Controlling the Photocorrosion of Zinc Sulfide Nanoparticles in Water by Doping with Chloride and Cobalt Ions

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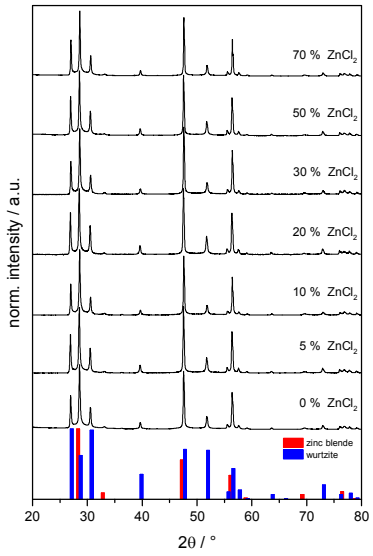

Figure S1. XRD patterns of ZnS with different levels of $ZnCl_2$ substitution after drying and annealing at 800 °C and acidic post-treatment.

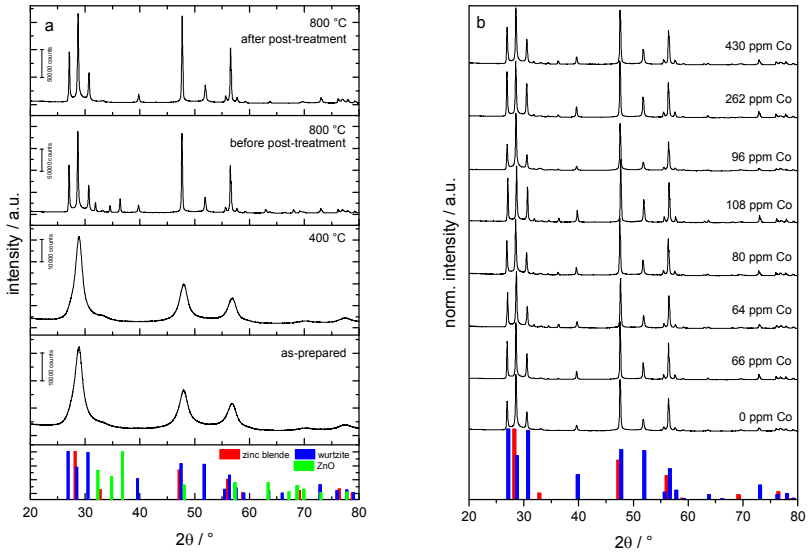

Figure S2. XRD patterns of ZnS doped with 262 ppm Co annealed at different temperatures (a) and with different levels of Co doping, annealed at 800 °C (b).

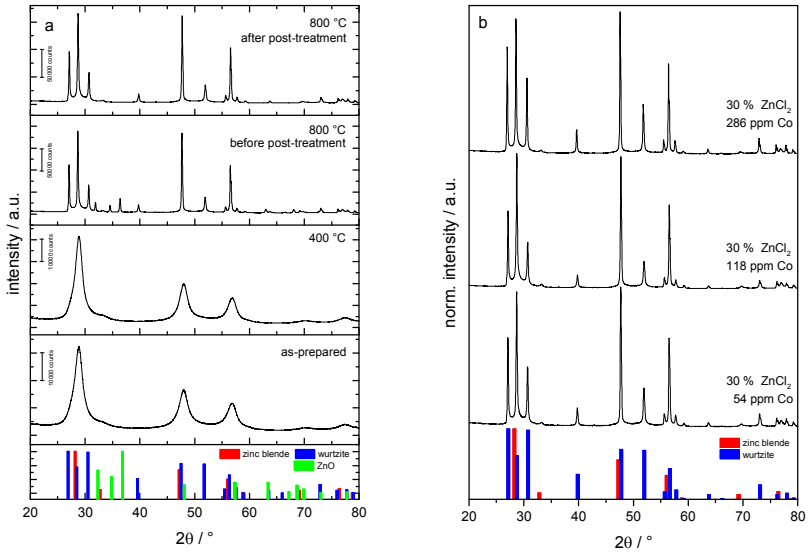

Figure S3. XRD patterns of ZnS co-doped with Cl and Co. (a) 30 % $ZnCl_2$ and 118 ppm Co annealed at different temperatures. (b) Effect of different Co doping.

