Electronic Supplementary Information (ESI)

Photoassisted formation of Cu_xS-based cathodes for CdS-sensitized solar cells with S^{2-}/S_x^{2-} electrolyte

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Electrodeposition of zinc hydroxyl chloride films on FTO.

Zinc hydroxyl chloride films were electrodeposited in a three-electrode cell with an FTO plate as a work electrode, zinc foil as a counter-electrode, and an Ag/AgCl reference electrode. The electrolysis was performed at 60 °C and a constant potential of –1.1 V vs. Ag/AgCl in a water/ethanol mixture (50 v% water) in the presence of 0.1 M $Zn(NO_3)_2$, 0.1 M KCl, and 4.0 g/L polyvinylpyrrolidone. After the electrode position the films were rinsed with distilled water and 2-propanol, dried at 70 °C and calcined on air at 450 °C.

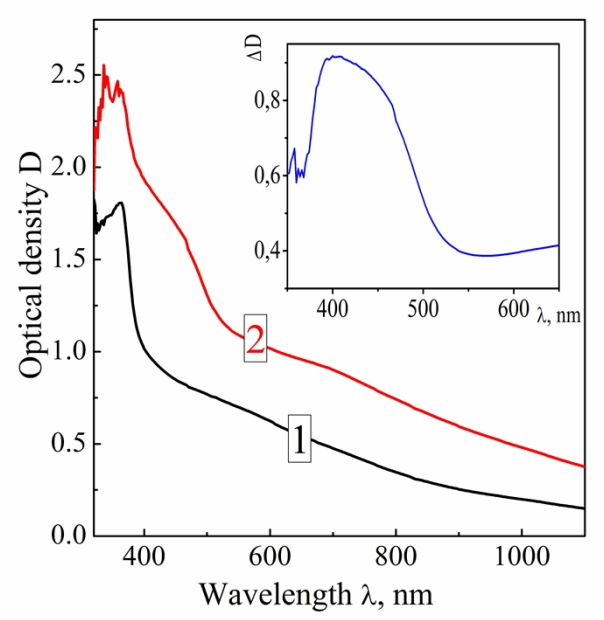


Figure S1. Extinction spectra of ZnO (curve 1) and ZnO/CdS (curve 2) films. Insert: differential CdS absorption spectrum obtained by subtracting curve 1 from curve 2.

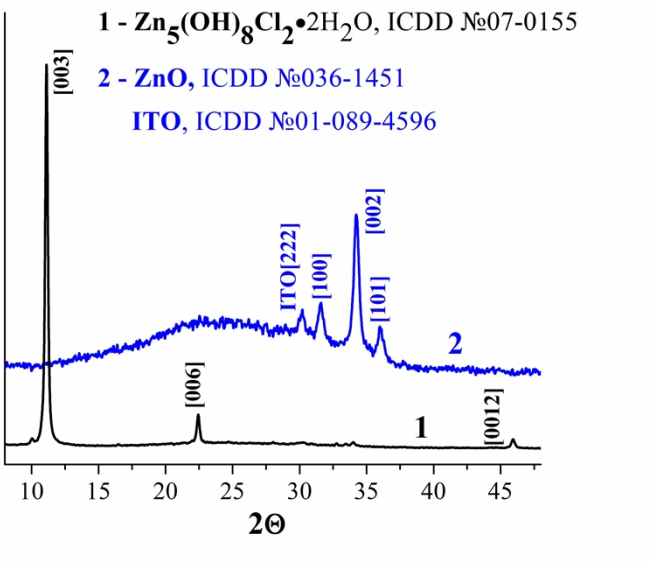


Figure S2. XRD pattern of as electrodeposited layered $Zn_5(OH)_8Cl_2 \times 2H_2O$ (curve 1), and ZnO (curve 2) formed after $Zn_5(OH)_8Cl_2 \times 2H_2O$ film calcination at 450 °C

