hydrogen

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Supplementary materials

Article

Role of the Sulphur Source in the Solvothermal Synthesis of Ag-CdS Photocatalysts: Effects on the Structure and Photoactivity for Hydrogen Production

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Materials and methods

Table S1. Standard deviation of the concentration (umr.) of Cd, S and Ag determined by TXRF for all the CdS-X and AgCdS-X samples.

	Cd (umr) ± Std.Dev.	S (umr) ± Std.Dev.	Ag (umr) ± Std.Dev.
CdS-S	112.41 ± 0.22	34.86 ± 0.13	--
AgCdS-S	112.41 ± 0.26	35.76 ± 0.16	0.82 ± 0.035
CdS-L	112.41 ± 0.23	32.44 ± 0.13	--
AgCdS-L	112.41 ± 0.23	35.37 ± 0.14	1.17 ± 0.028
CdS-T	112.41 ± 0.26	34.84 ± 0.17	--
AgCdS-T	112.41 ± 0.21	34.97 ± 0.12	7.53 ± 0.041

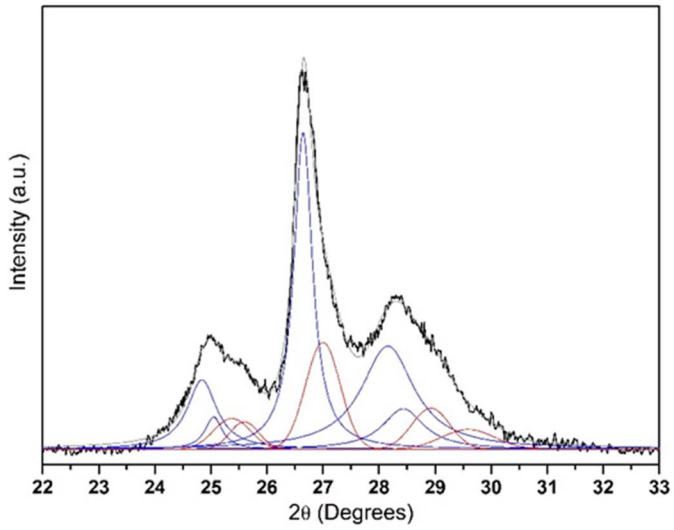


Figure S1. Representative example of the peak broadening deconvolution analysis of the XRD profiles (AgCdS-T sample).

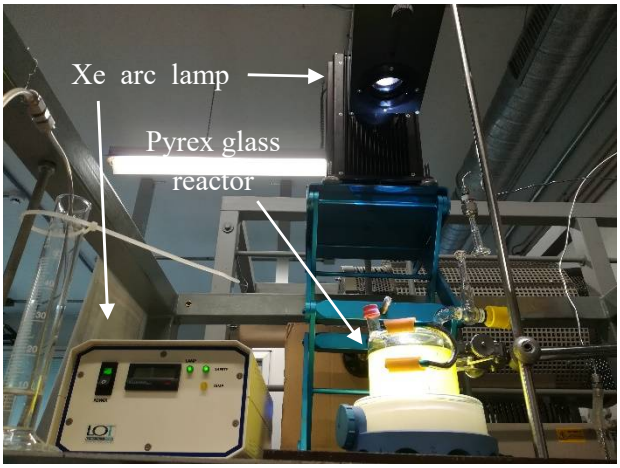


Figure S2. Experimental setup used for the photocatalytic activity measurements.