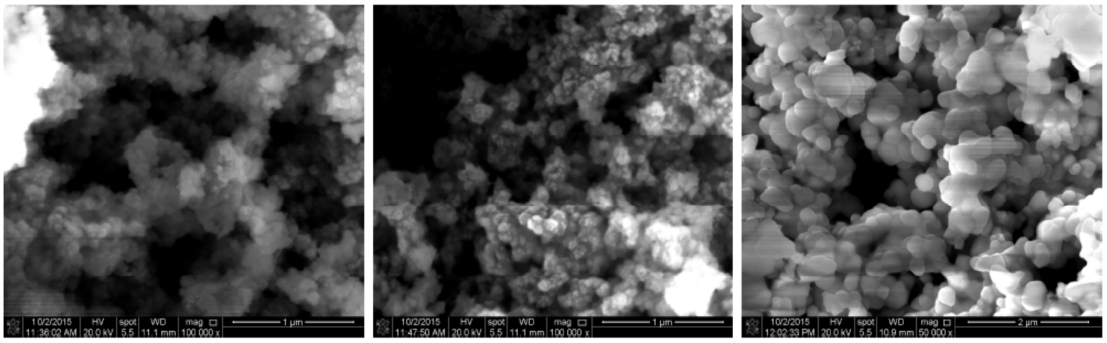

Figure S4.SEM images of Cl-doped ZnS obtained after drying (left) and after calcination at 400 °C (middle) and 800 °C (right).

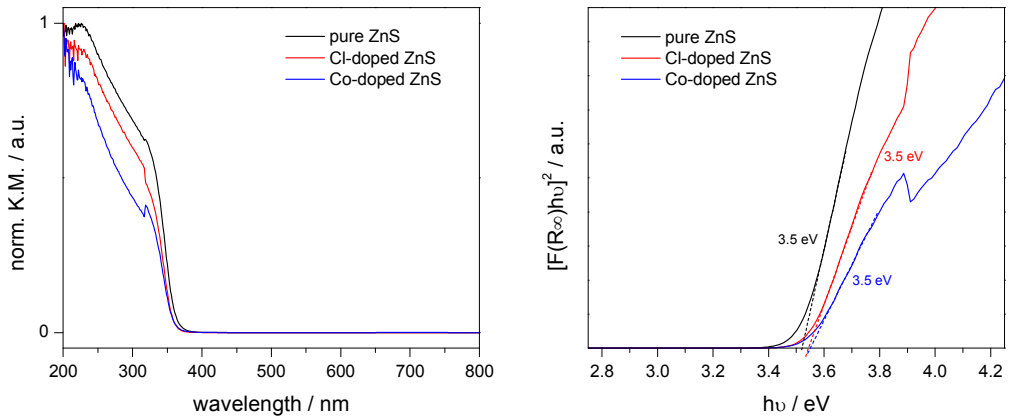

Figure S5. UV/Vis diffuse reflectance spectra (Kubelka-Munk function, left) and bandgap determination (Tauc plot, right) for as-prepared pure ZnS, Cl-doped ZnS and Co-doped ZnS.

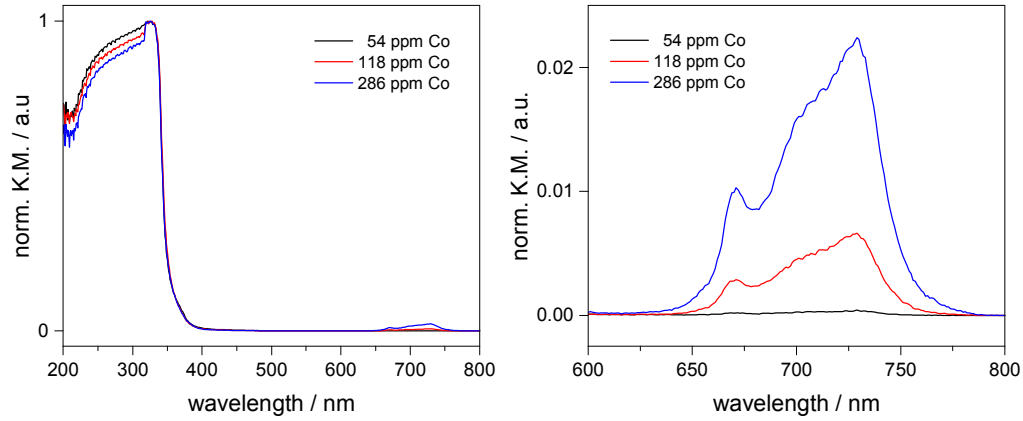

Figure S6. Full range (a) and enlarged (b) UV/Vis diffuse reflectance spectra of 30 % $ZnCl_2$ ZnS co-doped with different amounts of Co annealed at 800 °C.