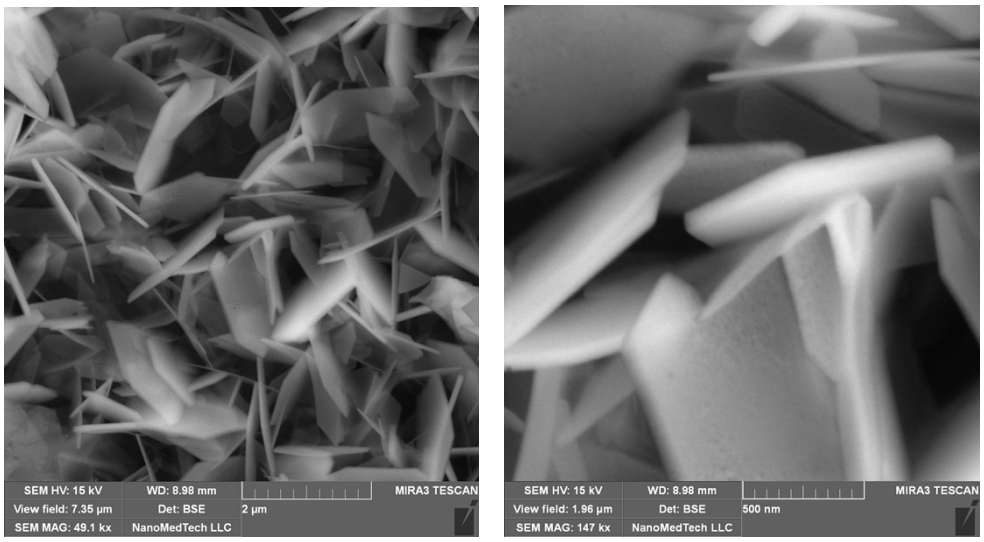


Figure S3. SEM images of FTO/$Zn_5(OH)_8Cl_2$ films

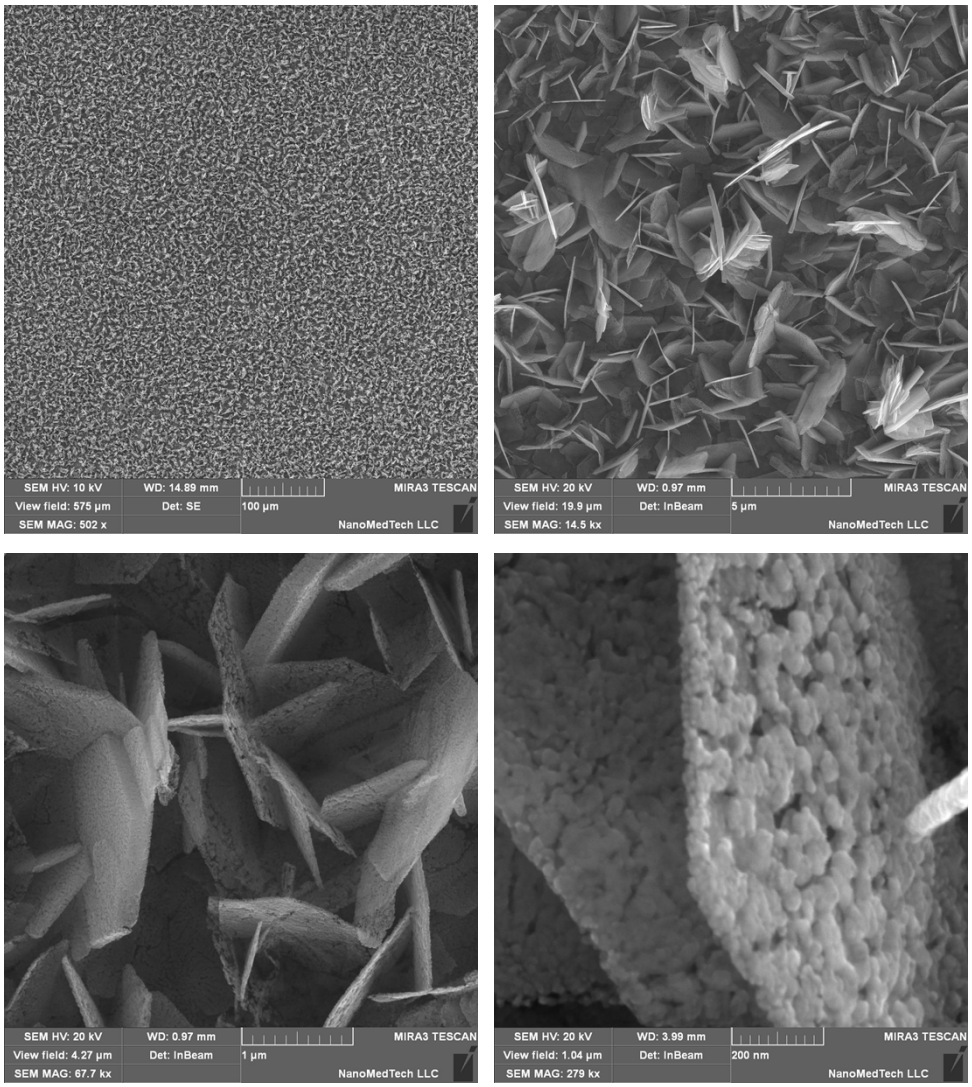


Figure S4. SEM images of electrodeposited and annealed FTO/ZnO film.

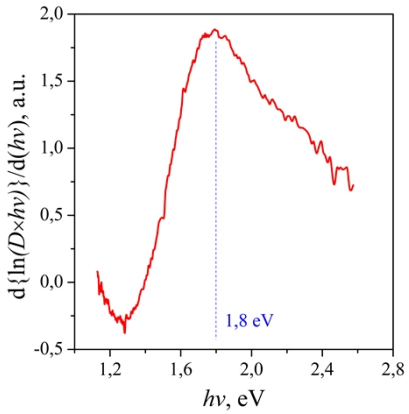


Figure S5. Absorption spectra of Cu_xS NPs in the film FTO/ZnO/Cu_xS in coordinates of differential form of Tauc equation for Cu_xS band gap determination.

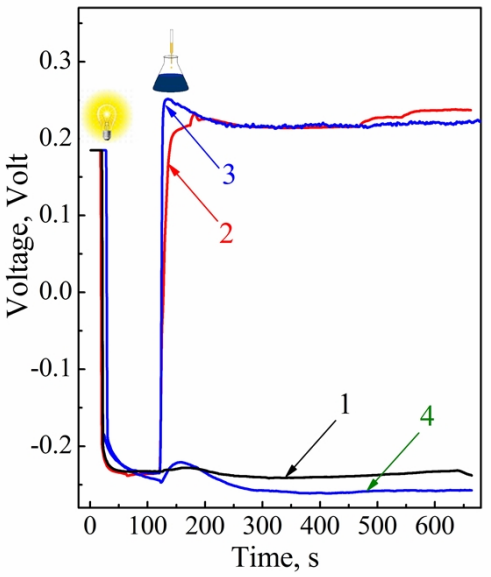


Figure S6. Temporal changes of the immersion potential of a FTO/ZnO film illuminated by white light (350−700 nm, the turn-on moment depicted by a lamp icon) after addition of 0.001 M S^0 (curve 1), 0.001 M $Cu(CH_3COO)_2$ (curve 2), mixture of copper(II) acetate and sulfur (curve 3), or 0.001 M CH_3COONa (curve 4). The moment of reactants addition depicted by a vial icon. The experiments were carried out in a three-electrode cell with a Pt counter-electrode and an Ag/AgCl reference electrode. The work electrode was immersed in 0.1 M solution of NH_4NO_3 in ethanol and illuminated in the open-circuit conditions.

