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An Insight into Enhanced Photocatalytic Properties of a Type-II MoS_2/ZnO Heterostructure and Tuning their Properties and Interfacial Charge Transfer by Strain

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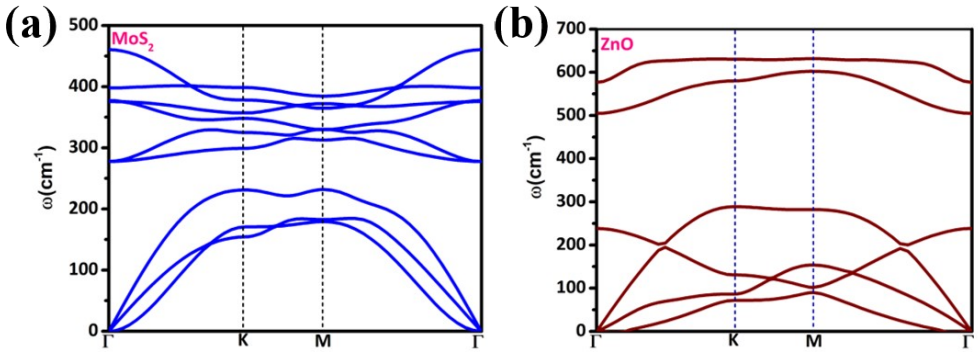

Figure S1: The calculated phonon band structure of the MoS_2 and ZnO monolayers.

Table S1: Summary of the reported MoS_2 and ZnO-based heterostructures and their parameters.

vdW heterostructure	Band alignment	CBO (eV)	VBO (eV)	ΔG_H (eV)	Mobility ($cm^2V^{-1}s^{-1}$)		Bandgap tuning	Ref.
					electron	hole		
MoS_2/ZnO	Type-II	1.55	0.57	-0.03	820	200	Strain	This work
MoS_2/ZnO	Type-II	2.49	0.58	-	-	-	-	[1]
MoS_2/ZnO	Type-II	2.49	0.58	-	-	-	-	[2]
ZnO/WSe_2	Type-II	-	-	-	480.32	1213.29	Strain	[3]
WS_2/ZnO	Type-II	0.97	0.34	-	-	-	Strain	[4]
ZnO/SeMoS	Type-II	0.86	0.11	-	-	-	Vertical strain	[5]

							and electric field	
BlueP/MoS_2	Type-II	0.79	0.44	-	-	-	-	[6]
InSe/MoS2	Type-II	-	-	-	-	-	Strain	[7]
g-ZnO/2H-MoS_2	Z-scheme	-	-	-	-	-	-	[8]
MoS_2/ZnO	Type-II	-	1.1	-	-	-	Electric field	[9]
GaN/ZnO	Type-II	-	-	-	-	-	Strain	[10]
AlN/ZnO	Type-II	-	-	-	-	-	Strain	[10]
MoS_2/BP	Type-I	0.17	0.73	-	-	-	-	[11]
MoS_2/BSe	Type-I	1.09	0.25	-	358.22	188.60	-	[12]
MoS_2/BP	Type-II	0.13	0.91	-	990	27670	Strain	[13]

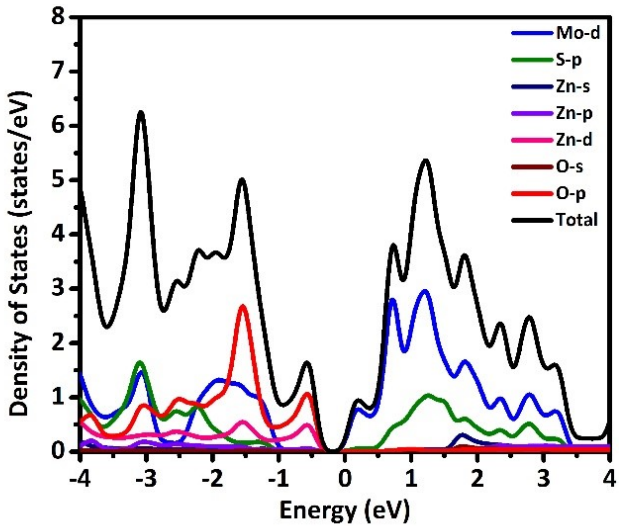

Figure S2: The calculated PDOS plot of the MoS_2/ZnO conf-5 heterostructure.

