

Supporting Information

Oxygen Vacancies Assisted 3DOM TiO₂-Zn_xCd_{1-x}S Heterojunctions for Enhanced Photocatalytic Hydrogen Production

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The AQY was calculated according to the equation¹:

$$\begin{aligned} \text{AQY (\%)} &= [\text{Number of the reacted electrons}] / [\text{Number of incident photons}] \times 100 \\ &= [\text{Number of evolved hydrogen molecules} \times 2] / [\text{Number of incident photons}] \times 100 \end{aligned}$$

$$\text{Number of evolved hydrogen molecules} = N_{\text{H}_2} \times N_{\text{A}}$$

$$\text{Number of incident photons} = P \times S \times \lambda \times t / (h \times c)$$

The factor of 2 accounts for the two electrons required per H₂ molecule

N_{H_2} = amount of H₂ produced (mmol), derived from GC quantification

N_{A} = Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$)

P = average light intensity at the sample surface (W/cm^2), measured as the mean of the center and edge values at 365 nm

S = irradiated area of the reactor = 38.5 cm^2 ($d = 7 \text{ cm}$)

λ = incident wavelength = 365 nm ($3.65 \times 10^{-7} \text{ m}$)

t = irradiation time = 3600 s (1 h)

h = Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$)

c = speed of light ($3 \times 10^8 \text{ m/s}$)

For the optimal 3DOM TiO₂-Zn_{0.5}Cd_{0.5}S sample under 365 nm irradiation, the measured light intensities were 0.86 W (center) and 0.276 W (edge).

$$\text{Average intensity} = (1/3 \times \text{center intensity} + 2/3 \times \text{edge intensity}) / (3.58 \times 3.14)$$

The average intensity is calculated to be $0.04187 \text{ W}/\text{cm}^2$. The hydrogen production rate was $7.48 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, yielding an AQY of 84.5%.

We confirm that the light intensity was carefully measured at multiple positions (center and edge) across the reactor surface. These computational details have been added to the Supporting Information.

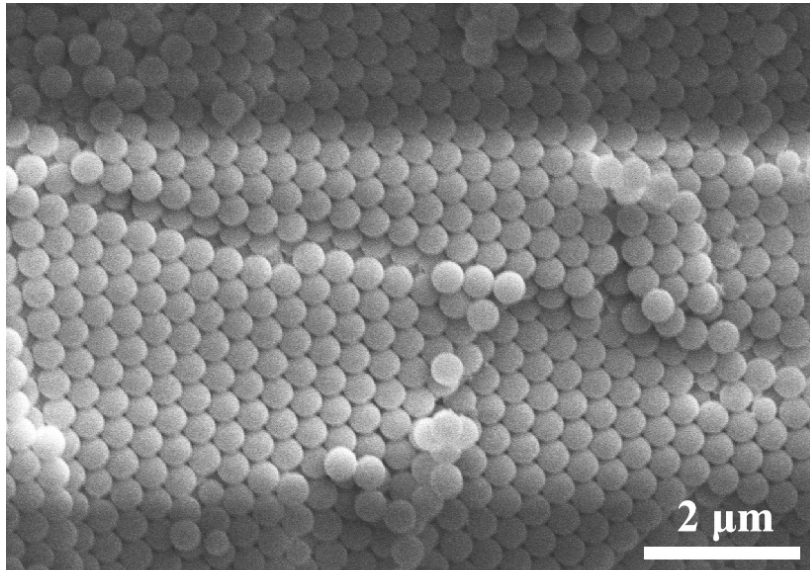


Fig. S1. SEM images of the samples PS template.

