

Electronic Supplementary Information

Doping La into the *depletion layer* of Cd_{0.6}Zn_{0.4}S photocatalyst for efficient H₂ evolution

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Experimental Section

1. Preparation of photocatalysts

$\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$: $x\%$ La photocatalysts were prepared via a solvothermal method (x is the molar percent of La in the starting materials). In a typical experiment of synthesizing $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$: 2% La photocatalyst, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (0.219 g), $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (0.399 g) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.022 g) were dissolved into 10 mL of ethylene glycol to form a clear solution under continuous stirring at 60–80 °C. Double excess of thioacetamide (0.295 g) was then dissolved into the former clear solution. The reaction mixture was adjusted to 12 mL and immediately transferred into an autoclave (Teflon cups with an inner volume of 15 mL). The autoclave was maintained at 180 °C for 24 h and then cooled down to room temperature. The product was washed several times with absolute ethanol, collected by centrifugation and finally dried in the air. Lanthanide compound coated CZS sample (0.305 g) was synthesized by adding undoped CZS powder into the ethylene glycol solution containing $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.022 g) and S^{2-} (from 0.011 g TAA) for comparison.

2. Characterization of photocatalysts

Crystal structures of products were investigated by a Rigaku D/max-2000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=0.15406$ nm, under a condition of 40 kV and 50 mA). The amounts of metals were determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin Elmer Optima 5300DV) after the sample was dissolved in a mixture of HNO_3 and HF. The microstructure and composition analyses were conducted on a field emission scanning electron microscope (FESEM, FEI Quanta 200F) working at 30 kV and a transmission electron microscope (TEM, FEI Tecnai G²) equipped with an energy-dispersive X-ray spectrometer (EDS) working at 300 kV. High angle annular dark field (HAADF) imaging was obtained in scanning TEM (STEM) mode. Transmission electron microscopy specimen was prepared as described in the literature¹ except that Epoxy Bond 110 was substituted for M-bond 610 to improve the dispersion of particles in the resin. And then, the cross-sections of the particles were obtained through a FEI Helios Nanolab 600i

dualbeam FIB/SEM system. XPS measurements were performed on a PHI 5700 XPS/ESCA system with a monochromatic Al K α (1486.6 eV). All binding energies were calibrated to C1s peak at 284.6 eV of the surface adventitious carbon. UV-vis diffuse reflectance spectra were acquired by a spectrophotometer (TU-1900) and were converted from reflection to absorbance by the standard Kubelka-Munk method. BaSO₄ was used as the reflectance standard. For the determination of the particle size distribution, 1 mg CZS: 2% La sample was dispersed in 10 mL 20% N-methyl-2-pyrrolidone (NMP) aqueous solution. The as-prepared solution was then measured at room temperature with a scattering angle of 90° by a Malvern Zetasizer Nano (Malvern Instruments Ltd.). The photoluminescence (PL) spectrum was obtained using an Edinburgh FLS 920 fluorescence spectrophotometer (Xe 900 lamp) at room temperature. The excitation wavelength was 390 nm.

3. Mott-Schottky measurement

The flat band potential (E_{fb}) of CZS: $x\%$ La photocatalysts were determined by Mott-Schottky method, which was carried out in a conventional three electrode cell using a PARSTAT-2273 advanced electrochemical system (Princeton Applied Research) equipped with an impedance analyzer. The as-prepared photocatalyst was deposited as a film on a 1 cm \times 1 cm area of a 1 cm \times 2 cm FTO glass as the working electrode, and the ohmic contact between the working electrode and the copper conductor was made on the non-photocatalyst coated part of FTO glass using conductive adhesives. A saturated calomel electrode (SCE) was used as the reference electrode, and Pt was used as the counter electrode. The electrolyte was 0.5 M Na₂SO₄ aqueous solution.