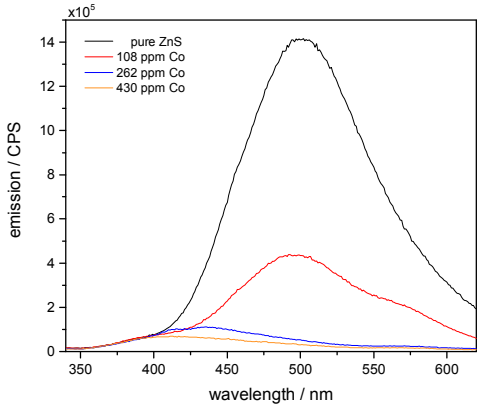

Figure S7. Photoluminescence emission spectra of differently Co-doped ZnS obtained at 800 °C.

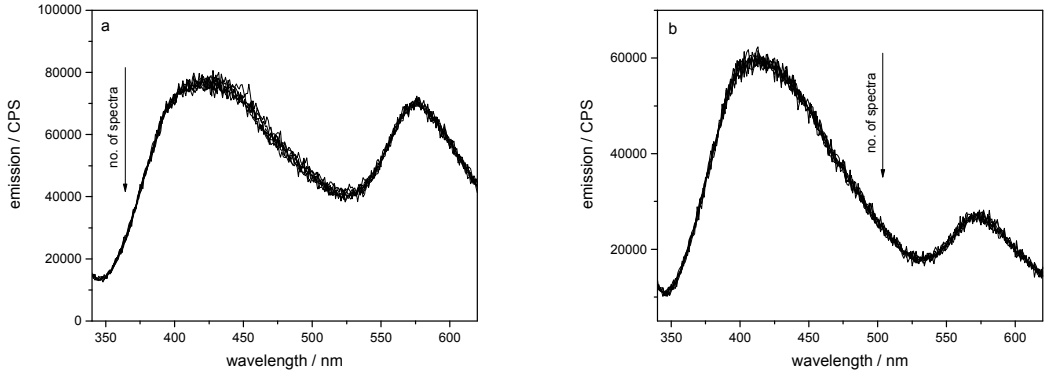

Figure S8. Consecutive photoluminescence emission spectra of Cl/Co-doped ZnS with 30 % $ZnCl_2$ and 118 ppm Co (a) and 286 ppm Co (b).

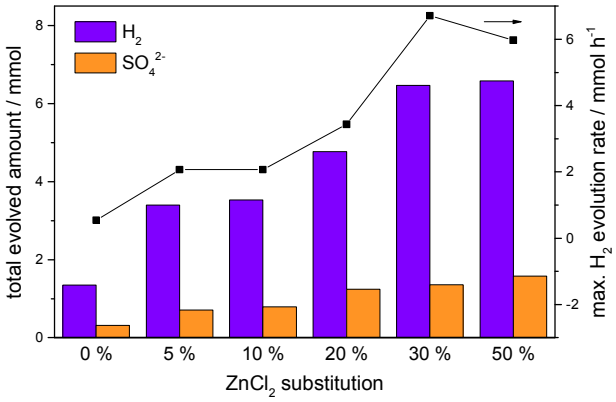

Figure S9. Photocatalytic H_2 evolution and SO_4^{2-} formation during irradiation of differently Cl-doped ZnS annealed at 800 °C. m_{cat} = 500 mg, t = 2.5 h, $V_{susp.}$ = 580 mL, 500 W Hg lamp.