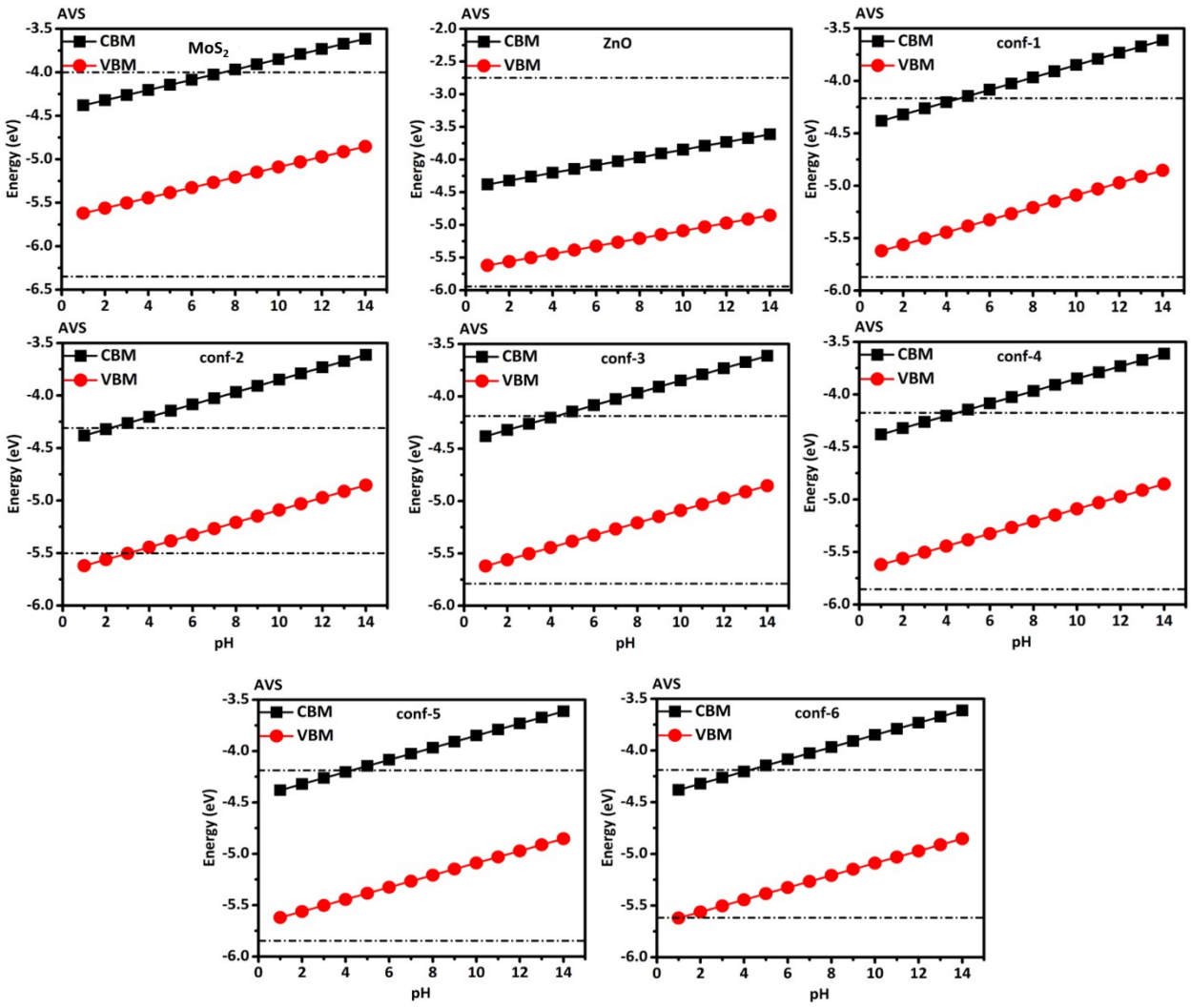

Figure S3: The effect of pH on the water redox potentials for the MoS_2, ZnO monolayers and heterostructures with six stacking patterns.