4. Photocatalytic reactions

The photocatalytic reaction was performed in a closed gas-circulation system with a side window. The photocatalyst powders were dispersed by ultrasonication for 30 min in an aqueous solution (330 mL) containing Na₂SO₃ (0.8 mol·L⁻¹) and Na₂S (0.6 mol·L⁻¹) as electron donors. Nitrogen was purged through the system for 30 min before reaction to remove oxygen. The reaction was carried out by irradiating the suspension with visible light from a 300 W Xe lamp (Trusttech PLS-SXE 300, Beijing)

which was equipped with an AM1.5 filter and a UV-cut filter ($\lambda > 400$ nm) to simulate sunlight irradiation and cut off the light in the ultraviolet region. Apparent quantum yields were tested under identical condition, except the AM1.5 filter and UV-cut filter was substituted for band-pass filter separately ($\lambda = 350$ nm and $\lambda = 420$ nm, half width = 15 nm). The amount of produced H₂ was measured by gas chromatography (Agilent 7890) with a thermal conductivity detector (TCD) and Ar was used as the carrier gas.

Figures S1-S9

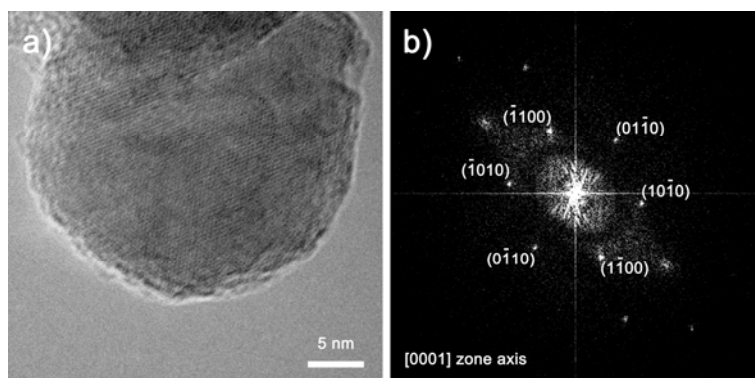


Fig. S1 a) HRTEM image and b) corresponding FFT pattern of a hexagonal wurtzite structure CZS: 2% La nanocrystal.

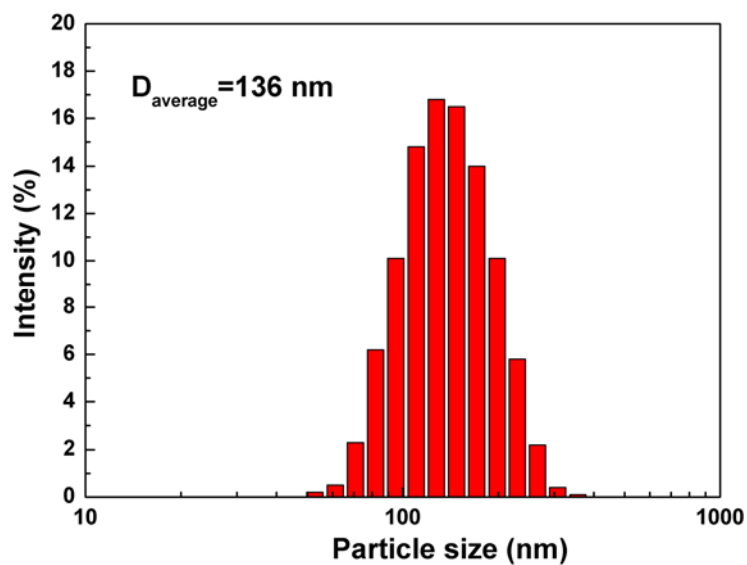


Fig. S2 Particle size distribution of CZS: 2% La photocatalyst.

