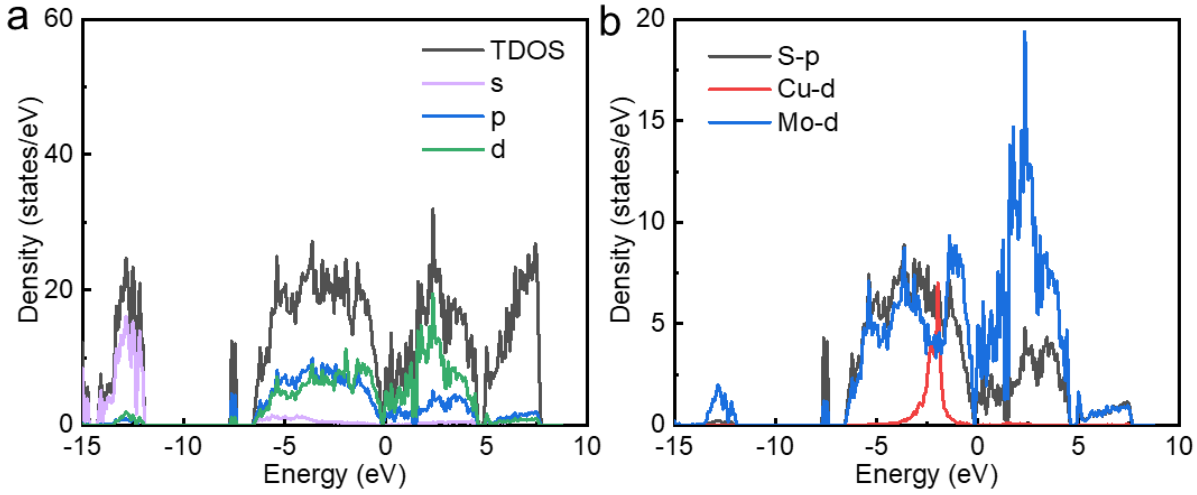

Figure S6 PDOS of Cu@MoS_2-Vs in acidic condition.

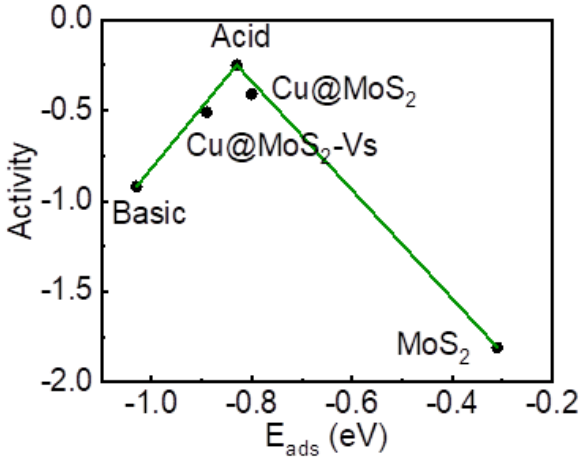

Figure S7 H_2O_2 decomposition reaction volcano plot for different MoS_2 supported nanozymes.

Table S1 S-S bonds, Mo-S bonds lengths and their average distance on MoS_2 and $Cu@MoS_2$ surfaces and Mo-Cu bond, Cu-S bonds lengths and their average distance on $Cu@MoS_2$.

Distance (Å)	MoS_2	$Cu@MoS_2$
S1-S2	3.245	3.341
S2-S3	3.203	3.356
S3-S1	3.245	3.341
S-S average	3.231	3.346
Mo1-S1	2.409	2.442
Mo1-S2	2.466	2.570
Mo1-S3	2.466	2.570
Mo-S average	2.447	2.527
Mo1-Cu	-	2.740
S1-Cu	-	2.274
S2-Cu	-	2.204
S3-Cu	-	2.204
S-Cu average	-	2.23

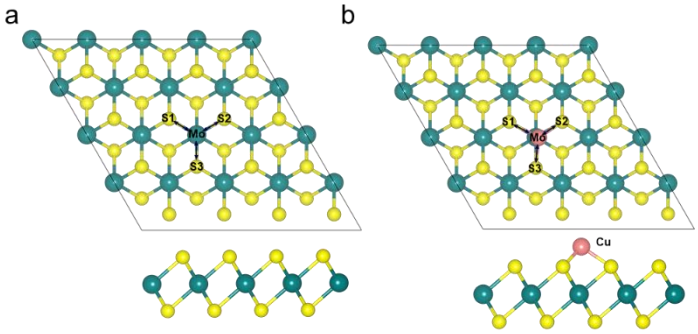

Table S2 Adsorption energy (E_{ads}, eV) of H_2O_2 molecule on different substrates.

