Supporting Information

One-step vulcanization of Cd(OH)Cl nanorods to synthesize CdS/ZnS/PdS nanotubes for highly efficient photocatalytic hydrogen evolution

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1. Materials

Sodium sulfite (Na_2SO_3), sodium hydroxide (NaOH) and sodium sulfate (Na_2SO_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. Polyvinyl pyrrolidone (PVP) and sodium tetrachloropalladate (Na_2PdCl_4) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Sodium sulfide ($Na_2S\cdot 9H_2O$) was obtained from Tianjin Tianli Chemical Reagent Co., Ltd. Cadmium chloride ($CdCl_2\cdot 2.5H_2O$) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Thioacetamide (TAA) was obtained from Tianjin Guangfu fine chemical research institute. Gelatin and zinc chloride ($ZnCl_2$) were purchased from Tianjin Shengao Chemical Reagent Co., Ltd. All of the reagents were analytically pure and used directly without further purification. Distilled water with a resistivity of 18.2 MΩ·cm was used throughout the experiments.

2. The chemical reaction processes

The detailed chemical reaction processes for one-step vulcanization of converting Cd(OH)Cl nanorods to CdS/ZnS/PdS nanotubes were proposed as follows:

$$Zn^{2+} + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ \qquad (1)$$

$$PdCl_4{}^{2-} + 2H_2O \rightarrow H_2PdCl_4 + 2OH^- \qquad (2)$$

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S \qquad (3)$$

$$CdOHCl + H_2S \rightarrow CdS + H_2O + H^+ + Cl^- \qquad (4)$$

$$Zn(OH)_2 + H_2S \rightarrow ZnS + 2H_2O \qquad (5)$$

$$H_2PdCl_4 + H_2S \rightarrow PdS + 4H^+ + 4Cl^- \qquad (6)$$

3. The calculation of apparent quantum efficiency

The apparent quantum efficiency (AQE) of the CZ_3P_1S sample was measured under the photocatalytic reaction condition (50 mg of catalysts in 100 mL solution of 0.35 M Na_2S and 0.25 M Na_2SO_3) using 225 W Xenon lamp equipped with different band-pass filters of wavelengths. The AQE was calculated by the following equation:

$$AQE = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{number\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{n_{H_2} \times N_A \times 2}{E\lambda/hc} \times 100\%$$

For instance, the above formula can be used to make the following calculation for the AQE at the wavelength of 365 nm with the required experimental parameters, including the power density of Xenon lamp at 365 nm (1.834 mW/cm^{-2}), the active area under irradiation light (28.3 cm^2) and the molar of generated hydrogen in 2 h (148.76 μmol).

$$AQE = \frac{148.76 \times 10^{-6} \times 6.02 \times 10^{23} \times 2}{1.834 \times 10^{-3} \times 28.3 \times 3600 \times 2 \times 365 \times 10^{-9}/\left(6.626 \times 10^{-34} \times 3 \times 10^{8}\right)} \times 100\%$$

$$= 26.1\%$$

4. Figures

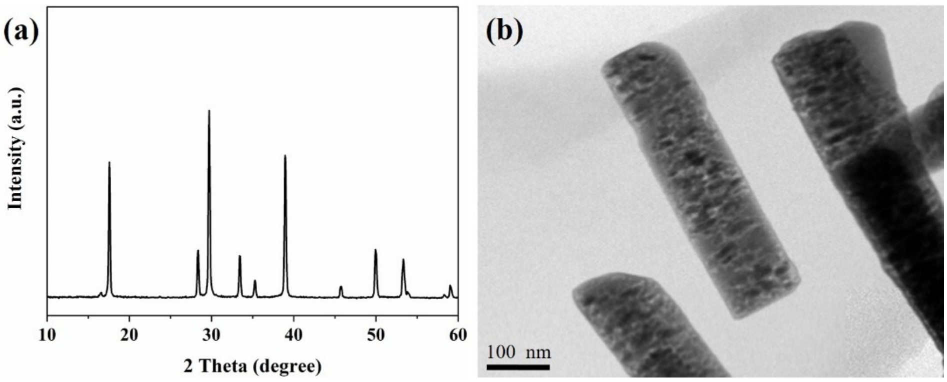

Fig. S1. The XRD pattern (a) and TEM image (b) of the as-prepared Cd(OH)Cl nanorods.