Text S1: Hydrogen evolution reaction (HER)

To describe the catalytic activity of any semiconductor, the exchange current density (ECD) is a crucial parameter for determining the efficiency of H_2 and O_2 generation in the water-splitting process. The adsorption free energy (AFE) of hydrogen or oxygen atoms directly relates to the ECD. Furthermore, the AFE is the most acceptable descriptor for evaluating the catalytic activity of photocatalysts for their use in the overall water splitting. The hydrogen adsorption energy (E_H) is obtained by the equation

$$\Delta E_H = E_{tot}\left({}^{MoS_2}/_{ZnO} + H\right) - E_{tot}\left({}^{MoS_2}/_{ZnO}\right) - \frac{1}{2}E(H_2)$$

Where, $E_{tot}\left({}^{MoS_2}/_{ZnO} + H\right)$, $E_{tot}\left({}^{MoS_2}/_{ZnO}\right)$ and $E(H_2)$ are the energies of the MoS_2/ZnO heterostructure with adsorbed hydrogen, MoS_2/ZnO heterostructure and hydrogen molecule respectively. The Gibb's free energy for the hydrogen adsorption is calculated by the equation;

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$$

ΔE_{ZPE} depicts the zero-point energy difference of the H_2 between adsorbed and the gas phase state; ΔS_H represents the entropy difference between the H_2 gas phase state and adsorbed state. The value of ΔE_{ZPE} is around 0.04 eV for the HER study. Moreover, From the previous reports, $\Delta E_{ZPE} - T\Delta S_H = 0.24\ eV$ is the acceptable value. The criterion of a semiconductor to be a great photocatalyst for HER activity is that the ΔG_H is close to zero. In addition, according to the reported literature, the optimum value of ΔG_H lies between $|\Delta G_H| \leq 0.25\ eV$ for an excellent HER activity[14,15].

A 3 × 3 × 1 supercell of the MoS_2/ZnO heterostructure is adopted for the study of hydrogen adsorption. We considered four different sites on the basal plane of the heterostructure for hydrogen adoption, i) Mo top, ii) S top, iii) Zn top and iv) O top. Figure S4 depicts the H adsorption on the surface of the MoS_2/ZnO heterostructure. Firstly, the distance between the H atom from the various sites is varied and optimized values are obtained. After that, the AFE is calculated for each site. The calculated values of ΔG_H and the optimized distance of the H atom from the heterostructure surface ($d_{surface\text{-}H}$) is listed in Table S2.

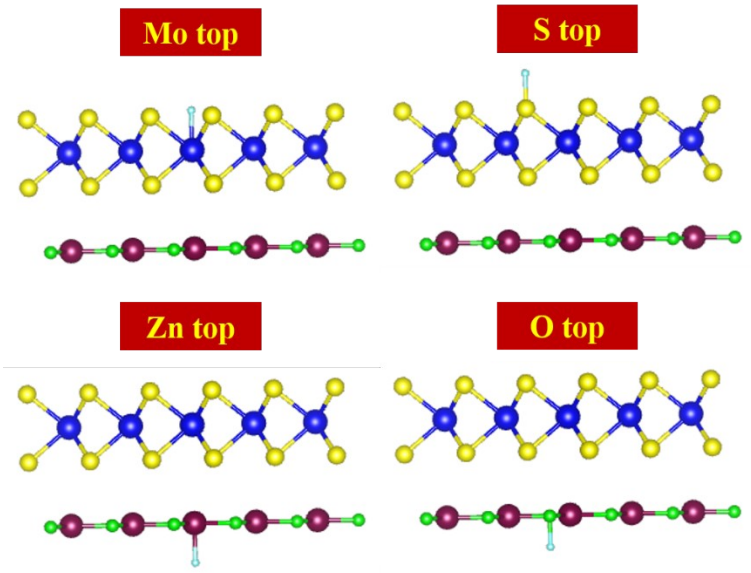

Figure S4: Different hydrogen adsorption sites on the surface of the heterostructure.

