Supplementary Materials

for

Effects of preparation conditions on the efficiency of visible-light-driven hydrogen generation based on $Cd_{0.25}Zn_{0.75}S$ photocatalysts

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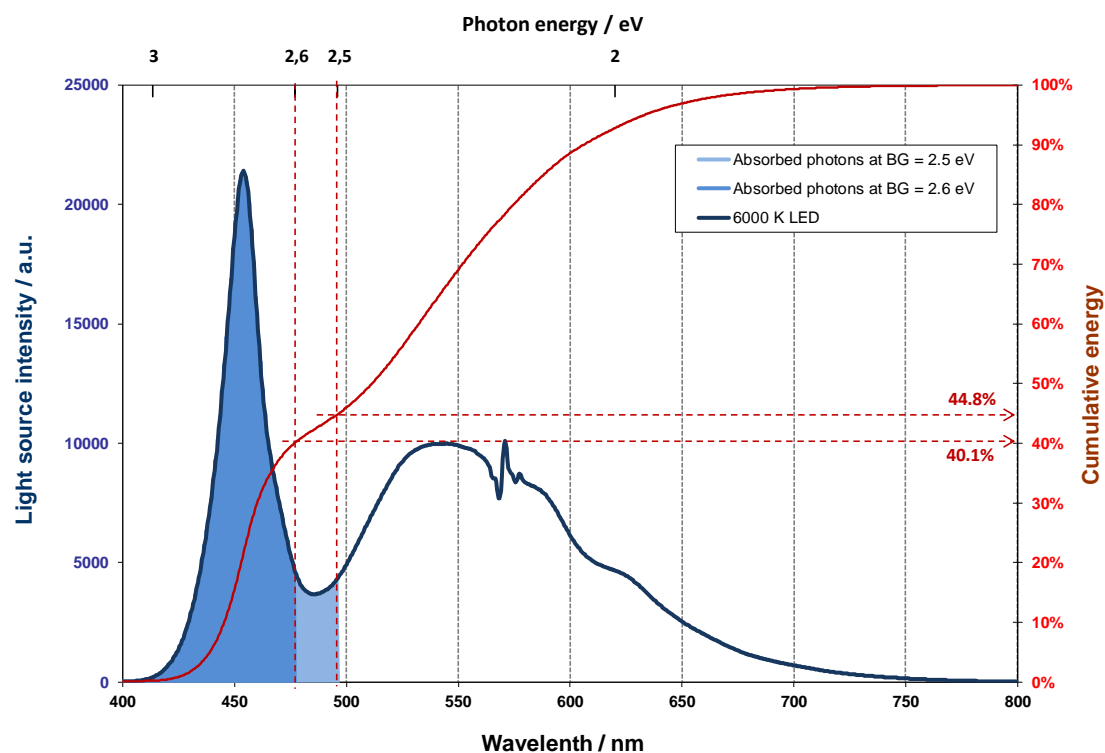
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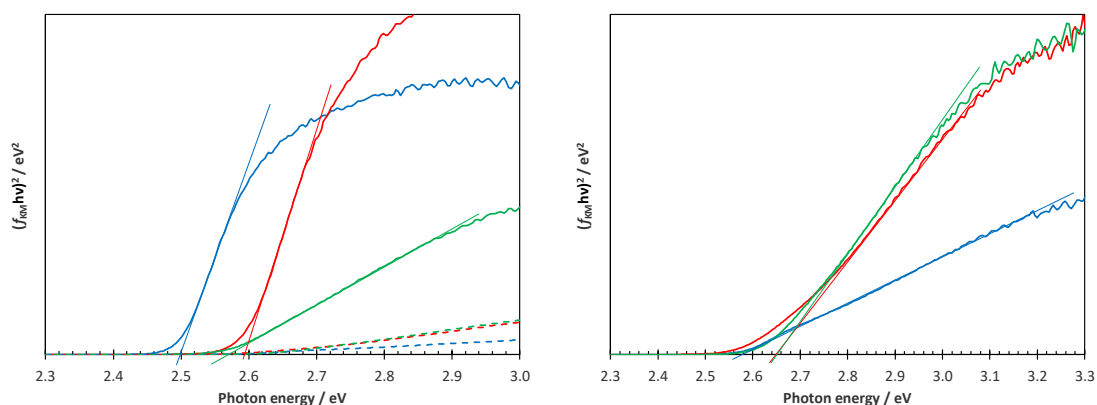