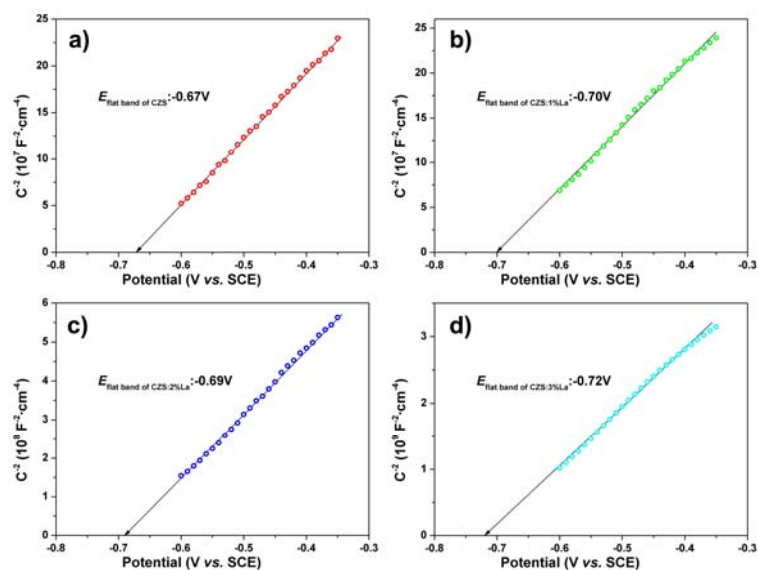


Fig. S3 Mott–Schottky plots for a) CZS, b) CZS: 1% La, c) CZS: 2% La and d) CZS: 3% La photocatalysts.

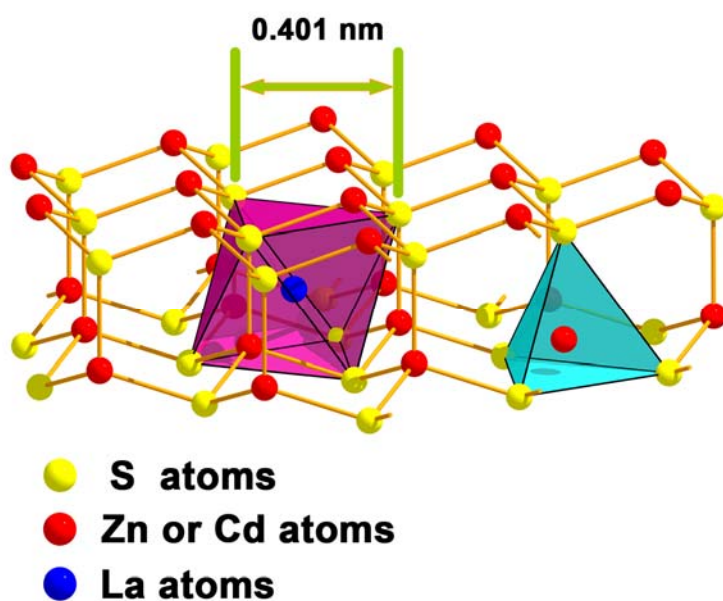


Fig. S4 Location of tetrahedral and octahedral sites in cubic sphalerite $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$: 2% La. The sizes of tetrahedral site and octahedral sites (diameter of the inscribed sphere) were calculated to be 1.64 \AA and 3.28 \AA , respectively.

$$R_{\text{tetrahedron}} = \frac{\sqrt{6}}{12} a; R_{\text{octahedral}} = \frac{\sqrt{6}}{6} a; a = \text{Bond}_{\text{S-S}} = 0.401 \text{ nm}$$

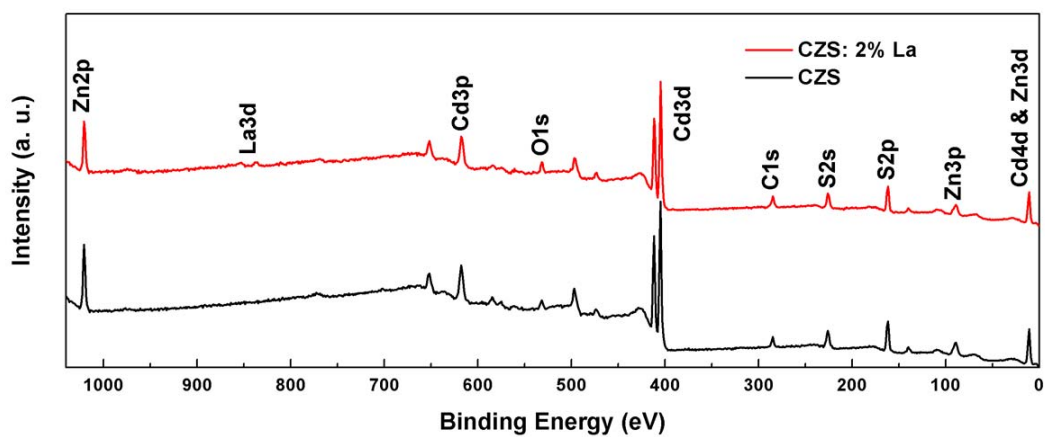


Fig. S5 Survey XPS spectra of undoped CZS and CZS: 2% La photocatalysts.