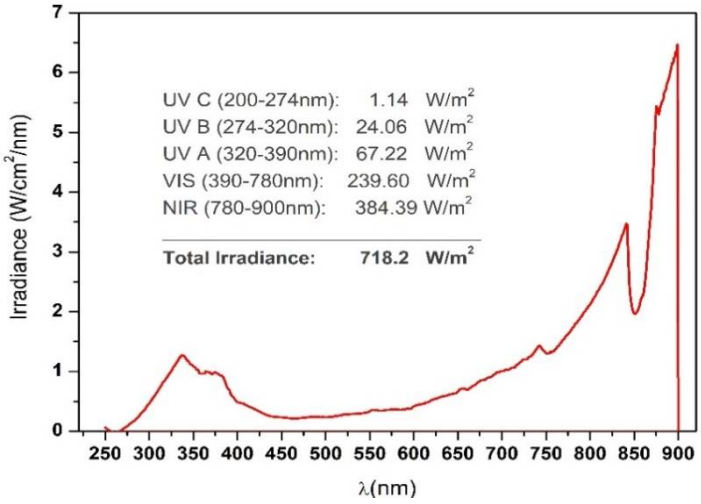
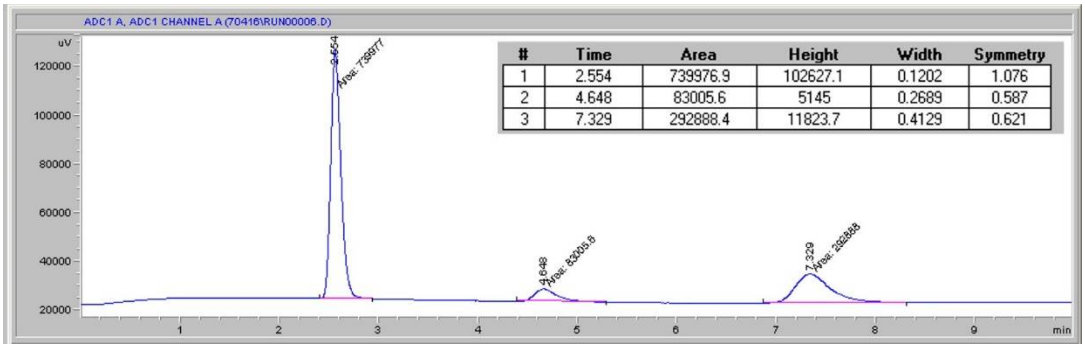


Figure S3. Irradiance spectra of the Xe arc lamp (150W, ozone Free, LOT Oriel GmbH & CO KG) measured with spectroradiometer (ILT550 LOT Oriel GmbH & Co. KG) at a focal distance equal to 26.5 cm.



#	Time	Area	Height	Width	Symmetry
1	2.554	739976.9	102627.1	0.1202	1.076
2	4.648	83005.6	5145	0.2689	0.587
3	7.329	292888.4	11823.7	0.4129	0.621

Figure S4. Representative chromatrogram (AgCdS-S sample) obtained in the GC Varian STAR CX3400 to quantify the produced H_2 (peak at retention time 2.55 min).

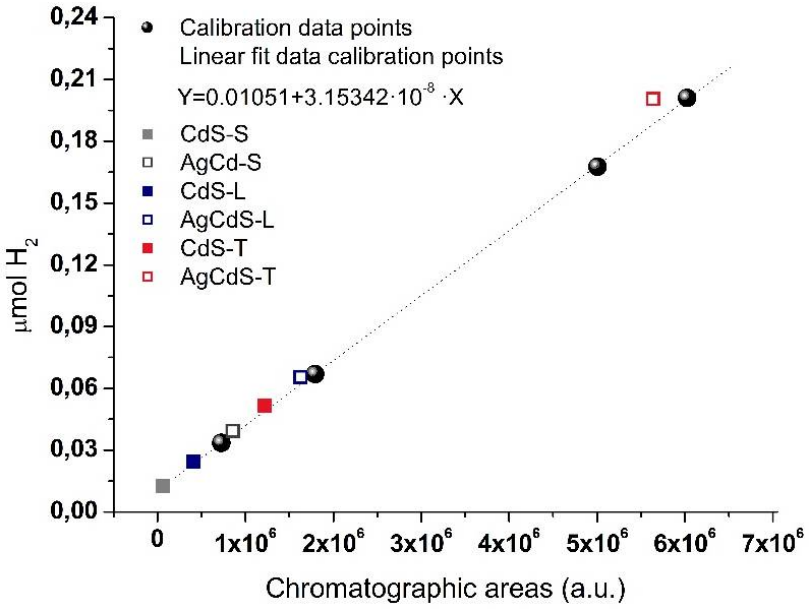


Figure S5. H_2 calibration curve for the quantification of the hydrogen produced from the chromatographic areas and experimental fitting of the results obtained in the CdS-X and AgCdS-X samples.