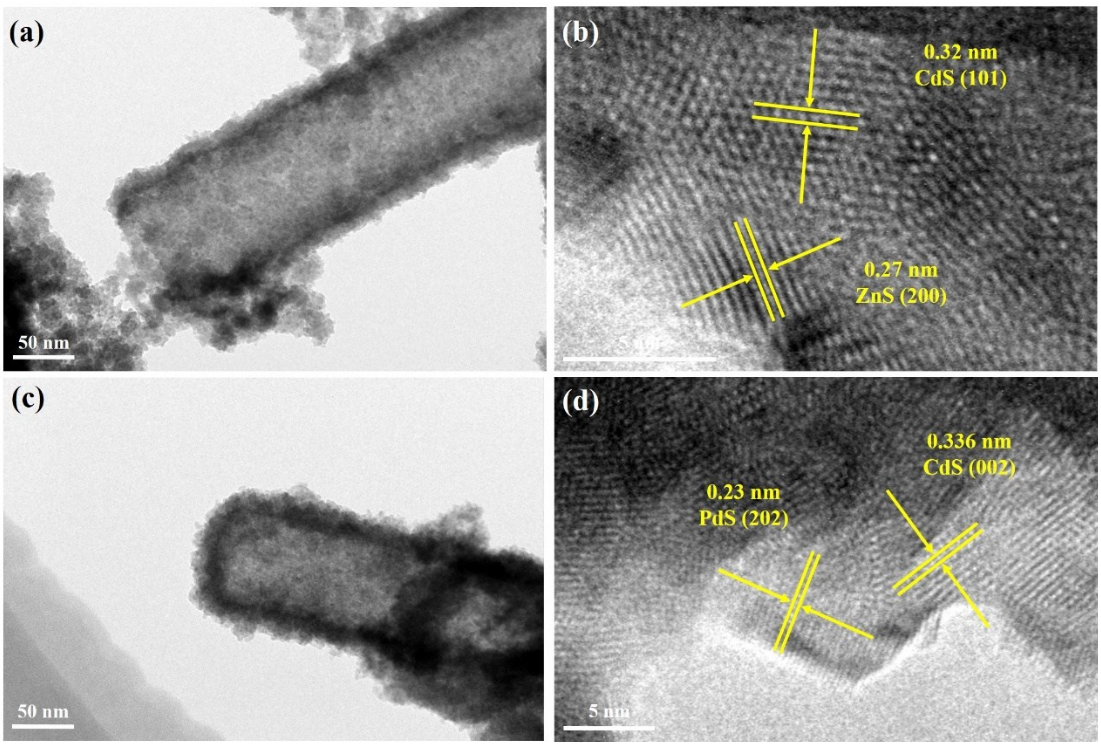

Fig. S2. TEM images of CZ_3S (a, b) and CP_1S (c, d).