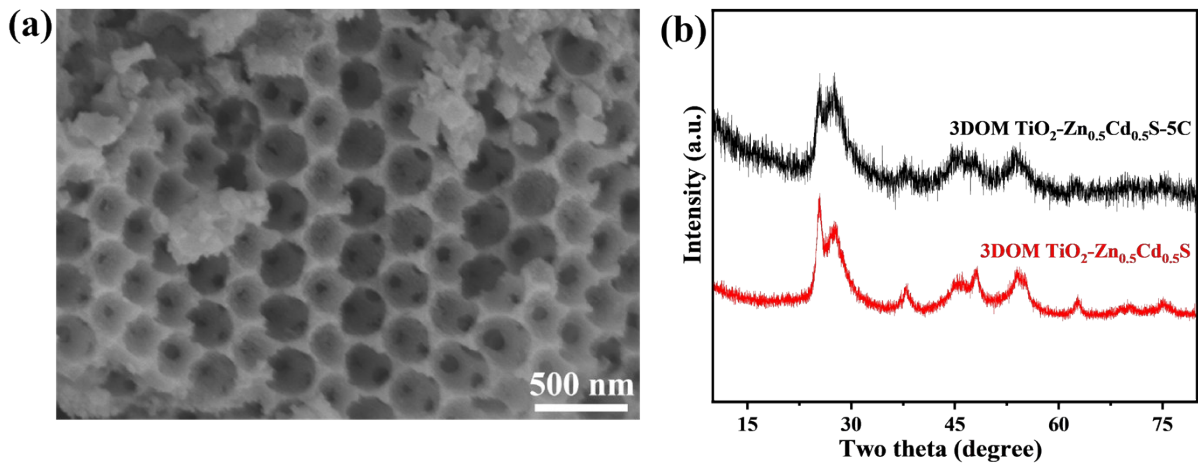


Fig. S2. (a) SEM of 3DOM $\text{TiO}_2\text{-Zn}_{0.5}\text{Cd}_{0.5}\text{S-5C}$ and (b) XRD of 3DOM $\text{TiO}_2\text{-Zn}_{0.5}\text{Cd}_{0.5}\text{S-5C}$ and 3DOM $\text{TiO}_2\text{-Zn}_{0.5}\text{Cd}_{0.5}\text{S}$.

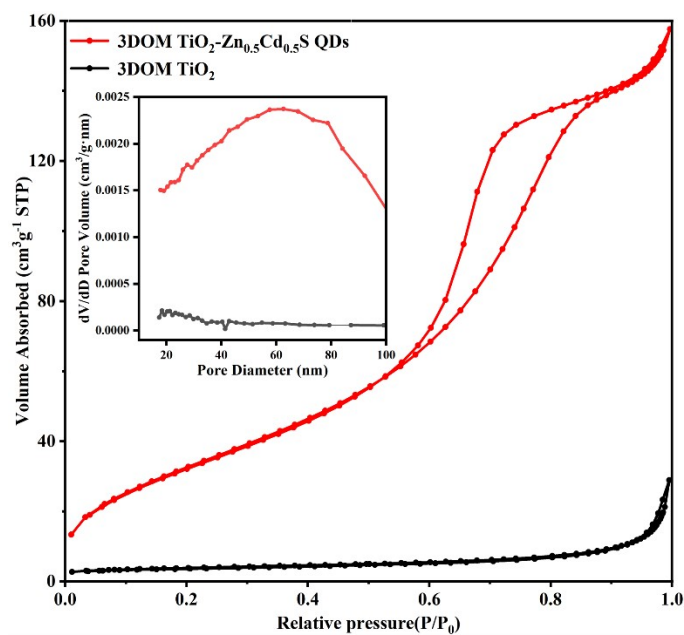


Fig. S3. N₂ absorption-desorption curves and corresponding pore size distribution of the 3DOM TiO₂-Zn_{0.5}Cd_{0.5}S and 3DOM TiO₂.

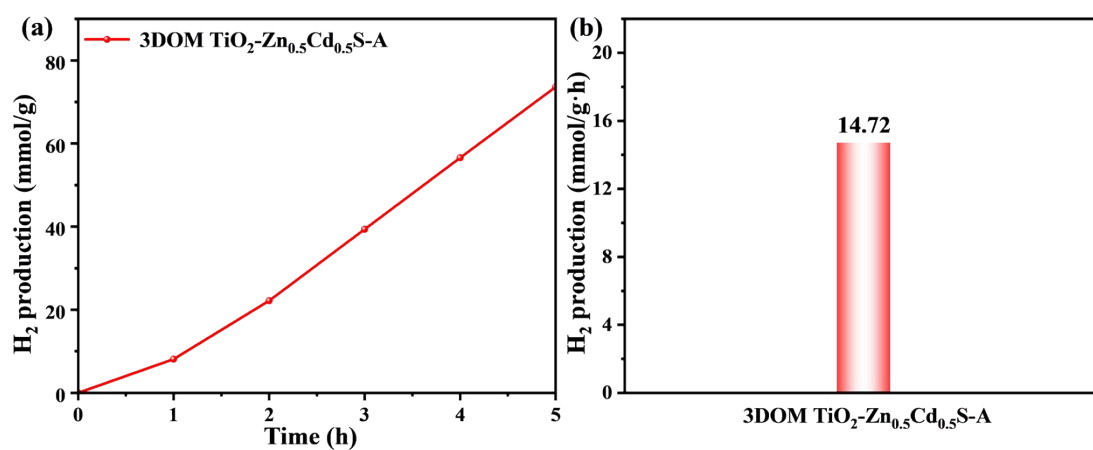


Fig. S4. (a) Hydrogen production amount within 5 hours, (b) Hydrogen production rate of 3DOM TiO₂-Zn_{0.5}Cd_{0.5}S-A.