Table S2: The optimized surface to adsorbed hydrogen atom distance and ΔG_H for different hydrogen adsorption site.

Hydrogen adsorption site	$d_{surface\text{-}H}$ (Å)	ΔG_H (eV)
Mo top	1.8	0.21
S top	1.6	-0.03
Zn top	1.8	0.45
O top	1.4	0.16

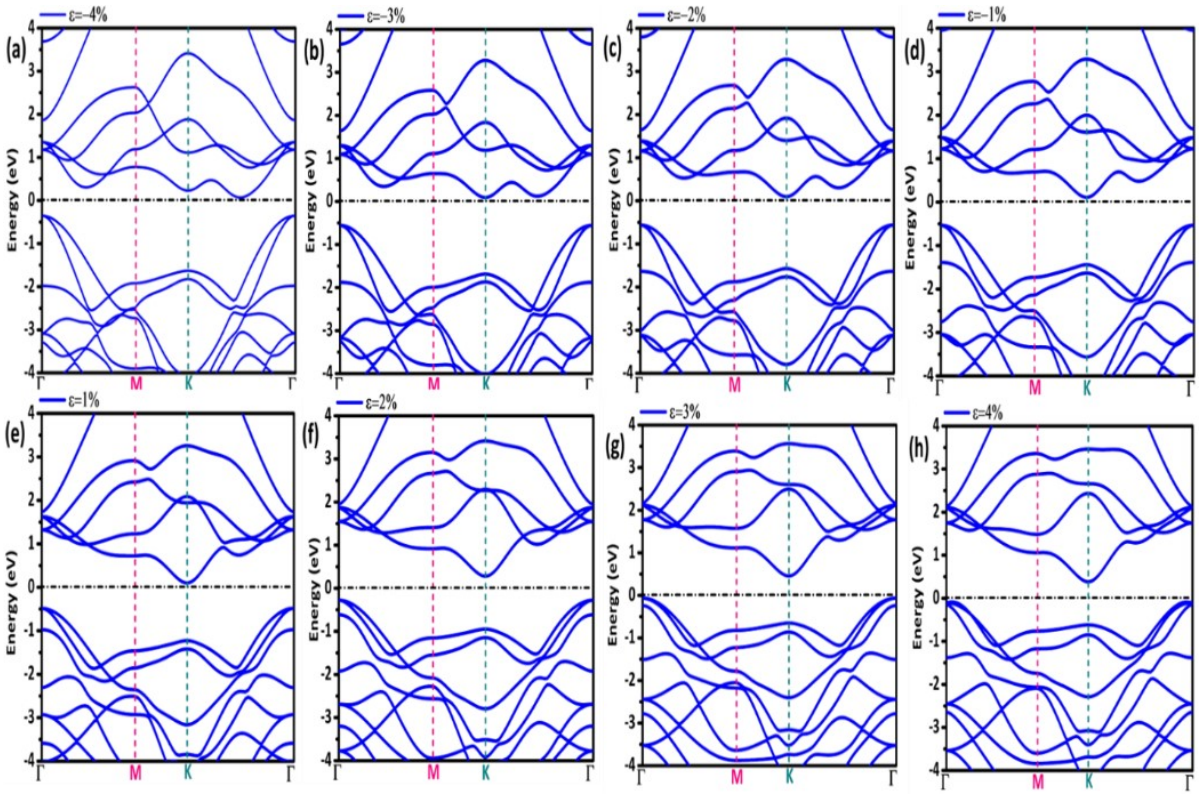

Figure S5: The electronic band structure of the MoS_2/ZnO heterostructure under biaxial strain.