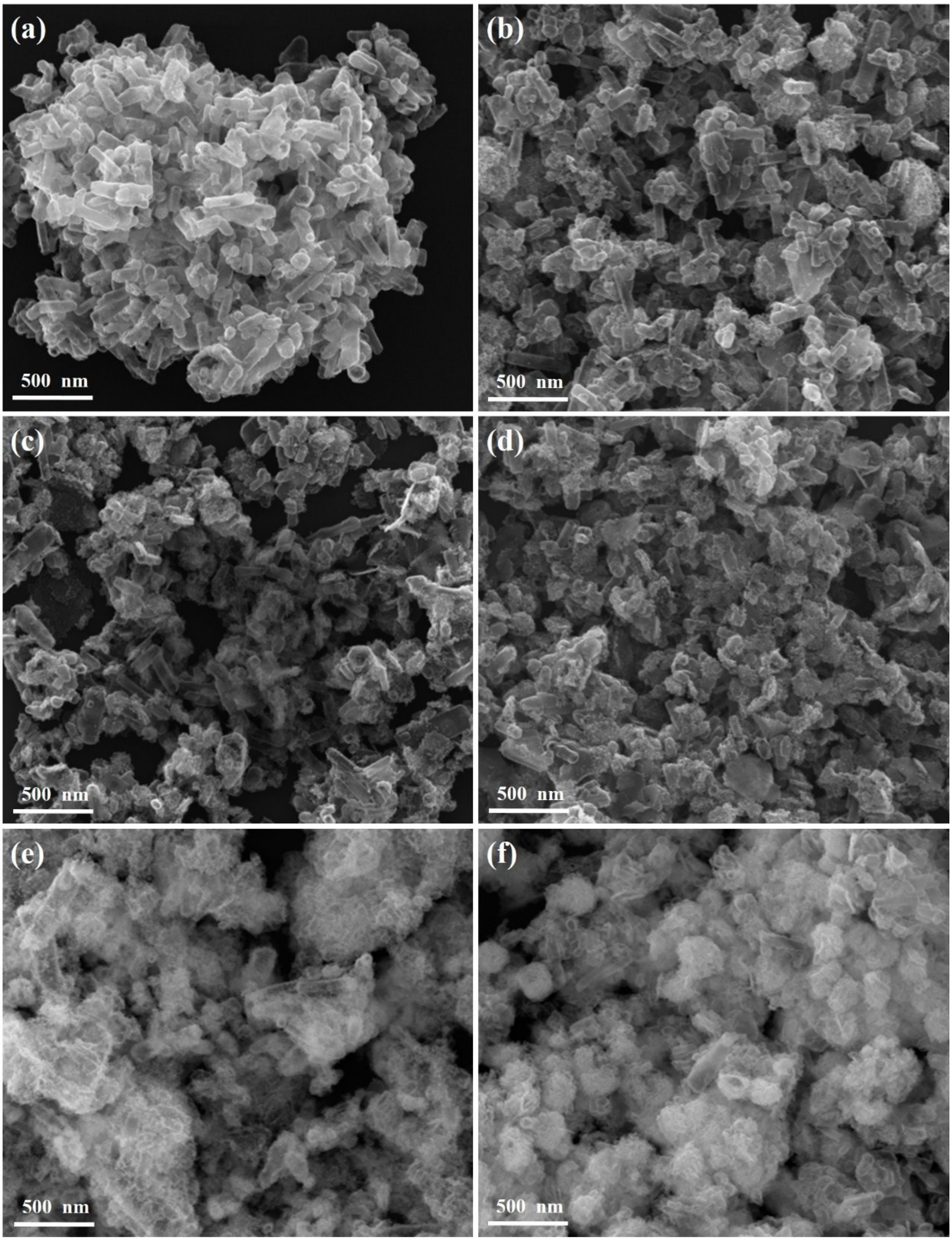

Fig. S3. SEM images of CdS (a), CZ_1S (b), CZ_3S (c), CZ_5S (d), CP_1S (e) and CZ_3P_1S (f).