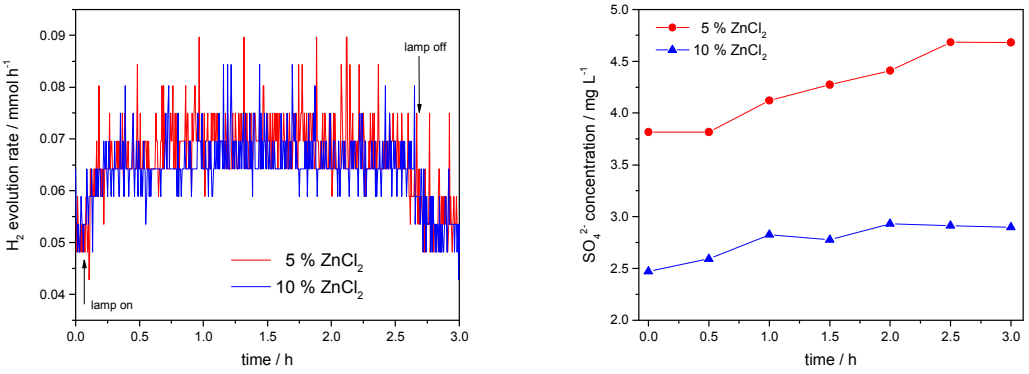

Figure S10. Photocatalytic H_2 evolution and SO_4^{2-}formation during irradiation of differently Cl-doped ZnS annealed at 400 °C. m_{cat} = 500 mg, t = 2.5 h, $V_{susp.}$ = 580 mL, 500 W Hg lamp.

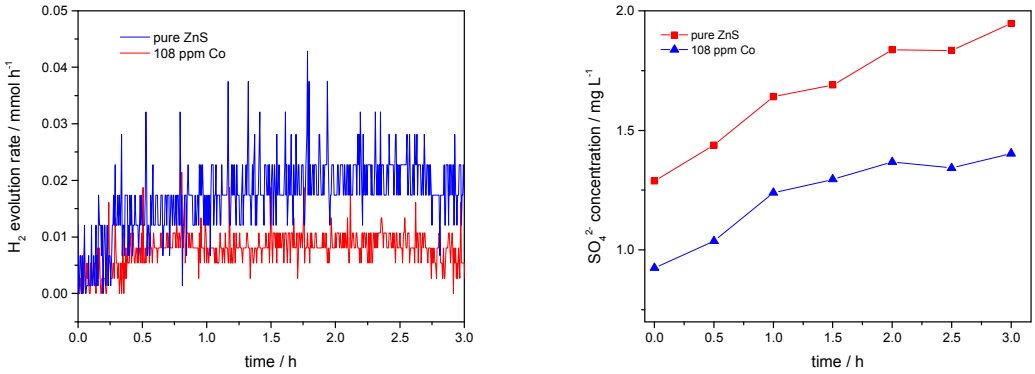

Figure S11. Photocatalytic H_2 evolution (a) and SO_4^{2-} formation (b) during irradiation of pure and Co-doped ZnS annealed at 400 °C.

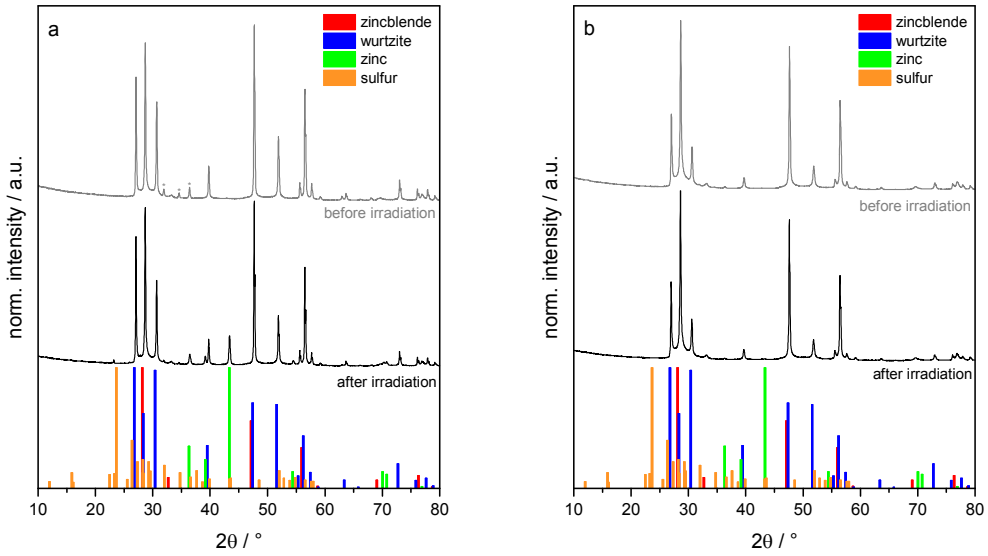

Figure S12. XRD patterns of ZnS doped with 108 ppm (a) and 262 ppm Co (b) annealed at 800 °C before and after photochemical experiments. The * denotes peaks from residual ZnO.

