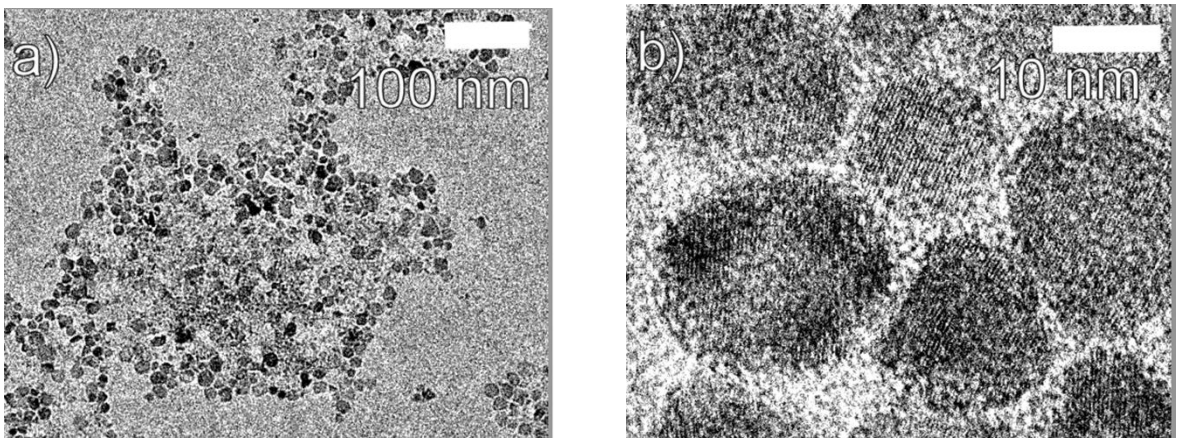
Supplementary Information

Transmission electron microscopy (TEM)

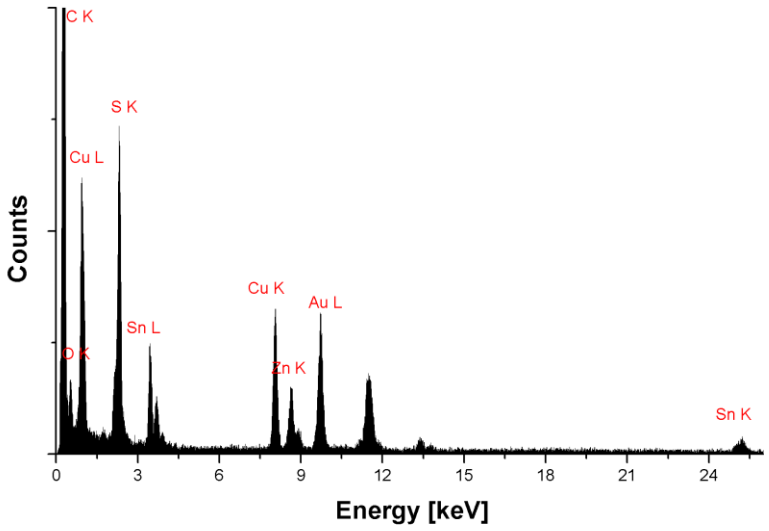
Transmission electron microscopy images of the used CZTS NCs are shown in Fig. Drops of diluted CZTS-dispersion were given onto a gold grid before being analyzed. Residual dispersant was removed by filter paper. A LaB6 cathodes electron source was operated at 120 kV acceleration voltage. The set up was also used to perform a compositional analysis of the particles via energy dispersive x-ray measurements (EDX). The data is shown in Tab. I. The analysis of the particles show a sulfur poor/ copper rich composition. The data was acquired inside the TEM.



[Figure A1]: TEM images of the CZTS NCs used for electrophoretic deposition. NCs show an average size of (18.0 ± 4.0) nm.

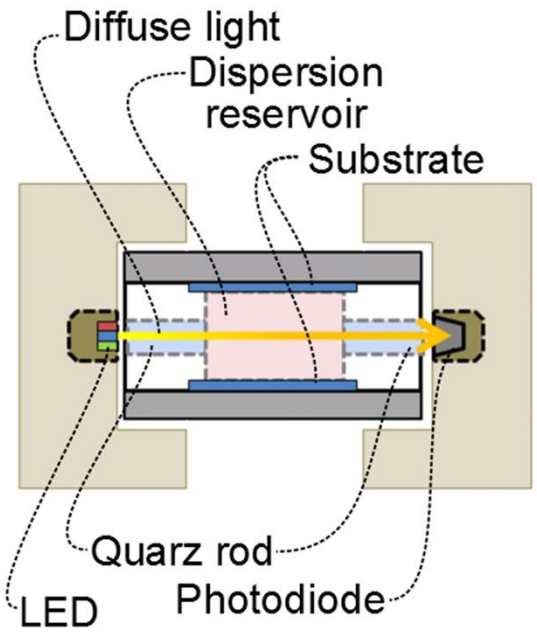
Tab. I Elemental composition of the used nanocrystals determined by EDX measurements

Element (Peak)	Weight %	Atomic %
S (K)	25.7	45.4
Cu (K)	31.7	28.2
Zn (K)	15.4	13.4
Sn (K)	27.2	13.00