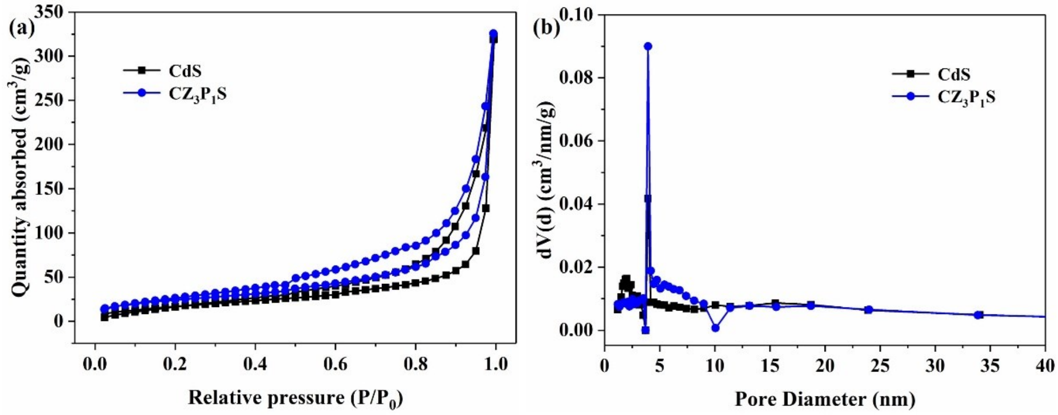

Fig. S4. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of CdS NTs and CZ_3P_1S catalyst.

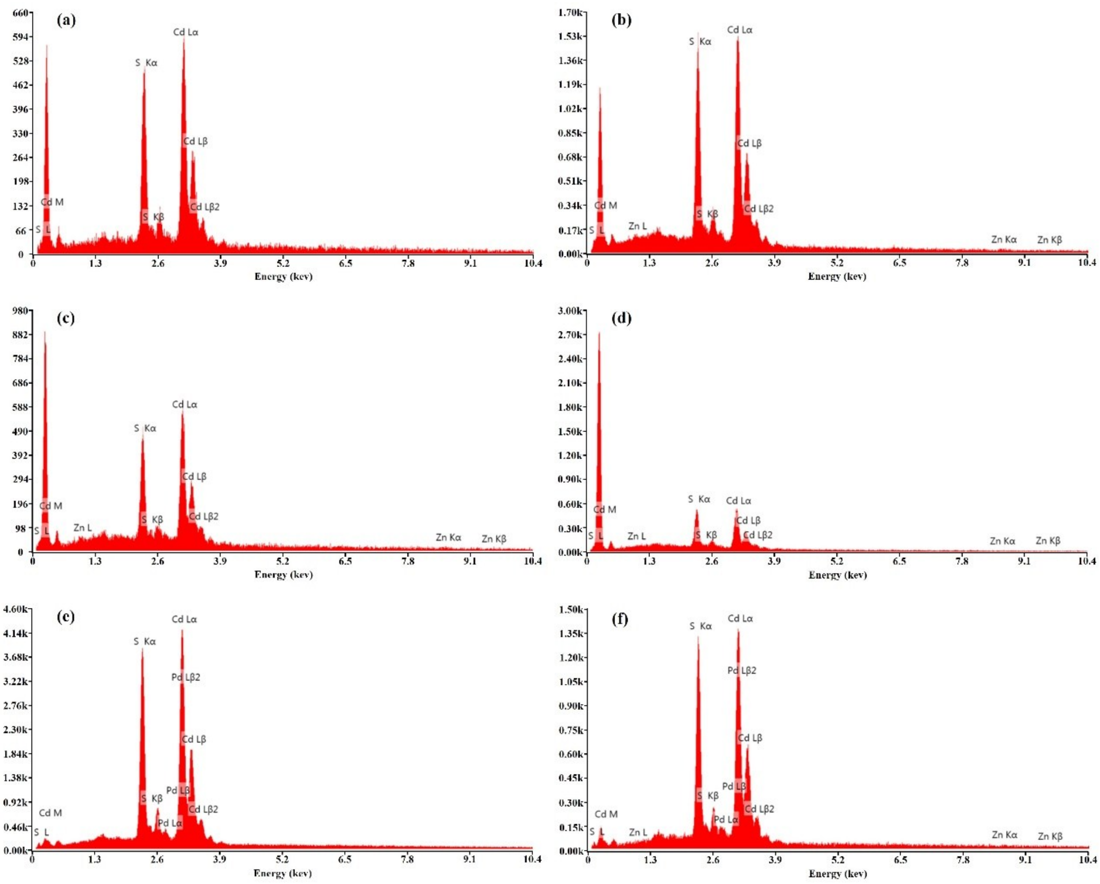

Fig. S5. EDX spectra of CdS (a), CZ_1S (b), CZ_3S (c), CZ_5S (d), CP_1S (e) and CZ_3P_1S (f).

