Supporting information

Implementation of 3D model for generation of simulated EQE spectra

The EQE can be simulated from EQE_R taking into account the filtering of photons through ZnSe and the collection losses of charge carriers in the absorber layer underneath ZnSe. To consider the collection losses it is necessary to compute the total volume of absorber layer underneath ZnSe and the fraction of it which is still subject to carrier collection.

Referring to the 3D geometrical model described in section 3.2 of the manuscript it is possible to calculate the volume $V_{collected}$. of absorber layer underneath type B ZnSe contributing to the photogenerated current. The rectangular section of absorber layer CZTSe underneath ZnSe shown in Fig. SI1 is seen in three dimensions as a cylinder which height and radius are known (L_{eff}, r).

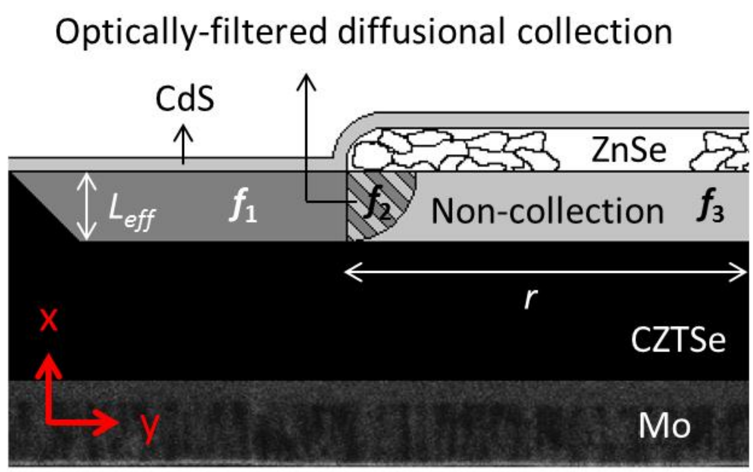

Fig. SI1 Cross section of the Mo/CZTSe/CdS interfaces where the CZTSe absorber layer is covered by a ZnSe island of radius *r*. The dashed area corresponds to the area underneath ZnSe to be calculated, which is subject to optical filtering and where collection of charge carriers still occurs. The charge carriers in the non-dashed light grey area underneath ZnSe are blocked due to ZnSe.

Thus, the total section of potentially active absorber below ZnSe has the volume: $V_Z = \pi \cdot r^2 \cdot L_{eff}$ with r being the radius of the ZnSe island and L_{eff} the estimated collection length of charge carriers, as discussed in section 3.2.

The fraction of V_Z being subject to collection, $V_{collected}$ (dashed area in Fig. SI1), can be calculated as a function of the ratio between r and L_{eff} and two cases (a) and (b) can be identified.

(a) $r \geq L_{eff}$

(b) $r < L_{eff}$

These two cases are shown schematically in Fig. SI2.