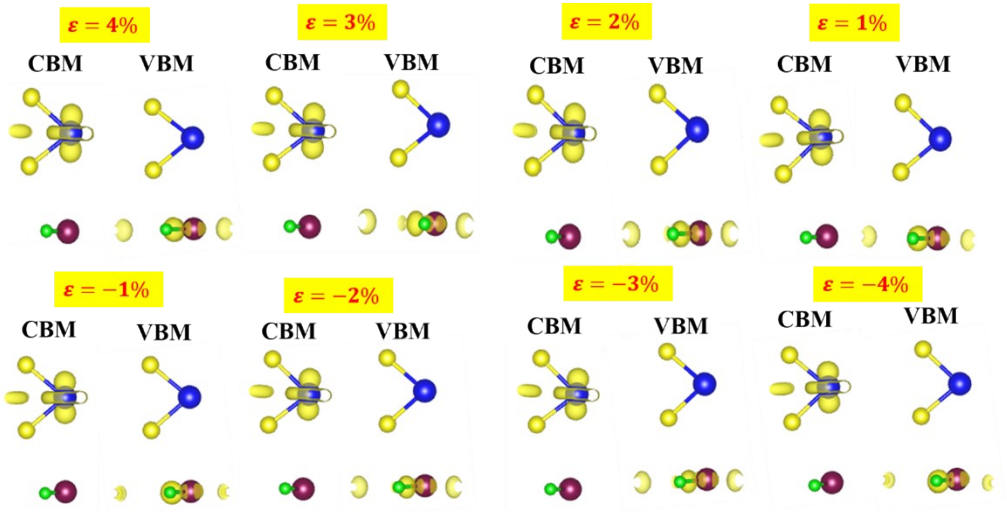

Figure S6: The partial charge density of the CBM and VBM of the MoS_2/ZnO heterostructure under biaxial strain.

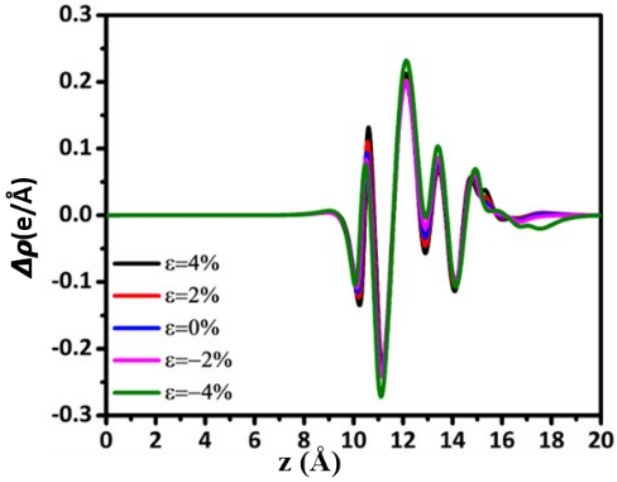

Figure S7: The CDD plot of the heterostructure under biaxial strain.