Substrate	pure MoS_2	Cu@MoS_2	Cu@MoS_2-Vs	Cu@MoS_2-Vs in acid	Cu@MoS_2-Vs in basic
E_{ads}	-0.31	-0.80	-0.89	-0.83	-1.03

The Cu loading surfaces have large adsorption energies (-0.80, -0.89, -0.83 and -1.03 eV for Cu@MoS2, Cu@MoS2-Vs, Cu@MoS2-Vs in acid and Cu@MoS2-Vs in basic, respectively) and much heat is released during the desorption and adsorption processes. According to the Gibbs free energy formula: ΔG=ΔH-TΔS, the difference of ΔG for H2O2 molecule in gas phase is - 0.75 eV under 37 ℃ and 0 K. After redressing by ΔG, the adsorption energy at 37 ℃ is - 0.80 - (- 0.75) eV = -0.05 eV, -0.89 - (- 0.75) eV = -0.14 eV, -0.83 - (- 0.75) eV = -0.08 eV, -1.03 - (- 0.75) eV = -0.28 eV respectively for Cu@MoS2, Cu@MoS2-Vs, Cu@MoS2-Vs in acid and Cu@MoS2-Vs in basic, which are all less than 0 eV, indicating that H2O2 molecule can be adsorbed on the surfaces. The temperature has little effect on the enzymatic activity for Cu loading surfaces. As for pure MoS2 surface (Eads = - 0.31 eV), increasing the temperature will decrease the enzymatic activity. The activity of pure MoS2 will further decrease at high temperature, which also further confirms that the pure MoS2 surface is almost reactive inert. As a result, the methodological limitation on temperature did not affect the study results through the analysis above.

Table S3 Adsorption energy (E_{ads}, eV) of Cu atom on different substrates.

Substrate	pure MoS_2	Cu@MoS_2	Cu@MoS_2-Vs	Cu@MoS_2-Vs in acid	Cu@MoS_2-Vs in basic
E_{ads} (eV)	-	-3.27	-4.96	-3.74	-2.79

Table S4 Important bond lengths on Cu@MoS_2-Vs surfaces in neutral, acidic and basic conditions.

Distance (Å)	Neutral	Acid	Basic
S1-S2	3.290	3.297	3.255
S2-S3	3.174	3.255	3.250
S3-S1	3.174	3.245	3.253
S-S Average	3.213	3.265	3.253
Mo1-Mo2	3.670	3.513	3.510
Mo2-Mo3	3.670	3.721	2.800
Mo3-Mo1	3.453	3.769	2.803
Mo-Mo Average	3.598	3.668	3.038
Mo1-Cu	2.644	2.638	2.218
Mo2-Cu	2.579	2.574	2.217
Mo3-Cu	2.645	2.651	2.120
Mo-Cu Average (or O-Cu)	2.623	2.621	2.185
S1-Cu	3.461	3.572	3.031
S2-Cu	3.461	3.430	3.589
S3-Cu	3.665	3.379	3.587
S-Cu Average （or S-O)	3.529	3.460	3.402
S-H1	-	1.362	-
S-H2	-	1.357	-
Mo3-Cu	-	-	2.847
S4-Cu	-	-	2.123
S5-Cu	-	-	2.122
O1-H1	-	-	0.978
O2-H2	-	-	0.990
O2-Cu	-	-	1.660

Table S5 Important bond lengths, angle and torsion of H_2O_2 on pure MoS_2, Cu@MoS_2 and Cu@MoS_2-Vs surfaces in neutral, acidic and basic conditions.

d (distance, Å), or angle or torsion	pure MoS_2	Cu@MoS_2	Cu@MoS_2-Vs	Cu@MoS_2-Vs-in-acid	Cu@MoS_2-Vs-in-basic
O1-O2	1.463	1.498	1.472	1.495	1.488
H1-O1	0.987	0.982	0.984	0.997	1.009
H2-O2	0.986	0.981	0.999	0.981	0.981
<H1O1O2	100.95	99.66	101.716	101.943	101.183
<H2O2O1	99.823	98.852	101.596	98.914	99.097
Torsion	-100.365	124.194	93.044	120.024	114.16
O1-Cu	-	2.031	2.068	2.045	2.007
Cu-S1 (Cu-Mo1)	-	2.303	2.711	2.666	2.161
Cu-S2 (Cu-Mo2)	-	2.212	2.681	2.619	2.17
Cu-S3 (Cu-Mo3)	-	2.275	2.628	2.706	-