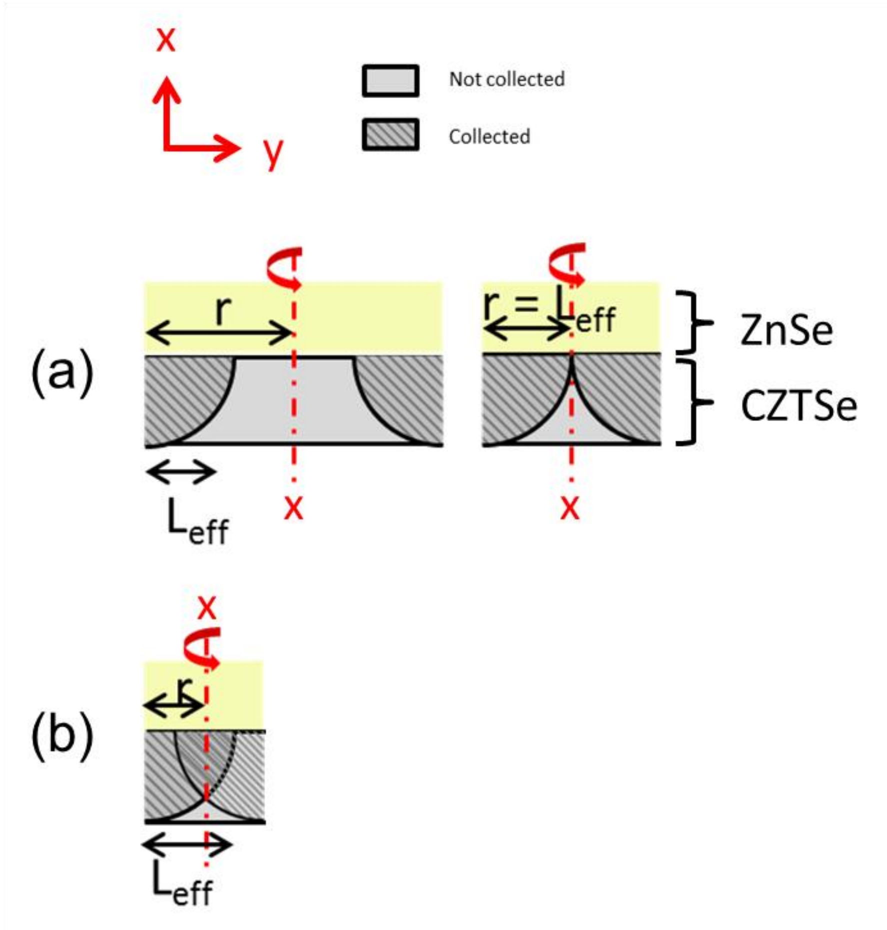

Fig. SI2 Two dimensional sketch of the model - cross section of the CZTSe absorber layer (grey) covered by a ZnSe island of radius *r* (light yellow). The dashed grey area corresponds to the collected area subject to optical filtering, which is to be calculated. The light grey area acts as current blocking area: due to the ZnSe there is no collection of charge carriers. The two cases with different r/L_{eff} ratio are identified as (a) $r \geq L_{eff}$ and (b) $r < L_{eff}$.

As seen in Fig. SI2 the collected volume $V_{collected}$ is created by revolution of a quarter of a circle (dashed area) around the x axis located at a distance r from the center of the circle (red x axis shown in Fig. SI1).

Figs. SI3 and SI4 show the procedures employed to obtain an expression for $V_{collected}$ in terms of r and L_{eff} for cases (a) ($\boldsymbol{r \geq L_{eff}}$) and (b) ($\boldsymbol{r < L_{eff}}$), respectively. As explained below, an intermediate step is needed; this implies using the theorem of revolution of a surface around an axis. If the surface is delimited by an axis, a function $y = f(x)$ and two lines of equations $x = k_1$ and $x = k_2$, the volume generated inside these borders by revolution around the axis can be calculated as: $\pi \int_{k_1}^{k_2} f(x)^2 \, dx$.

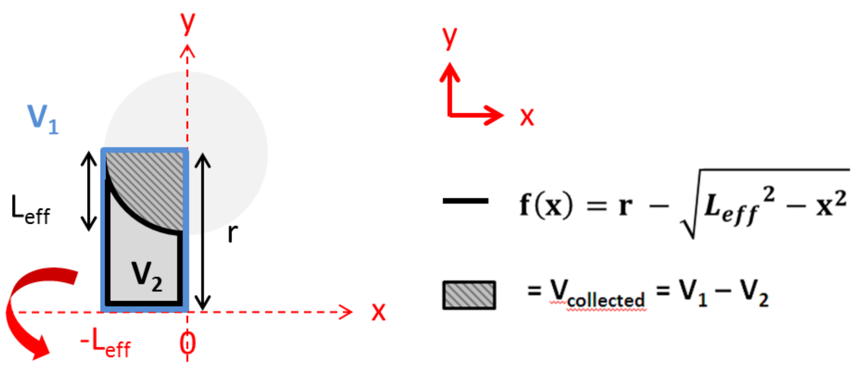

Fig. SI3 Mathematics employed to calculate the collected volume underneath ZnSe for case (a), $\boldsymbol{r \geq L_{eff}}$

The equation *f(x)* for the curve delimiting the quarter of a circle is determined. The first step is made by calculating the volume V_2 generated by the surface lying between that curve and the x-axis (light grey area in Fig. SI3). The rectangular surface of width L_{eff} and length *r* (blue rectangle in Fig. SI3) generates by revolution around the x axis a cylinder with the volume V_1. The volume $V_{collected}$ is then obtained by subtracting V_2 from V_1.

For case (b), where $r < L_{eff}$, the procedure to calculate $V_{collected}$ follows the same principle. The difference is just lying in the fact that the quarter of circle crosses the x axis. The volume generated by revolution of the surface lying between the x axis, the curve of equation *f(x)* and the two lines of equation x = - L_{eff} and x = $\sqrt{L_{eff}^2 - r^2}$ has to be subtracted from the volume of the cylinder V_1 with radius equals to L_{eff} and height equals to r (the radius of the original ZnSe cluster) (see Fig. SI4).