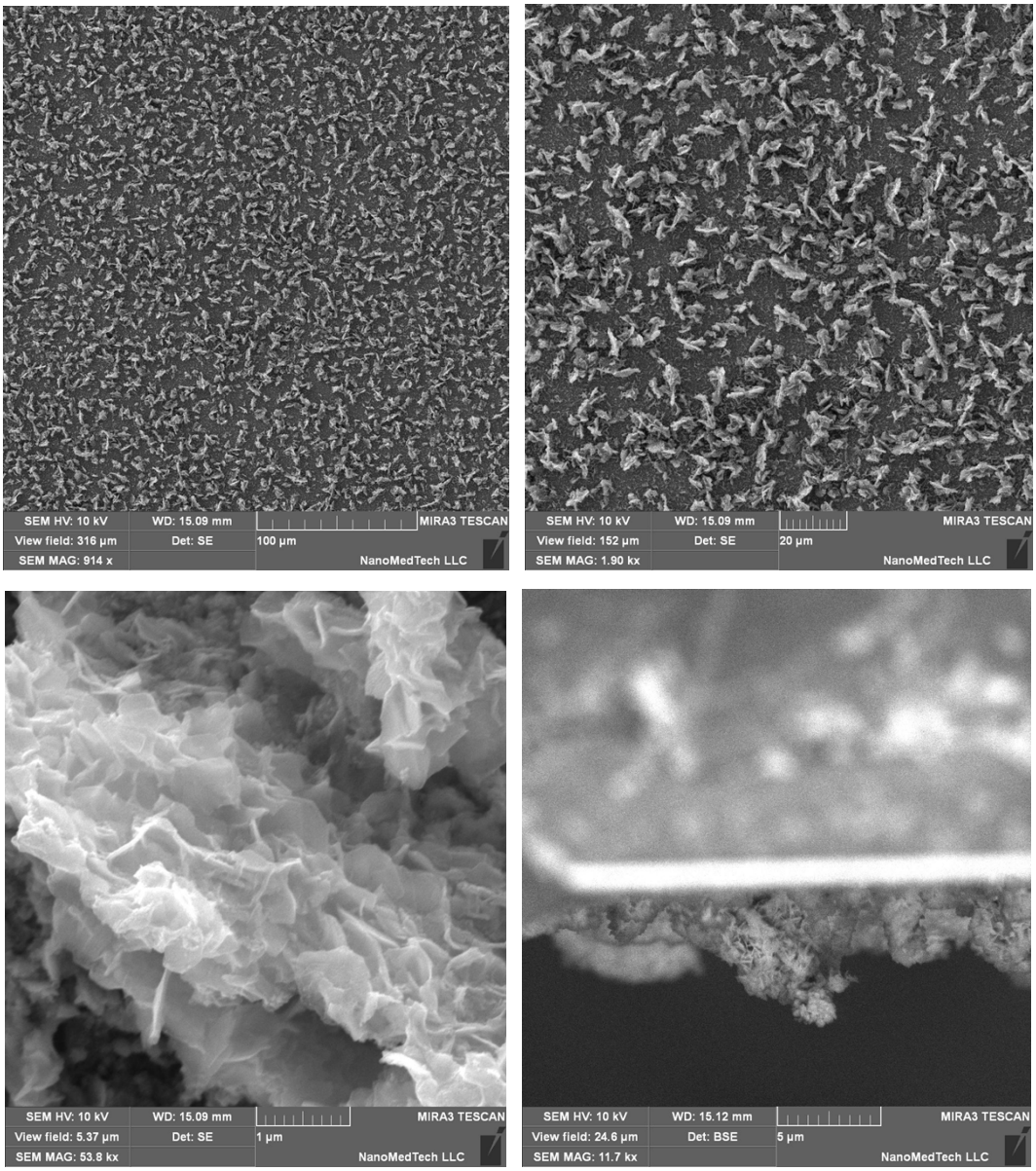
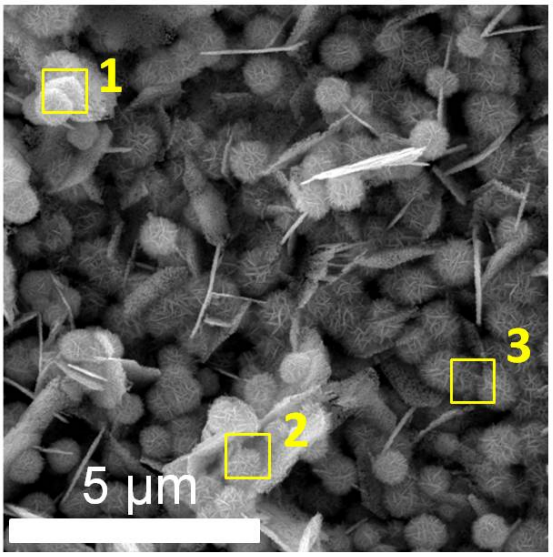