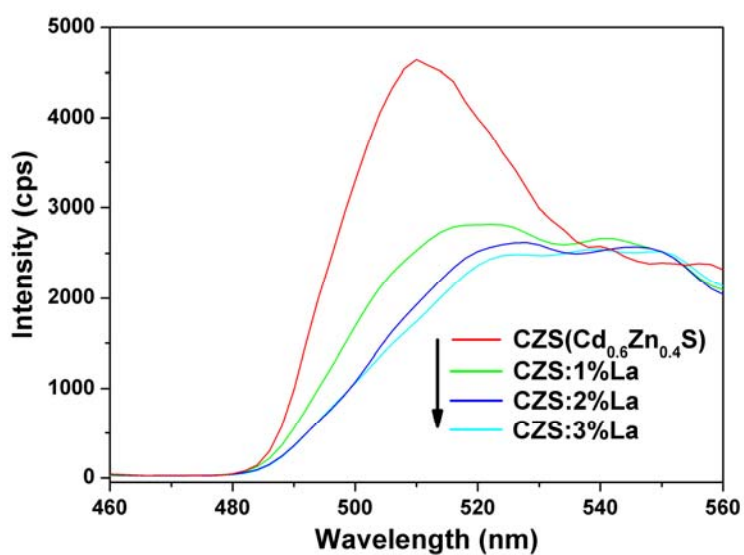


Fig. S6 Room temperature PL spectra of CZS: 0–3% La photocatalysts.

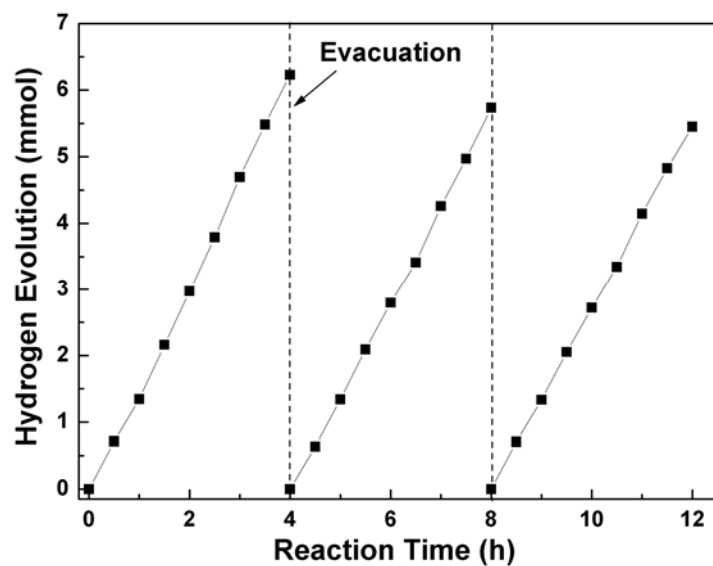


Fig. S7 Amount of hydrogen evolution according to reaction time for CZS: 2% La photocatalyst.

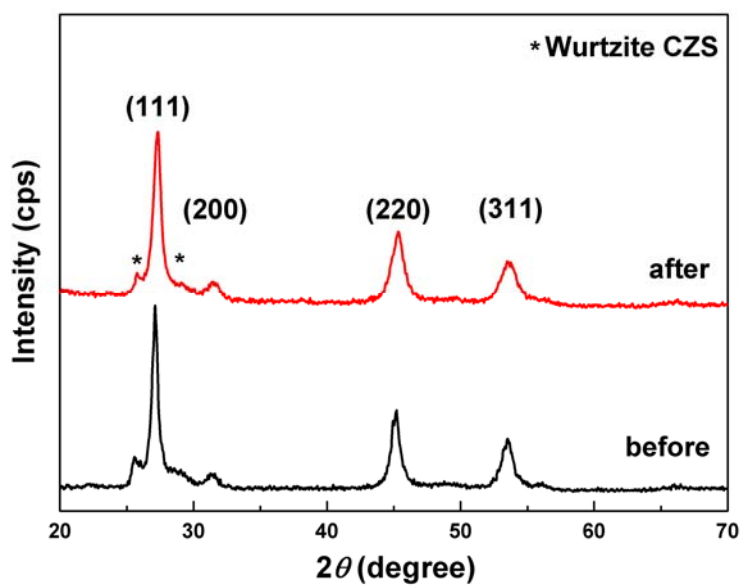


Fig. S8 XRD patterns of CZS: 2% La photocatalyst before and after 12 h of the photocatalytic H₂ evolution test.