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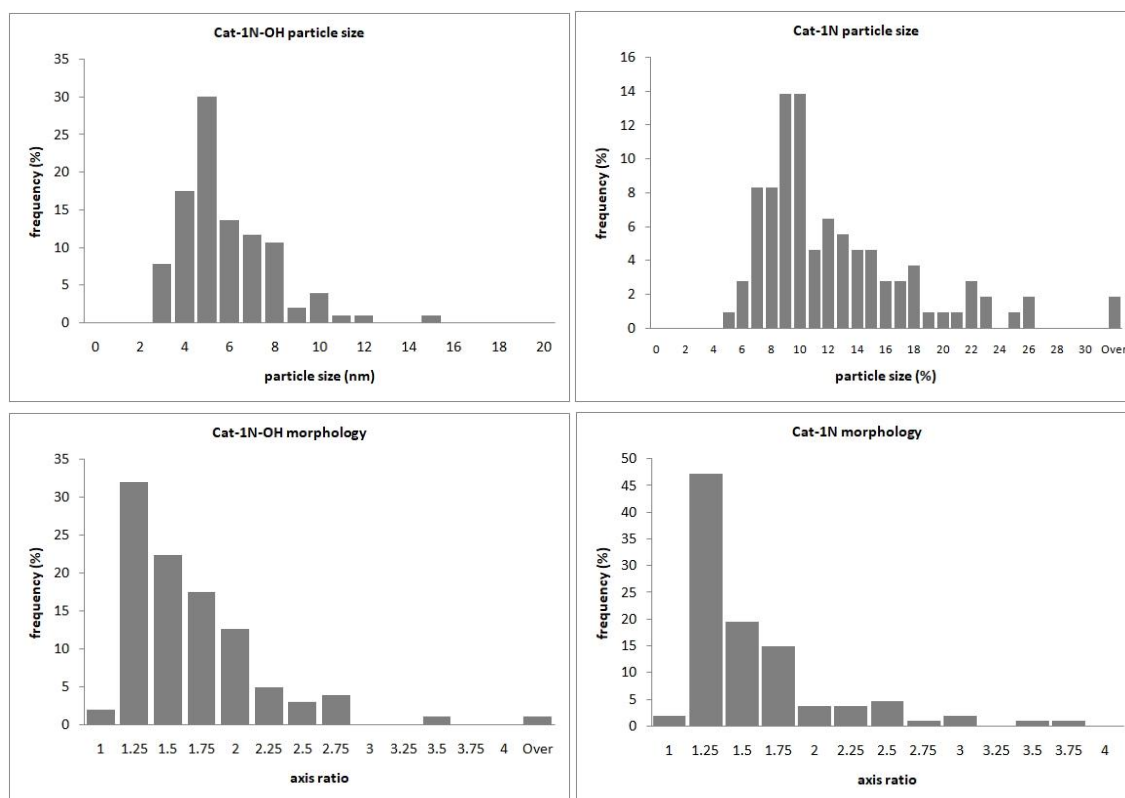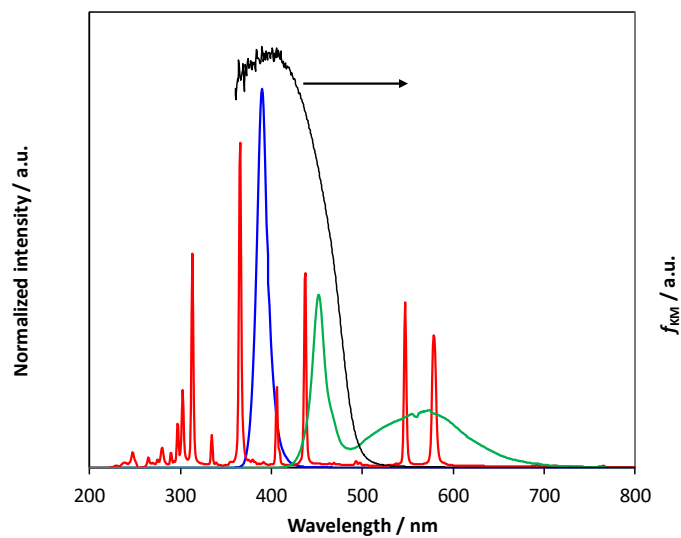**Figure S1.** Normalized (blue line) and cumulative (red line) intensity of the vis LED applied for illumination. The red dashed lines indicate the difference between the energies absorbed at 2.5 eV and 2.6 eV band gaps.