Figure S7. SEM images of FTO/ZnO/Cu_xS films produced by partial sulfidation of zinc oxide followed with substitution of Zn(II) in ZnS with copper ions (see in more details in [23]).



Spect-rum	Cu	S
1	1,42	1
2	1,34	1
3	1,39	1

Figure S8. SEM image of FTO/ZnO/Cu_xS film with three separate sections chosen for the EDX analysis (left part). Ratio of copper-to-sulfur atoms in the selected areas, according to the EDX analysis.

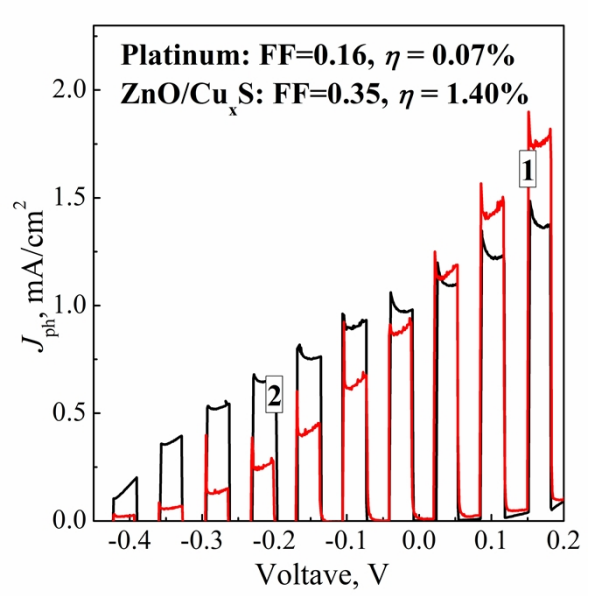


Figure S9. Illumination-modulated photocurrent−voltage dependences for ZnO/CdS photoanode coupled with platinum (curve 1) and ZnO/Cu_xS heterostructure (curve 2). The ZnO/Cu_xS film was produced by by partial sulfidation of zinc oxide followed with substitution of Zn(II) in ZnS with copper ions (see in more details in [23]).

Table S1. Influence of parameters of photocatalytic deposition of Cu NPs on SPR band maximum position of Cu NPs λ_{max}, optical density of copper sulfide film D at 1000 nm, and short-circuit photocurrent density J_{SC} observed in solar cells with ZnO/Cu_xS films as cathodes in a tandem with a ZnO/CdS photoanode.

№	ZnO electro-deposition time, min	Cu^0 photo-deposition time, min	$[Cu(OAc)_2]\times10^3$, M	I, %	D	J_{SC}, mA/cm^2
1	2	60	5.0	100	1.04	1.92
2	4				0.83	1.90
3	6				0.84	1.87
4	8				0.56	1.83
1	10	15	2.5	100	0.13	1.77(*)
2		30			0.22	1.82
3		60			0.27	1.91
4		90			0.38	1.93
5		120			0.43	1.95
1	5	60	1.0	100	0.10	1.61(*)
2			2.5		0.20	1.88
3			5.0		0.50	1.88
4			10.0		0.80	1.89
1	5	60	5.0	100	0.55	1.87
2				50	0.71	1.93
3				20	0.66	1.94

Notes: I − relative intensity of UV light used to photodeposit Cu NPs, 100% corresponds to 20 mW/cm^2; (*) photocurrent is not stable in time. Accuracy of E_g and J_{SC} determination is 0.01 eV and 0.005 mA/cm^2, respectively.