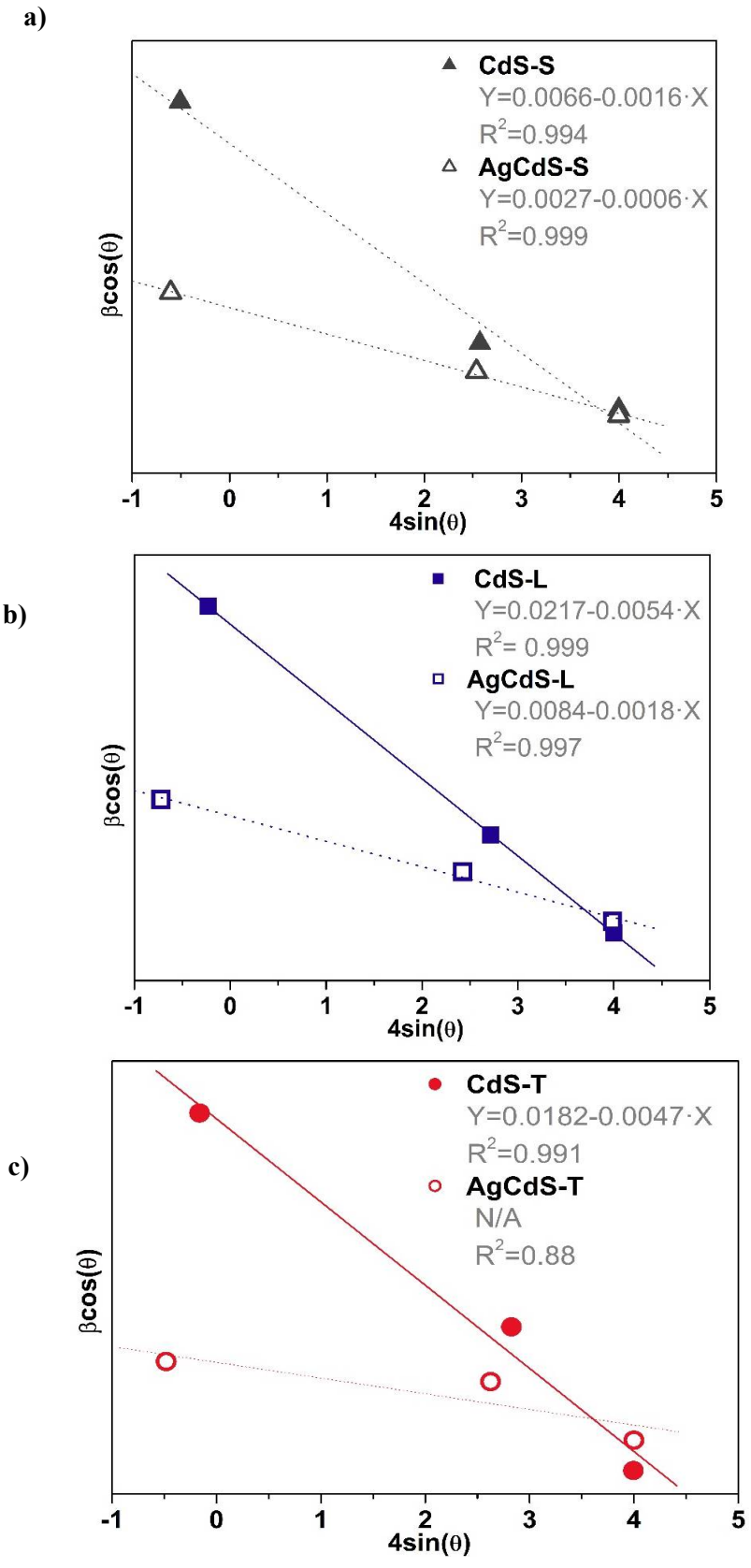


Figure S6. Williamsom-Hall plot linear fit for the CdS-X and AgCdS-X photocatalysts prepared with different sulphur source: a) Elemental sulfur, b) L-cysteine and c) Thiourea.