Figure S2. Tauc representation of Cat-xN (solid lines in part „a") and Cat-xN-0H (dashed lines in part „a" and solid lines in part „b" (blue: x=0, red: x=1, green x=2). Part „b" is the magnification of part „a" regarding Cat-xN-0H catalysts.

Figure S3. Particle size distribution (longest diameter) and axis ratio distribution (longest diameter/perpendicular diameter) of the *Cat-1N-OH* sample (left diagrams) and Cat-1N sample (right diagrams) calculated from 103 and 108 particles, respectively.

Figure S4. Normalized emission spectra of the light sources applied for illumination (blue line: UV-LED, red: Hg-Xe arc lamp, green: vis LED). The solid black line represent the KM-function.

Figure S5. RHP of hydrothermally treated catalysts during illumination with vis LED (orange) and UV LED (violet) and the ratio of the RHPs measured with UV and vis LED.

Table S1. Measured data for the calculation of IPCE and QY of Cat-xN catalysts illuminated by 50W UV-LED, and the resulting IPCE and QY values.

	Catalyst		
	Cat-0N	**Cat-1N**	**Cat-2N**
$n_{photons}$/t **(mmol/h)**	18.76	18.76	18.76
RHP (mmol H_2/h)	0.479	1.078	0.900
RHP (mmol H_2/g/h)	26.6	59.9	50.0
IPCE	5.11%	11.49%	9.59%
Ratio of abs. photons	99.8%	99.8%	99.8%
QY	5.12%	11.51%	9.61%

Since we were not able to measure with the LED lamp we used for the previous measurements (the intensity of UV LEDs decreases significantly over time, so we used another LED with a higher light intensity as a light source (50 W, but with the same spectral properties as the other one). Therefore, $n_{photons}$ was 18.76 mmol/h (instead of 12.06 mmol/h as in Table 5). This caused only slight deviations in the IPCE and QY values for the Cat-2N catalyst, compared to those in Table 5.

Comparing the RHP values obtained with the UV LED to those obtained with the vis LED, they increased by a factor of 3.1, 3.1, and 3.4 for the Cat-0N, Cat-1N, and Cat-2N catalysts, respectively (Fig S3). The similar magnitude of change suggests that there are no differences in BG that significantly affect the fraction of photons absorbed by the vis LED.

The highest measured QY (at 380 nm) is 11.5% for Cat-1N.

Text S1. Determination of the intensity of light sources

The intensity of light sources was determined by trioxalato-ferrate(III) actinometer. Since our light sources were not monochromatic, we have taken account the energy (wavenumber ($\tilde{v}$)) dependence of the quantum yield of trioxalato-ferrate(II) ($\Phi(\tilde{v})$), the ratio of the absorbed photons ($I_A(\tilde{v})$), and the normalized spectra of light source ($I_L(\tilde{v})$).

The amount of Fe(II) produced per unit volume of reactor ($[Fe(II)]$) during unit time:

$$\frac{d[Fe(II)]}{dt} = \frac{dc_{Ph,ab}}{dt} \cdot \Phi_{Fe} \qquad (1)$$

The amount of absorbed photons ($n_{Ph,ab}$) per unit volume ($c_{Ph,ab} = n_{Ph,ab}/V_{Rea}$) per unit time ($dc_{Ph,ab}/dt$) can be written as the product of the ratio of absorbed photons by trioxalate ferrate(III) (I_A) and the amount of incident photon ($n_{Ph,in}$) per unit volume ($c_{Ph,in}$) per unit time ($dc_{Ph,in}/dt$). When calculating the absorbed fraction, the light path in the reactor (l_{Rea}) and the absorbance of the $[Fe(ox)_3]^{3-}$ ($A_{Fe(III)}$) measured in a 1 cm cuvette must be taken into account!

$$\frac{d[Fe(II)]}{dt} = \frac{dc_{Ph,in}}{dt} \cdot I_A \cdot \Phi_{Fe} = \frac{dc_{Ph,in}}{dt} \cdot (1 - 10^{-l_{Rea}A_{Fe(III)}}) \cdot \Phi_{Fe} \qquad (2)$$