Comments to Table S1.

Earlier, in a study of ZnO/ZnSe heterostructures the present authors showed that an increase in the thickness of ZnO film results in a corresponding increment in the ZnSe concentration in the final films [A. Kozytskiy, O. Stroyuk and S. Kuchmiy, *Catal. Today*,

2013, **230**, 227.]. An opposite trend was observed in the present work for ZnO/Cu_xS heterostructures. As underlined in the Materials and Methods, the zinc oxide films were illuminated from the FTP side to deposit Cu nanoparticles. Figure S9 shows the absorption spectra of ZnO films electrodeposited for 2, 4, 6, and 8 min. As can be seen, even the ZnO film with a minimal ZnO thickness (2-min eloectrodeposition) absorbs almost completely the light with λ = 320−370 nm. So, further increment in the film thickness (longer electrolysis times) does not increase a portion of absorbed light but at the same time creates a growing barrier between the light-absorbing ZnO layer near the FTO−ZnO interface and copper acetate and ethanol on the interface ZnO−electrolyte. The barrier slows the photocatalytic deposition of Cu nanoparticles, decreases the amount of photodeposited copper and, as a result, decreases the amount of copper sulfide in the final ZnO/Cu_xS heterostructures.

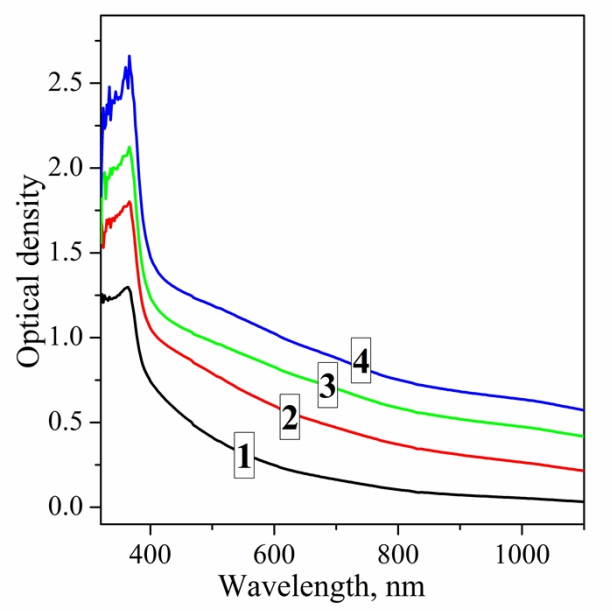


Fig. S10. Absorption spectra of ZnO films obtained at different electrodeposition duration − 2 min (curve 1), 4 min (2), 6 min (3), and 8 min (4). FTO spectrum is subtracted from curves 1−4.

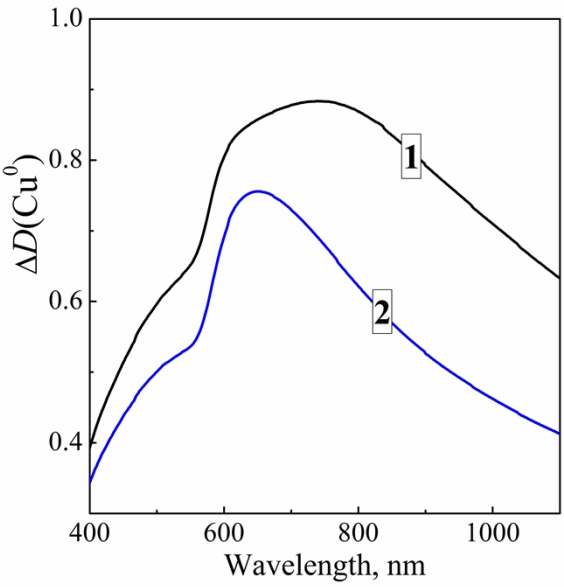


Fig. S11. Differential absorption spectra of Cu in FTO/ZnO/Cu films produced at 20% (curve 1) and 100% (2) UV light intensity. The spectra were obtained by subtracting absorption spectra of starting FTO/ZnO films.