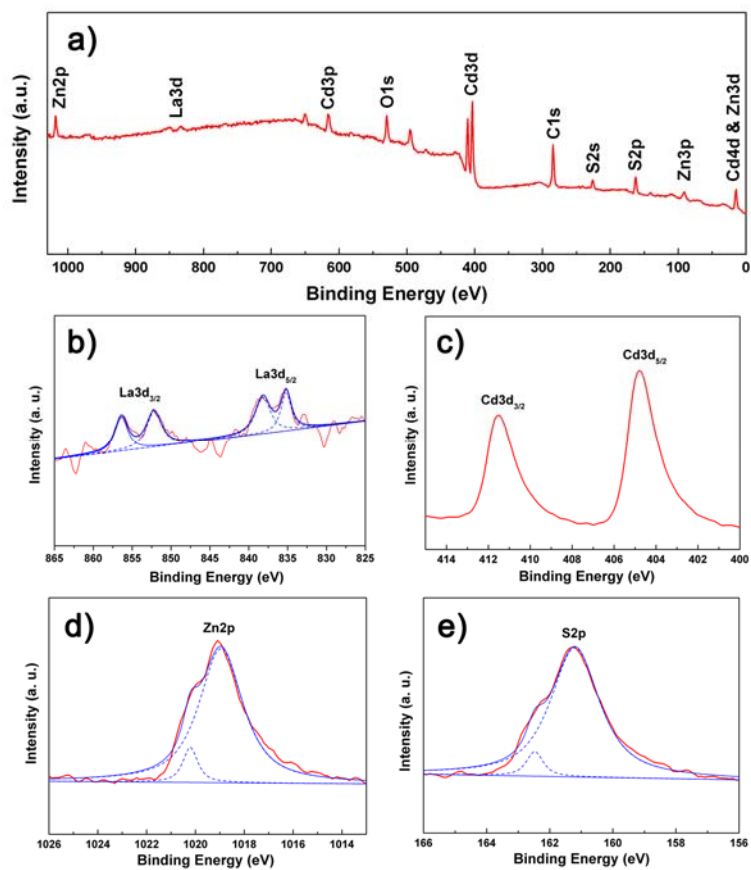


Fig. S9 XPS spectra of CZS: 2% La photocatalyst after 12 h of the photocatalytic H₂ evolution tset: a) survey spectra, b) La 3d, c) Cd 3d, d) Zn 2p and e) S2p core levels.

Tables S1-S4

Table S1 Bulk and surface compositions of CZS: $x\%$ La photocatalysts.

Samples	Atom percentage (%)					
	Cd ^a	Zn ^a	La ^a	Cd ^b	Zn ^b	La ^b
CZS	57.23	42.77	0	61.13	38.87	0
CZS:1%La	57.46	42.37	0.17	61.36	37.77	0.87
CZS:2%La	56.88	42.86	0.26	60.19	36.87	2.94
CZS:3%La	58.14	41.49	0.37	60.05	34.62	5.33

^a: measured by ICP-AES

^b: measured by XPS

Table S2 The depths of the depletion layer of CZS: 0-3% La photocatalysts and the values of slope and flat band potential calculated from the Mott–Schottky plots.

Samples	Slope k	E_{fb} (V)	d_{dl} (nm)
	($10^8 \text{ F}^{-2} \cdot \text{cm}^{-4} \cdot \text{V}^{-1}$)		
CZS	7.13	-0.67	10.8
CZS:1%La	7.06	-0.70	11.0
CZS:2%La	16.9	-0.69	16.9
CZS:3%La	87.5	-0.72	39.3

Table S3 Apparent quantum yields of undoped CZS and CZS: 2% La photocatalysts and the parameters of the incident monochromatic lights. The apparent quantum yields were calculated based on the amounts of H₂ evolved under monochromatic light irradiation in one hour.

