Supplementary Information

The Z-scheme transfer of photogenerated electron for CO₂ photocatalytic reduction over g-ZnO/2H-MoS₂ heterostructure

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Computational equations

In the work, all the calculation formulas used are as follows

Binding energy $(E_b)^1$

$$E_{b} = E_{(g - ZnO/2H - MoS_{2})} - E_{(g - ZnO)} - E_{(2H - MoS_{2})}$$
(S1)

where $E_{(g-ZnO/2H-MoS_2)}$, $E_{(g-ZnO)}$, and $E_{(2H-MoS_2)}$ are the total energies of g-ZnO/2H-MoS₂, g-ZnO, and 2H-MoS₂, respectively.

The mobility of carriers $(\mu)^{2,3}$

$$\mu = \frac{q\tau}{m^*} \tag{S2}$$

where q is the charge number, τ is the scattering time, and m^{*} is the effective mass.

The effective mass of photoexcited electron and hole⁴

$$m^{*} = \hbar^{2} \left(\frac{d^{2}E}{dk^{2}}\right)^{-1}$$
(S3)

where E is the band edge energy; k is the wave vector; and \hbar is the reduced Planck constant.

The charge density difference⁵

$$\Delta \rho = \rho_{(g - ZnO/2H - MoS_2)} - \rho_{(g - ZnO)} - \rho_{(2H - MoS_2)}$$
(S4)

where $\rho_{(g-ZnO/2H-MoS_2)}$, $\rho_{(g-ZnO)}$, and $\rho_{(2H-MoS_2)}$ represent the charge densities of g-ZnO/2H-MoS₂, g-ZnO, and 2H-MoS₂, respectively.

Gibbs free energy $(\Delta G)^6$

$$\Delta G = \Delta E + \Delta E_{ZEP} - T\Delta S \tag{S5}$$

where ΔE is the total electronic and ionic energy obtained from DFT total energies of the catalysts, ΔE_{ZEP} is the change of zero-point energy, T is the temperature (298.15 K), and ΔS is the entropy change. Zero-point energies and entropies of photocatalytic reduction of CO₂ intermediates were computed from the vibrational frequencies.

Band edge distances7-9

The photocatalyst of semiconductor for CO_2 reduction must have suitable band edges to match the redox potential of CO_2 /hydrocarbons. Referring to the normal hydrogen electrode (NHE), we calculate the potentials of band edges corresponding to the CBM

and VBM of g-ZnO and 2H-MoS $_2$ by the work function method:

$$E_{CBM} = -\Phi + 0.5E_{g}$$
(S7)

$$E_{\rm VBM} = -\Phi - 0.5E_{\rm g} \tag{S8}$$

$$E_{CBM} = -E_{CBM} (PH = 7) - 4.5$$
 (S9)

$$E_{VBM} = -E_{VBM} (PH = 7) - 4.5$$
 (S10)

where, Φ is the work function, E_g is the band gap, and E'_{CBM} , E'_{VBM} are the potentials versus NHE.



Fig. S1 Structural models of (a) 2H-MoS₂ and (b) g-ZnO, and plane diagrams of (c) S-Mo-S and (d) O-Zn-O.

After structural optimization, the bond length of O-Zn is 1.764 Å and its bond angle is 119.984°, while the planar bond length of S-Mo is 1.825 Å and the bond angle is 119.961°, which show the S-Mo-S six-membered ring displayed on the plane of 2H-MoS₂ being very similar to the O-Zn-O six-membered ring of g-ZnO.



Fig. S2 Energy band structures of (a) monolayer 2H-MoS₂ and (b) monolayer g-ZnO.

Both 2H-MoS₂ and g-ZnO are direct bandgap semiconductors, where the band gap of 2H-MoS₂

is 1.759 eV, the CBM and VBM are at the high symmetry point Γ . Our calculation results are supported by the literatures, ^{10,11} where the band gap of a single-layer MoS₂ is between 1.7-1.9 eV. Our calculated band gap of g-ZnO is 2.629 eV, 18% error from the 3.2 eV in the experiment.¹² Although the bandgap value is corrected by Ueff=7.5 eV, it still has an error with the experimental value. But if the Ueff value is increased excessively, the CBM and VBM on g-ZnO will be dislocated to even change the physical properties of the band structure by losing its actual physical meaning. By referring to the most suitable Ueff verified in literatures to compensate the spin repulsion of DFT between the d electrons of the Zn atom, this error is reduced, and the ZnO maintains a reasonable band structure. Therefore, we guarantee the electronic structure accuracy.



Fig. S3 Optical absorption behaviors of (a) 2H-MoS₂, (b) g-ZnO, (c) g-ZnO/2H-MoS₂.



Fig. S4 Band decomposed charged density of the (b) CBM and (c) VBM



Fig. S5 g-ZnO/2H-MoS₂ for planar-averaged electrostatic potential along the Z axis.

Table S1. Calculated Free energies of CO2 reduction into CH4 on2H-MoS2, g-ZnO and g-
ZnO/2H-MoS ₂

Intermediate	Free energy (eV)		
products	2H-MoS ₂	g-ZnO	g-ZnO/2H-MoS ₂
Surface+*COOH	3.935	2.801	2.016
Surface+*CO	1.186	0.901	0.461
Surface+*COH	4.089	4.476	3.787
Surface+*CHO	3.186	2.742	1.778
Surface+*CHOH	3.126	3.173	1.59
Surface+*CH ₂ O	1.48	1.433	0.352
Surface+*OCH ₃	2.281	1.808	1.536
Surface+*CH ₂ OH	2.304	2.227	1.421
Surface+*CH ₃ OH	0.449	0.445	-0.473
Surface+*CH ₃	1.013	1.499	0.694
Surface+ CH ₄	-1.019	-0.865	-1.654

Notes and references

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