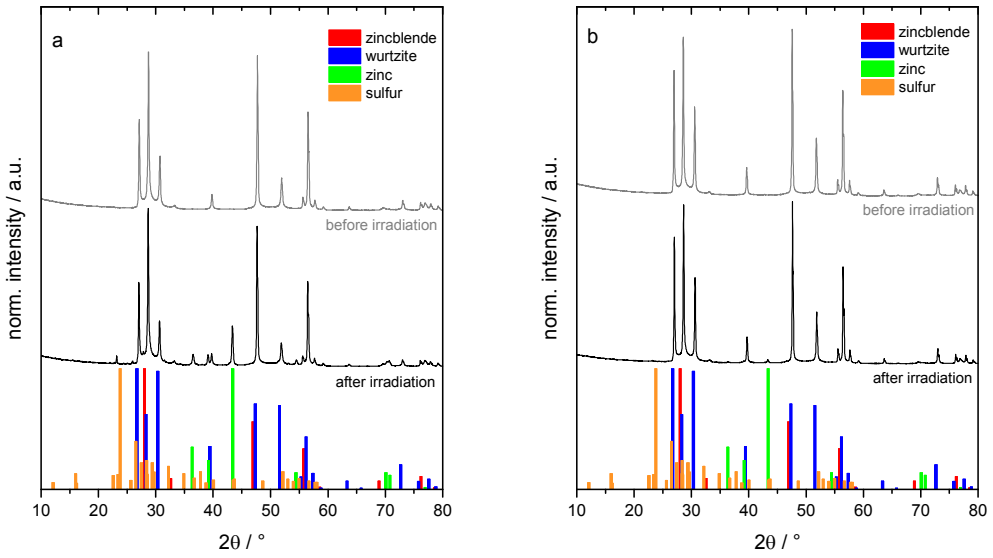

Figure S13. XRD patterns of 30 % $ZnCl_2$ ZnS co-doped with (a) 118 ppm Co and (b) 286 ppm Co before and after photochemical experiments.

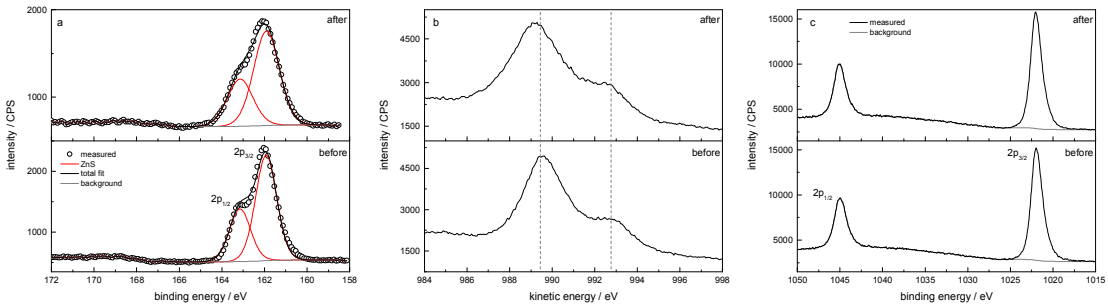

Figure S14. X-ray photoelectron spectra of Cl-doped ZnS before and after 2.5 h UV irradiation in the slurry-reactor. a) S 2p b) Zn LMM Auger c) Zn 2p.

Table S1. Evolved H_2 and SO_4^{2-} during photochemical experiments with Cl-doped ZnS (800 °C). m_{cat} = 500 mg, t = 2.5h, $V_{susp.}$ = 580 mL.

$ZnCl_2$ substitution [%]	H_2 max [mmol h^{-1}]	H_2 after 2.5 h [mmol h^{-1}]	H_2 total [mmol]	SO_4^{2-} [mg mL^{-1}]	SO_4^{2-} total [mmol]
-	0.54	0.51	1.35	51.7	0.31
5	2.07	1.15	3.40	116.7	0.71
10	2.07	1.20	3.53		
20	3.43	1.28	4.77	176.2	1.25
30	6.71	1.24	6.47	224.3	1.35
50	5.97	1.38	6.58	262.0	1.58

Table S2. Surface atomic concentrations and S^{2-}/SO_4^{2-} ratios of 30% $ZnCl_2$-ZnS before and after UV irradiation in ambient air derived from the XP spectra.

irradiation time [min]	atomic concentration[%]				S^{2-}/SO_4^{2-}
	C	O	S	Zn	
0	17.9	8.1	37.0	37.0	∞
0.5	15.3	18.4	32.5	33.8	7.0
5	14.2	27.7	26.3	31.8	2.2
60	13.0	36.1	23.4	27.5	1.3