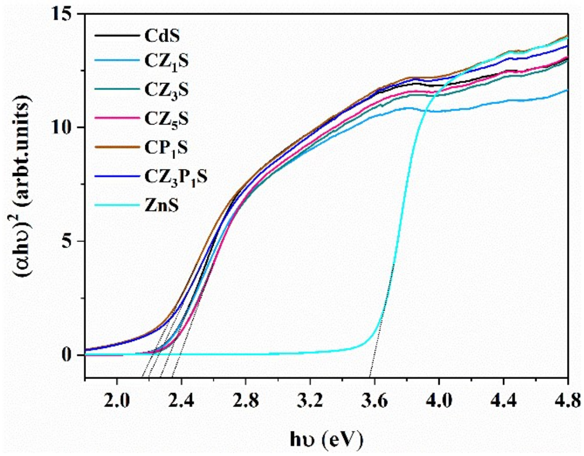

Fig. S6. Tauc plots of the as-prepared samples.

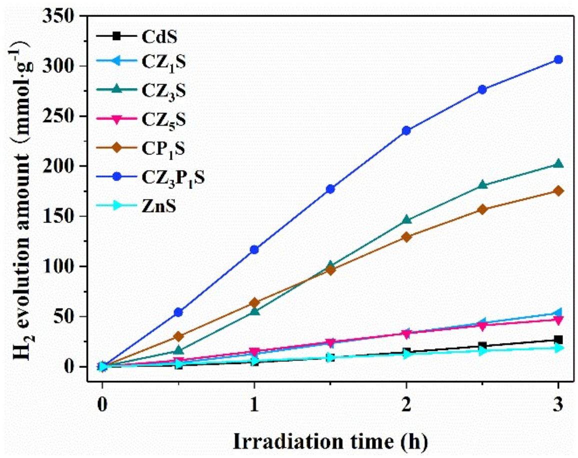

Fig. S7. Time courses of H_2 evolution over the as-synthesized samples.

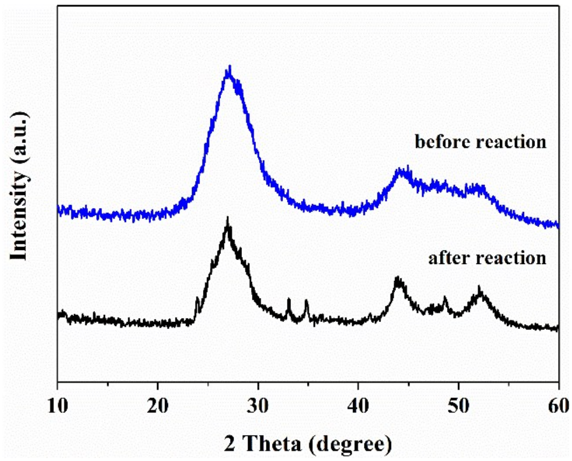

Fig. S8. XRD patterns of the CZ_3P_1S before and after cycling tests.