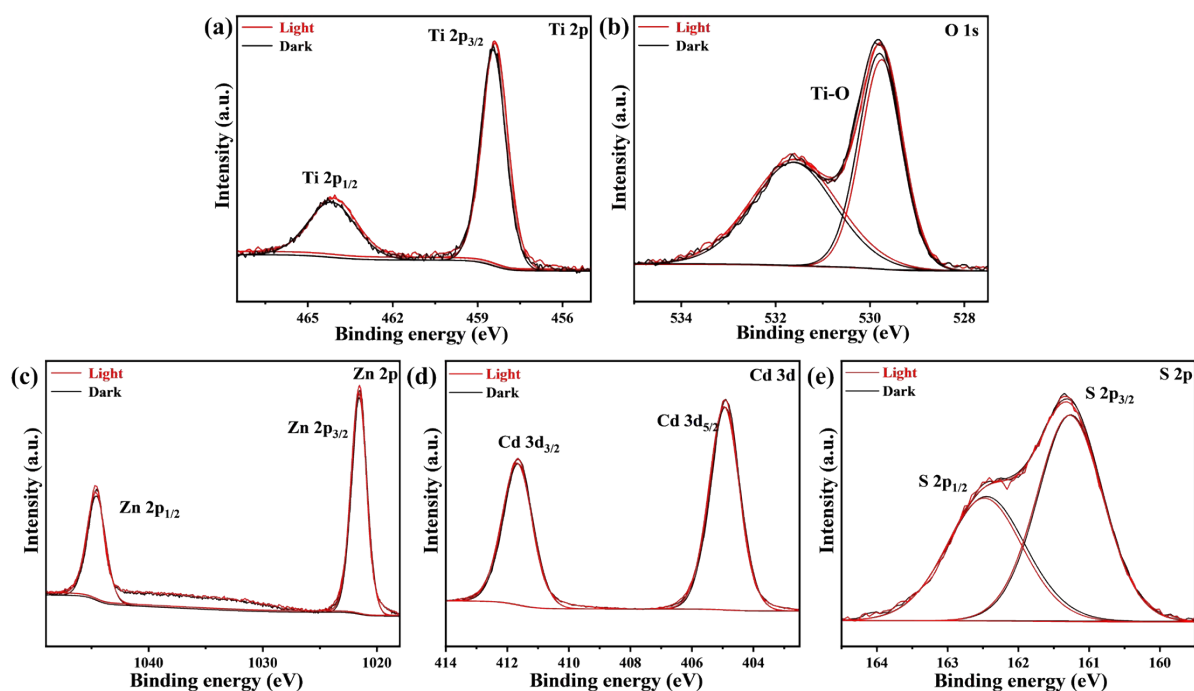


Fig. S5. High-resolution XPS spectra of (a) Ti 2p, (b) O 1s, (c) Zn 2p, (d) Cd 3d, and (e) S 2p of 3DOM TiO₂-Zn_{0.5}Cd_{0.5}S with and without light irradiation.

Note: The sample was first characterized under dark conditions to obtain the reference spectra. Subsequently, the sample was irradiated in situ using a 300 W Xe lamp for 10 minutes, after which the XPS spectra were immediately acquired under the same conditions.

TableS1. ICP test of the sample.

Sample	Zn (%)	Cd (%)	S (%)	Ti (%)
3DOM TiO ₂ -Zn _{0.5} Cd _{0.5} S	18.16	18.19	16.87	46.78

Table S2. Comparison of photocatalytic H₂ production performance between our work and other reported results.

Samples	Hydrogen Production System	H ₂ Rate (mmol • g ⁻¹ • h ⁻¹)	References
3DOM TiO₂-Zn_{0.5}Cd_{0.5}S	20 % Methanol	20.33	Our work
20 %-ZnCdS/O _V -NiCo ₂ O ₄	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	8.44	2
CoWO ₄ /V _{Zn} -Zn _{0.3} Cd _{0.7} S	Cl-PhCH ₂ OH/DMF	15.58	3
TiO ₂ -Zn _{0.5} Cd _{0.5} S	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	16.68	4
HAu/3DOM-TiO ₂	Methanol	6.42	5
3DOM LaFeO ₃ /Cd _{0.7} Zn _{0.3} S	Na ₂ S/Na ₂ SO ₃	0.28	6
3DOM TiO ₂ -g-C ₃ N ₄ -Cu ₂ O ₂	10 % Triethanolamine	12.11	7
3DOM In ₂ O ₃ -TiO ₂	Methanol	0.43	8
3DOM N/TiO ₂ -CdS QDs	Na ₂ S • H ₂ O/Na ₂ SO ₃	2.08	9
3DOM SrTiO ₃ -TiO ₂ /CQDs	Na ₂ S/Na ₂ SO ₃	0.58	10
RGO/TiO _{2-x}	Glycerol	13.6	11
O _{Vs} -TiO ₂ -NiS	20 % Methanol	3.95	12

Table S3. Mesoporous parameters of the 3DOM TiO₂-Zn_{0.5}Cd_{0.5}S and 3DOM TiO₂.

Samples	Surface Area (m ² • g ⁻¹)	Pore Volume (cm ³ • g ⁻¹)	Pore Size (nm)
3DOM TiO ₂ - Zn _{0.5} Cd _{0.5} S	129.11	0.23	54.16
3DOM TiO ₂	12.77	0.04	150.94

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