Since

$$c_{Fe(phen)_3^{2+}} = \frac{A^{510}_{Fe(phen)_3^{2+}}}{\varepsilon^{510} \cdot l_{cuv}} \qquad (3)$$

where ε^{510} is the molar absorption coefficient of $[Fe(phen)_3]^{2+}$ at 510 nm (11600 M^{-1}cm^{-1}) and l_{cuv} (= 1 cm) is the optical path length in the cuvette. Since the sample taken out of the reactor was diluted 50 times ($D = 50$), the amount of Fe(II) produced per unit volume of reactor during the unit time is:

$$\frac{d[Fe(II)]}{dt} = \frac{d(A_{Fe(phen)_3^{2+}})}{dt} \cdot \frac{D}{\varepsilon^{510} \cdot l_{cuv}} \qquad (4)$$

The differential quotient on the right side of this equation is the slope (S) obtained by actinometry, so based on the equations 2 and 4, the following equation can be derived:

$$\frac{S \cdot D}{\varepsilon^{510} \cdot l_{cuv}} = \frac{dc_{Ph,in}}{dt} \cdot (1 - 10^{-l_{Rea}A_{Fe(III)}}) \cdot \Phi_{Fe} \qquad (5)$$

Of this, the amount of incident photons per unit volume per unit time is as follows:

$$\frac{dc_{Ph,in}}{dt} = \frac{S \cdot D}{\Phi_{Fe} \cdot \varepsilon^{510} \cdot l_{cuv} \cdot (1 - 10^{-l_{Rea}A_{Fe(III)}})} \qquad (6)$$

The molar amount of incident photons to the volume of the sacrificial solution (V_r) in the reactor per unit time (I_R) is:

$$I_R := \frac{dc_{Ph,in}}{dt} \cdot V_r = \frac{S \cdot D \cdot V_r}{\Phi_{Fe} \cdot \varepsilon^{510} \cdot (1 - 10^{-l_{Rea}A_{Fe(III)}})} \qquad (7)$$

The I_R, Φ_{Fe} and $A_{Fe(III)}$ values depend on the energy (or wavenumber) of the incident photons, so the above formula is correct only for actinometry of a monochromatic light source. The correct formula for the entire spectral range of a light source can be obtained by integration on an energy scale (wavenumber). To do this, we can exploit the fact that the energy distribution spectra of the light source ($E(\tilde{\upsilon})$) are proportional to $I_R(\tilde{\upsilon})$. Let the proportionality factor be k, so:

$$I_R(\tilde{\upsilon}) = k \cdot E(\tilde{\upsilon}) \tag{8}$$

After substituting I_R and sorting the energy dependent parameters to the left and integrating:

$$k \int E \cdot \Phi_{Fe} \cdot (1 - 10^{-l_{Rea} A_{Fe(III)}}) \; d\tilde{\upsilon} = \frac{S \cdot D \cdot V_r}{\varepsilon^{510}} \tag{9}$$

All of the parameters but k are known, so k can be expressed. Since the total incident photons to the reactor per unit time can be obtained by the following equation:

$$\int I_R(\tilde{\upsilon}) \, d\tilde{\upsilon} \;=\; k \cdot \int E(\tilde{\upsilon}) d\tilde{\upsilon}, \tag{10}$$

Substituting the k parameter according to the equotion (9) gives:

$$\int I_R(\tilde{\upsilon}) \, d\tilde{\upsilon} \;=\; \frac{\int E(\tilde{\upsilon}) d\tilde{\upsilon}}{\int E \cdot \Phi_{Fe} \cdot (1 - 10^{-l_{Rea} A_{Fe(III)}}) \; d\tilde{\upsilon}} \cdot \frac{S \cdot D \cdot V_r}{\varepsilon^{510}} \tag{11}$$

where the quotient of the two integrals gives an apparent quantum yield of the photoproduction of Fe(II) (Φ'_{Fe}), which is a constant value for a given light source at a given geometrical arrangement.

$$\Phi'_{Fe} \;:=\; \frac{\int E \cdot \Phi_{Fe} \cdot (1 - 10^{-l_{Rea} A_{Fe(III)}}) \; d\tilde{\upsilon}}{\int E(\tilde{\upsilon}) d\tilde{\upsilon}} \tag{12}$$

Thus, the number of incident photons on the reactor per unit time is:

$$\int I_R(\tilde{\upsilon}) \, d\tilde{\upsilon} \;=\; \frac{S \cdot D \cdot V_r}{\Phi'_{Fe} \cdot \varepsilon^{510}} \tag{13}$$