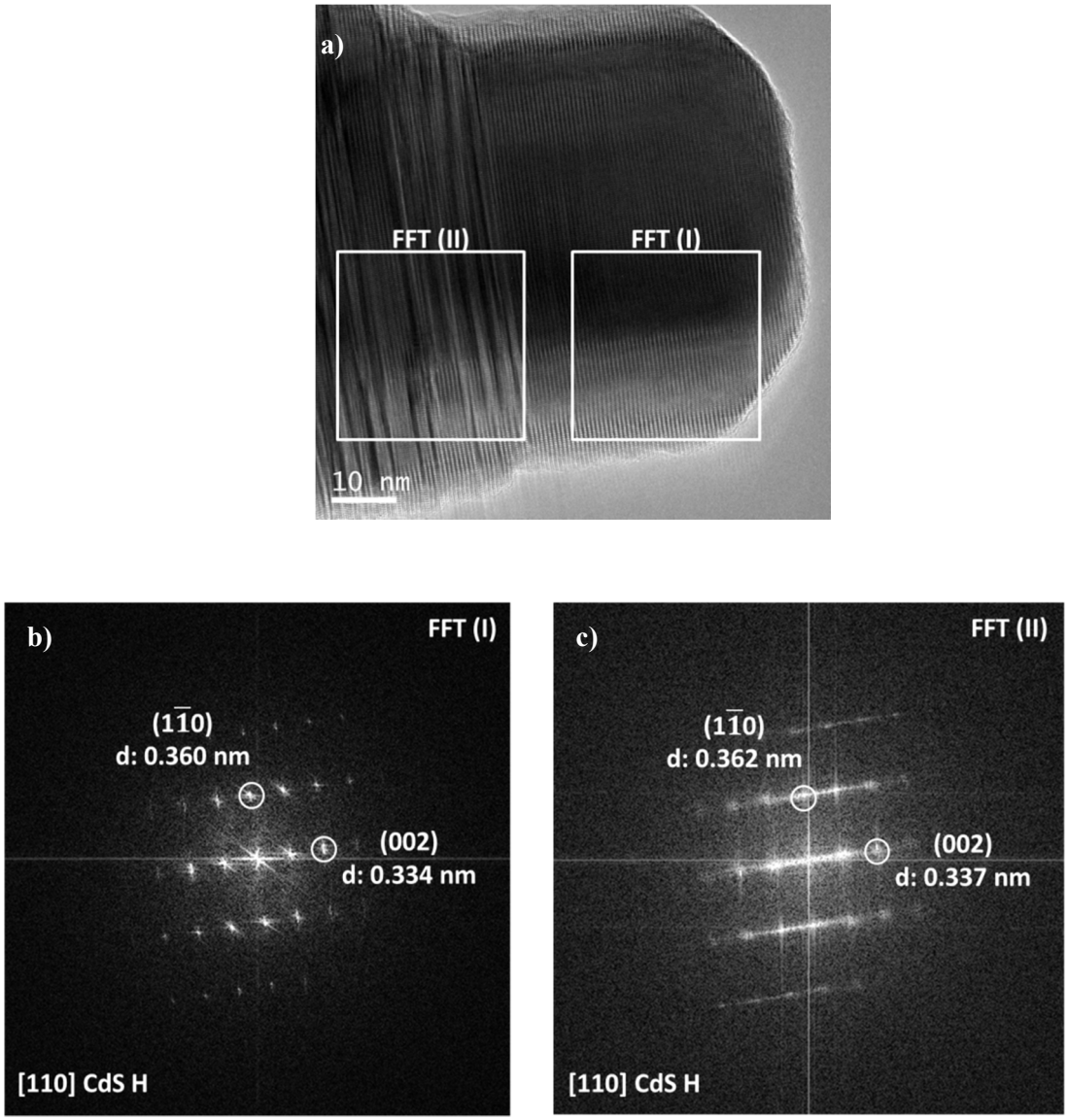


Figure S7. HR-TEM images of the FFT analysis for the determination of the crystalline planes of the (a) AgCdS-S for the region FFT I (b) and FFT II (c).