[Figure A2] EDX spectra of the CZTS NCs

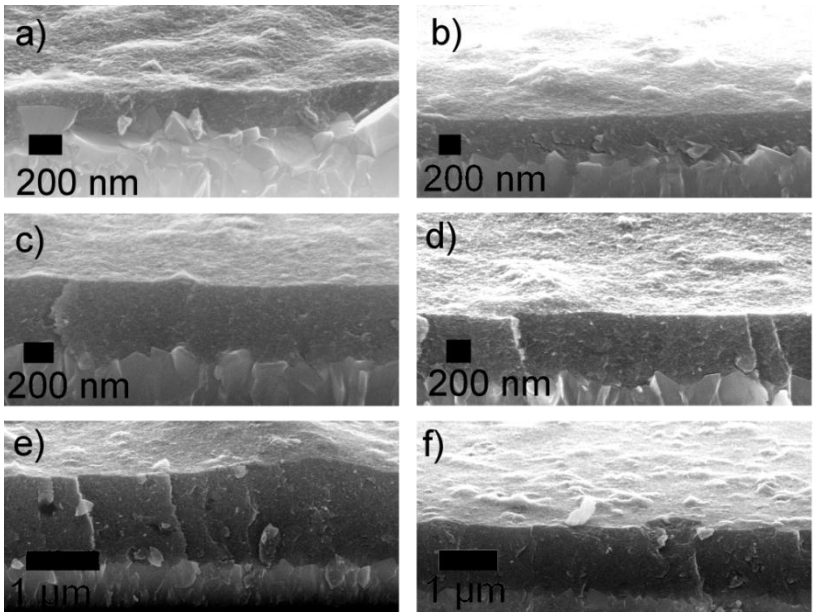
EPD and monitoring set-up



[Figure A3] Top view representation of the Set-up used for the electrophoretic deposition and process monitoring.

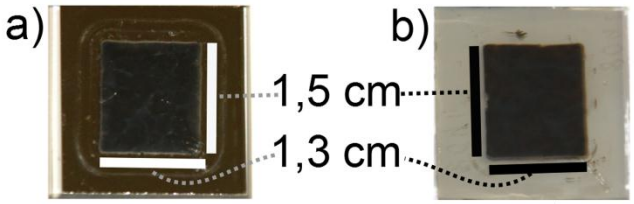
Cu_2ZnSnS_4 layers

The layer thickness was determined by SEM cross section images. Values concerning the thickness were taken at 8 – 12 positions. An average value was calculated and the standard deviation served as an error. The samples were analyzed with a tilt of α = 16 °, considered by multiplying the measured data by $cos\alpha \cong 1.4$ during thickness determination. Cross section SEM images of the layers are shown in Fig. A3.



[Figure A4] Cross section SEM-micrographs of deposited layers for different CZTS concentration: a) 1.5 µl b) 3 µl c) 4 µl d) 6 µl e) 10 µl f) 15 µl of mother dispersion were dissolved in a mixture of acetonitrile and toluene.

Figure A4 shows photographs of Cu_2ZnSnS_4 layers on Mo and FTO Substrates.



[FigureA5] Photographs of Cu_2ZnSnS_4 layers on a) Mo and b) FTO Substrates

Fitting procedure and parameters

The data obtained from the In-situ transmission measurements was fitted by a Formula derived from the combination of two formulas. The first is Lambert-Beers law a

$$I = I_0 \exp(-\alpha c x), \quad (1)$$

where I is the light intensity of a light source with initial intensity I_0 at a distance x after crossing a medium with the absorption coefficient α of concentration c. The second formula describes the time evolution of the NC concentration in dispersion during the EPD as presented in [1]:

$$c(t) = \frac{w_0}{V} \exp(-kt), \quad (2)$$

with the Volume: *V*, the initial weight of NC in dispersion: w_0, the time: *t* and the kinetic parameter: *k* = $S \cdot \mu / V$, where *S* denotes the deposited area and μ the electrophoretic mobility. By combining (1) and (2) we obtain:

$$I = I_0 \exp(-C \cdot exp(-kt)), \quad (3)$$

where the absorption parameter *C* is defined as $C = \frac{\alpha x w_0}{V}$. The values of C depend on the initial conditions $C = -ln\,(I(0))$. In order to imply the possibility of retardation, the variable t_i was introduced resulting in

$$I = I_0 \exp(-C \cdot \exp(-k(t - t_i)). \quad (4)$$

Before fitting the data was normalized by dividing the whole dataset by an average of the stable domain (after depletion), to obtain $I_0 \sim 1$. This follows from the assumption that all the dispersions lead to the same intensity when depleted. The absorption parameter *C* was determined by the initial transmission value: $C = -\ln(I(O))$. The Parameters of the fitted curves are given below in Tab. II and Tab. III together with the respective value of R^2.

Tab. II: Acetonitrile variation

Acetonitrile ratio	I_0	Absorption parameter *C*	Kinetic Parameter *k*	Retardation time t_i	R^2
			[$s^{-1} \times 10^{-2}$]	s	
0	-	-	-	-	-
25	1.02	2.77	1.34 ± 0.01	69.4 ± 0.7	0.993
50	1.03	2.51	1.14 ± 0.01	0.0 ± 0.6	0.994
75	0.99	3.16	2.06 ± 0.02	1.9 ± 0.4	0.994
100	0.99	3.90	3.08 ± 0.03	0.7 ± 0.4	0.990

Tab.III: Voltage variation

Voltage	I_0	Absorption parameter *C*	Kinetic Parameter *k*	Retardation time t_i	R^2
			[$s^{-1} \times 10^{-2}$]	s	
10	-	-	-	-	-
25	1.01	2.05	9.92 ± 0.06	53.8 ± 0.8	0.993
50	1.00	1.92	8.62 ± 0.05	32.4 ± 0.8	0.989
75	1.02	1.79	7.81 ± 0.04	20.8 ± 0.7	0.994
100	1.01	2.02	7.14 ± 0.02	8.8 ± 0.4	0.994
250	1.03	2.60	6.09 ± 0.02	6.5 ± 0.6	0.980