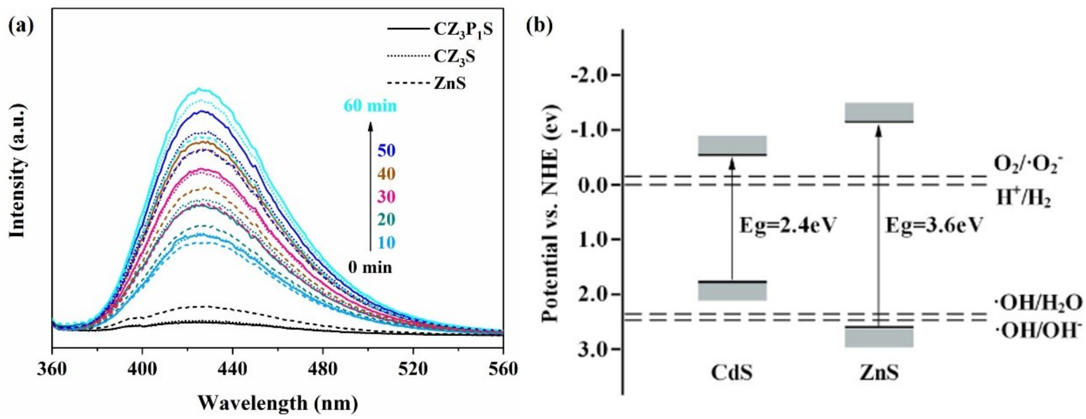

Fig. S9. PL spectra (a) of CZ_3P_1S, CZ_3S and ZnS samples in a TA solution irradiated by simulated sunlight at di□erent irradiation time (excitation at the wavelength of 315 nm), and the schematic diagram (b) of the band positions of CdS and ZnS.

5. Tables

Table S1 The percentages of S, Cd, Zn and Pd in the as-prepared samples measured by the EDX.

Sample	CdS	CZ_1S	CZ_3S	CZ_5S	CP_1S	CZ_3P_1S
S K (wt. %)	22.51	23.76	21.83	24.56	23.53	22.94
Cd L (wt. %)	77.49	74.44	75.39	72.03	75.95	74.14
Zn K (wt. %)	-	1.8	2.78	3.41	-	1.44
Pd L (wt. %)	-	-	-	-	0.52	1.48

Table S2 The percentages of S, Cd, Zn and Pd in the CZ_3P_1S sample measured by XPS.

Element	S	Cd	Zn	Pd
Percentage (at. %)	48.88	46.85	2.98	1.29
Percentage (wt. %)	21.87	73.49	2.72	1.92

Table S3 The band gap values of the as-prepared samples.

Sample	CdS	CZ_1S	CZ_3S	CZ_5S	CP_1S	CZ_3P_1S	ZnS
Band gap (eV)	2.32	2.35	2.39	2.42	2.22	2.26	3.6

Table S4 Comparison of the photocatalytic H_2 evolution rates over different CdS-based photocatalysts.

Catalyst	$R(H_2)$ (mmol/g/h)	Sacrificial agents	Reference
CdS NTs	8.9	0.35 M Na_2S and 0.25 M Na_2SO_3	This work
CZ_3P_1S	102.1	0.35 M Na_2S and 0.25 M Na_2SO_3	This work
CdS nanoplates/Pt	3.75	0.25 M Na_2S and 0.25 M Na_2SO_3	[1]
Pt-PdS/CdS NPs	29.23	0.5 M Na_2S and 0.5 M Na_2SO_3	[2]
CdS NRs/NiS	1.131	0.35 M Na_2S and 0.25 M Na_2SO_3	[3]
Au/CdS/TiO_2	1.97	0.25 M Na_2S and 0.25 M Na_2SO_3	[4]
TiO_2-Au-CdS	1.81	0.1 M Na_2S and 0.1 M Na_2SO_3	[5]
$Cd_{0.5}Zn_{0.5}S/MoO_2$	25.24	0.1 M Na_2S and 0.1 M Na_2SO_3	[6]
ZnO/CdS/ZnS	44.7	0.35 M Na_2S and 0.25 M Na_2SO_3	[7]
ZnO/CdS/ZnS	2.077	0.35 M Na_2S and 0.25 M Na_2SO_3	[8]
Pd/CdS/PdS	89.2	0.1 M Na_2S and 0.1 M Na_2SO_3	[9]
CdS/ZnS	0.792	0.35M Na_2S and 0.25 M Na_2SO_3	[10]

References

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Table S5 AQE over the CZ_3P_1S sample at different wavelengths.

λ (nm)	365	380	420	500
AQE (%)	26.1	20.51	6.9	1.63