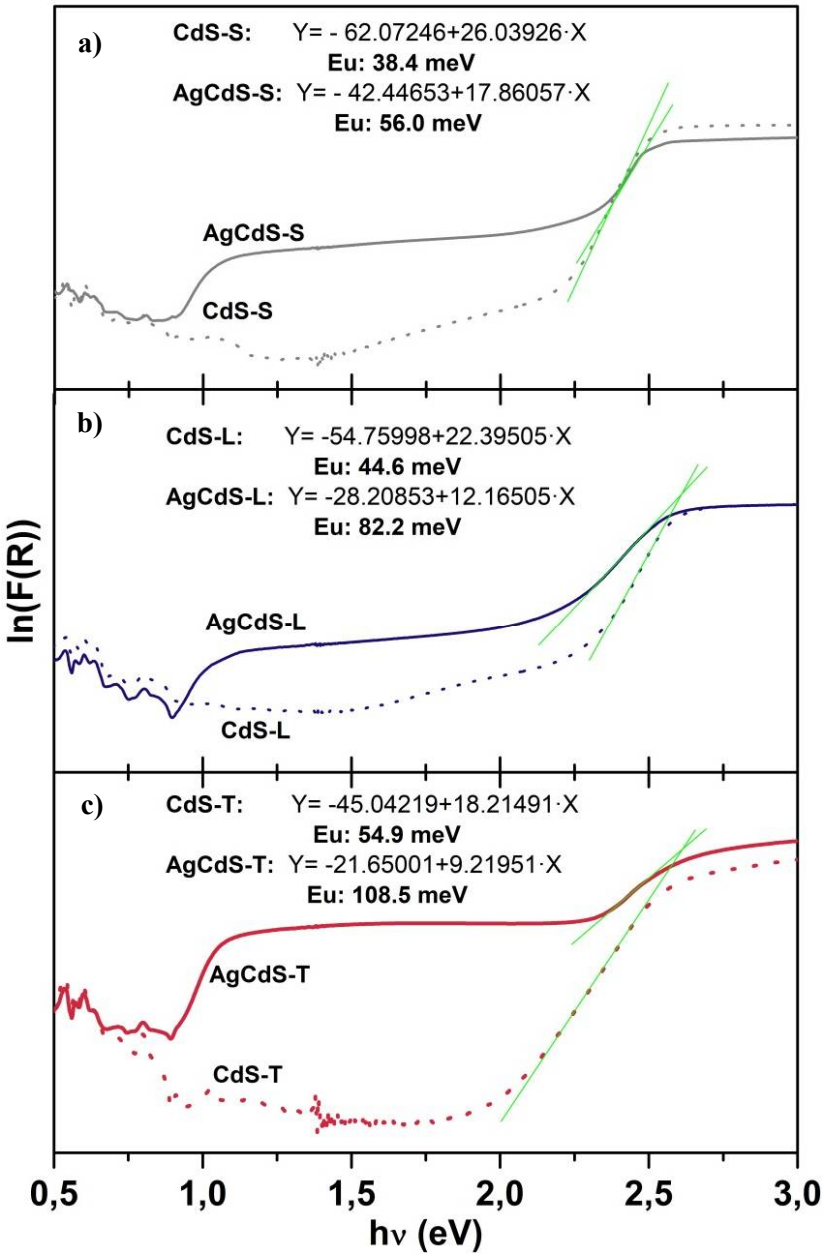


Figure S8. Urbach tails linear fit of CdS-X and AgCdS-X photocatalysts prepared with different sulphur sources: a) Elemental sulfur b) L-cysteine and d) thiourea.

Table S2. Complex stability constants extracted from reference [4].

Complexing Agent	Log K	
	Cd^{2+}	Ag^{+}
Ethylenediamine	10.09	4.7
Thiourea	1.6	7.4
L-cysteine	19.63	11.4

$$SO_3^{2-} + H_2O + 2h^+(BV) \rightarrow SO_4^{2-} + 2H^+$$

$$2S^{2-} + 2h^+(BV) \rightarrow S_2^{2-}$$

$$S_2^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S^{2-}$$

$$SO_3^{2-} + S^{2-} + 2h^+(BV) \rightarrow S_2O_3^{2-}$$

Figure S9. Sacrificial reagents equilibrium reactions [5].

Experimental

The theoretical calculation of the relative position of the valence band and conduction band of CdS and Ag_2S was carried out by applying the Equations 1 and 2 [1]:

$$E_{VB} = E_{CB} + BG \quad (1)$$

$$E_{CB} = \chi - (0.5 \cdot BG) + E_0 \quad (2)$$

Where E_0 is the scale factor that relates the reference electrode redox level to the absolute vacuum scale and is equal to -4.5 eV for NHE, meanwhile χ represents the electronegativity of the semiconductor calculated based on the method proposed by Nethercot et al.[2] (Equation 3) as a geometrical average of the electronegativity of the individual constituent atoms:

$$\chi = (xA^a \cdot xB^b)^{\frac{1}{a+b}} \quad (3)$$

The electronegativity of the individual constituent atoms (x, table SI 3) was calculated according to Mulliken´s method, based on the arithmetic mean of the first ionization energy (EIE, eV) and the electronic affinity (EA, eV) (Equation 3):

$$x = \frac{1}{2} \cdot (EIE + EA) \quad (3)$$

Table S3. Electronegativity of Cd, Ag and S calculated from EIE and EA, extracted from reference [3].

	EIE (eV)	**EA (eV)**	$\boldsymbol{x}$
Cd	8.9938	0	4.4969
Ag	7.5762	1.302	4.4391
S	10.36	2.077	6.2185

References

[1] Tang R., Su H., Sun Y., Zhang X. Li L., Liu C., Zeng S and Sun D., Enhanced photocatalytic performance in Bi_2WO_6/SnS heterostructures: Facile synthesis, influencing factors and mechanism of the photocatalytic process, Journal of Colloid and Interface Science, 2016, 466, 388–399

[2] Nethercot, A.H. Jr., Prediction of Fermi Energies and Photoelectric Thresholds Based on Electronegativity Concepts, Physical Review Letters, 1974, 33, 1088

[3] David R. Lide, Handbook of Chemistry and Physics,84th Edition, CRC Press

[4] Dean, J. A.; Lange´s Handbook of Chemistry; McGraw-Hill, 5th Edition, ISBN: 0-07-016384-7

[5] Reber J.F. and Meier K., Photochemical production of hydrogen with zinc sulfide suspensions, J. Phys. Chem., 1984, 88, 5903–5913