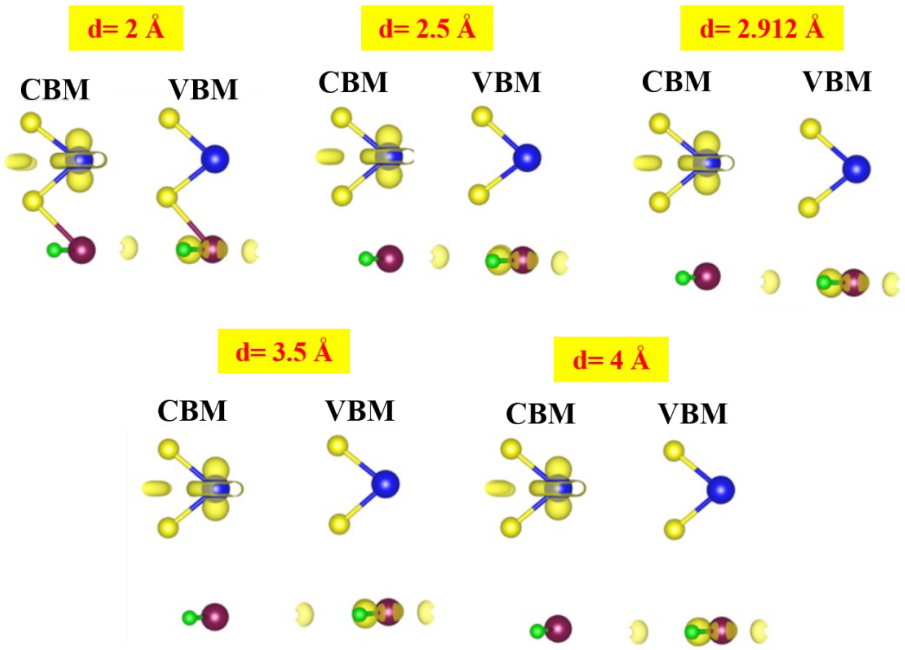

Figure S8: The band decomposed charge density of the MoS_2/ZnO heterostructure with the variation of the interlayer distance.

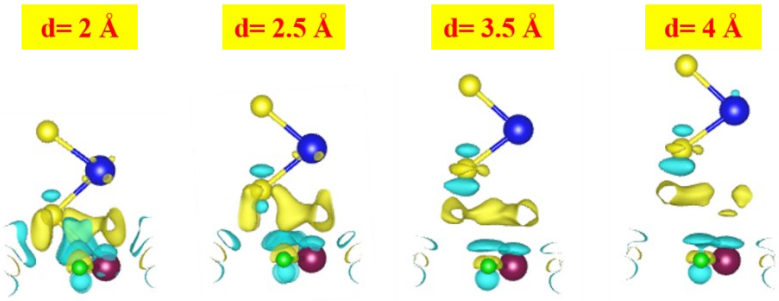

Figure S9: Calculated CDD isosurfaces of the MoS_2/ZnO heterostructure with the variation of interlayer distance.

Table S3: XYZ files of MoS_2 and ZnO monolayers, MoS_2/ZnO heterostructure with six configurations.

	Element	X	Y	Z
MoS_2	Mo	0.666667118	0.333332882	0.750000000
	S	0.333331441	0.666668559	0.828344968
	S	0.333331441	0.666668559	0.671655032
ZnO	Zn	0.666666000	0.333332000	0.524659588
	O	0.333332000	0.666666000	0.524648487
MoS_2/ZnO (conf-1)	Mo	0.6664298050	0.3330758083	0.7500614771
	S	0.3331518506	0.6664611202	0.8275589922
	S	0.3330813997	0.6663910823	0.6726417600
	Zn	0.6836553252	0.3503678654	0.5102406341
	O	0.3504216195	0.6837841238	0.5078071366
MoS_2/ZnO (conf-2)	Mo	0.673398775	0.339813472	0.748844428
	S	0.340065785	0.673145221	0.826214123
	S	0.340064801	0.673145292	0.671774619
	Zn	0.339938199	0.673656594	0.524666218
	O	0.673272440	0.340319422	0.521810611
MoS_2/ZnO (conf-3)	Mo	0.668112348	0.334064134	0.749118813
	S	0.334726452	0.667367221	0.826588069
	S	0.334738371	0.667373329	0.671805219
	Zn	0.009082965	0.004539000	0.523986088
	O	0.675609864	0.337796316	0.521811812
MoS_2/ZnO (conf-4)	Mo	0.6660769289	0.3321577424	0.7504260592
	S	0.3327531684	0.6655102900	0.8279307821
	S	0.3327063087	0.6654166097	0.6730034820

	Zn	0.0064249564	0.0128486600	0.5096592458
	O	0.3398386375	0.6796766979	0.5072904308
MoS_2/ZnO (conf-5)	Mo	0.671183846	0.335605068	0.748236609
	S	0.337869016	0.668950663	0.825705623
	S	0.337844867	0.668930427	0.671008563
	Zn	0.671033174	0.335497643	0.525130655
	O	0.004339097	0.002156199	0.523228549
MoS_2/ZnO (conf-6)	Mo	0.669049994	0.338106480	0.747996052
	S	0.335704383	0.671444390	0.825437599
	S	0.335726104	0.671429995	0.670975027
	Zn	0.335322671	0.670619889	0.525841533
	O	0.001996848	0.003969247	0.523059789

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