λ_{inc} (nm)	Irradiation area (cm ²)	Power density (mW·cm ⁻²)	Amount of H ₂ production (mmol)		Apparent quantum yield (%)	
			CZS	CZS:2%La	CZS	CZS:2%La
350±7.5	19.6	0.53 ^a	0.019	0.051	34.8	93.3
420±7.5		6.67 ^b	0.091	0.3	11.0	36.3

^a: measured by a radiometer (Photoelectric Instrument Factory, Beijing Normal University, model UV-A in $\mu\text{W}\cdot\text{cm}^{-2}$)

^b: measured by a radiometer (Photoelectric Instrument Factory, Beijing Normal University, model FZ-A in $\text{mW}\cdot\text{cm}^{-2}$).

Table S4 Apparent quantum yields of ZnS, CdS, ZnS: 2% La and CdS: 2% La samples

λ_{inc} (nm)	Apparent quantum yields (%)			
	ZnS	ZnS:2%La	CdS	CdS:2%La
350±7.5	8.5	21.3	5.5	11.0
420±7.5	0	0	2.3	5.1

Calculation details of the depletion layer depth (d_{dl})

According to the well known Mott–Schottky relation, the depletion layer depth (d_{dl}) can be calculated through the following equation³:

$$d_{dl} = \varepsilon_r \varepsilon_0 \sqrt{k(E_{bias} - E_{fb})}$$

where $\varepsilon_0 = 8.854 \times 10^{-14} \text{ F cm}^{-1}$ is the vacuum permittivity, ε_r denotes the dielectric constant of the material, k is the slope of the Mott–Schottky plot, E_{bias} is the applied potential and E_{fb} is the flat band potential.

Herein, E_{bias} is set to be zero, because only the photoinduced open circuit potential works. All of the ε_r of CZS: 0–3% La samples is set to be 5.6,² because the doping amount is relatively low.

Calculation details of the apparent quantum yield (A.Q.Y.)

The energy of one photon (E_{photon}) with wavelength of λ_{inc} (nm) is calculated using the following equation³:

$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{inc}}}$$

where h (J·s) is Planck's constant, c ($\text{m}\cdot\text{s}^{-1}$) is the speed of light and λ_{inc} (m) is the wavelength of the incident monochromatic light. And the total energy of the incident monochromatic light (E_{total}) is calculated using the following equation:

$$E_{\text{total}} = PSt$$

where P ($\text{W}\cdot\text{m}^{-2}$) is the power density of the incident monochromatic light, S (m^2) is the irradiation area and t (s) is the the duration of the incident light exposure. The number of incident photons can be obtained through the following equation:

$$\text{Number of incident photons} = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{PS\lambda_{\text{inc}}t}{hc}$$

Quantum yield (Q.Y.),⁴ which is widely used to evaluate the performance of photocatalysts for water splitting, is defined by the following equation:

$$\text{Q.Y.(\%)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$$

However, it is difficult to directly determine the number of reacted electrons via experimental methods. As a result, the apparent quantum yield (A.Q.Y.) is defined as follow by substituting twice the number of H_2 molecules evolved for the number of reacted electrons.

$$\text{A.Q.Y.(\%)} = \frac{2 \times \text{Number of } \text{H}_2 \text{ molecules evolved}}{\text{Number of incident photons}} \times 100$$

Finally, the apparent quantum yield is calculated using the following equation:

$$\text{A.Q.Y.(\%)} = \frac{2n_{\text{H}_2,t} N_{\text{A}} hc}{PS\lambda_{\text{inc}}t} \times 100$$

where $n_{\text{H}_2,t}$ (mol) is the amount of H_2 evolved over the duration t of the incident light exposure, N_{A} (mol^{-1}) is Avogadro's constant.

References

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- 4 X. B. Chen, S. H. Shen, L. J. Guo and S. S. Mao, *Chem. Rev.*, 2010, **110**, 6503.