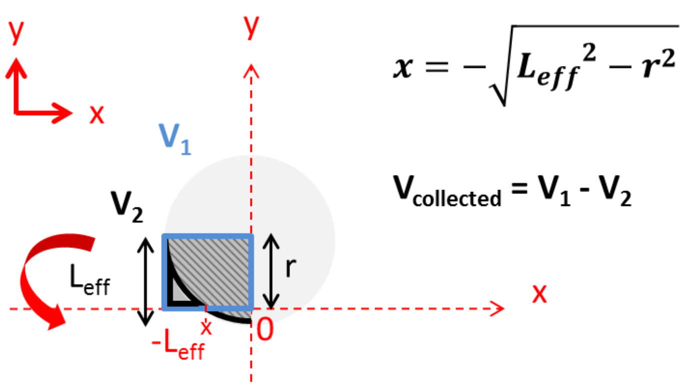

Fig. SI4 Mathematics employed to calculate the collected volume underneath ZnSe for case (b), $\boldsymbol{r < L_{eff}}$

Thus, for the two cases, (a) and (b), Eq (1) and (2) are obtained, respectively ($L = L_{eff}$):

(1) $V_{collected} = -\frac{2\pi L^3}{3} + \frac{r\pi^2 L^2}{2}$

(2) $V_{collected} = -\frac{2\pi L^3}{3} + \pi \cdot \sqrt{L^2 - r^2} \cdot \left(\frac{4r^2+2L^2}{3}\right) + \frac{rL\pi^2}{2} - rL\pi \cdot \arcsin\sqrt{1-\left(\frac{r}{L}\right)^2} - r\pi^2 \cdot \sqrt{1-\left(\frac{r}{L}\right)^2}$

The ratio $\frac{V_{collected}}{V_Z}$ leads in each of the two cases to a percentage of carrier collection underneath ZnSe for a fixed pair of r and L_{eff} values.

The volume of potentially active absorber material can now be divided into three volume fractions: f_1 is the volume fraction of active absorber without ZnSe surface coverage, f_2 is the fraction of active absorber layer underneath ZnSe and f_3 is the remaining volume fraction of potentially active absorber layer where carrier collection is impossible due to the ZnSe surface coverage. The cross section schematic of the absorber layer represented in Fig. SI1 is now shown in Fig. SI5 as top view, together with the three volumes fractions f_1 f_2 and f_3.

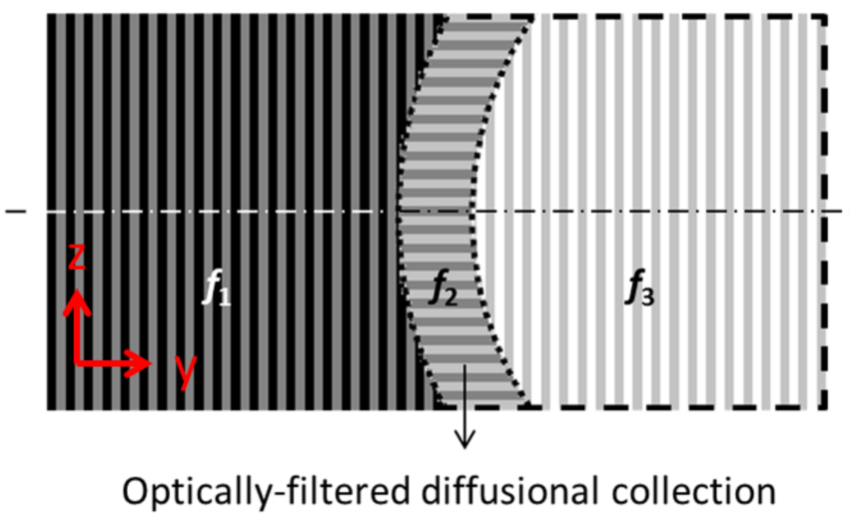

Fig. SI5 Top view of the CZTSe absorber layer, separated into the three volume fractions f_1, f_2 and f_3

The fractions f_1 and f_2 can be defined as a function of the ZnSe surface coverage χ as follows:

(3) $f_2 = \frac{V_{collected}}{V_Z} \cdot \chi$

(4) $f_3 = \frac{V_Z - V_{collected}}{V_Z} \cdot \chi$

(5) $f_1 = 1 - f_2 - f_3$

The linear dependence of f_2 and f_3 on the ZnSe surface coverage χ is shown in Fig. 7a for fixed *r* and L_{eff}. The slope of such lines is apparent from Eqs (3-4).

The fraction f_2 of active absorber layer contributing to the EQE spectrum of the device and lying underneath ZnSe is subject to optical filtering by the ZnSe aggregate. It is possible to estimate the spectrum profile of the photons transmitted by the ZnSe T_{ZnSe} via the *Lambert-Beer* law. For a defined ZnSe thickness *x* and taking into account the absorption coefficient α of ZnSe reported in the literature [23], T_{ZnSe} is calculated as follows:

(6) $$T_{ZnSe} = e^{-\alpha \cdot x}$$

In summary, the EQE of a CZTSe cell with charge carrier collection length L_{eff} with ZnSe clusters of mean radius *r* located between CZTSe and CdS is expressed as follows:

(7) $$EQE = EQE_R \cdot (f_1 + f_2 \cdot T_{ZnSe}) = EQE_R \cdot \left(1 - \frac{V_Z + V_{collected} \cdot T_{ZnSe}}{V_Z} \cdot \chi\right)$$

where EQE_R is a reference ZnSe-free EQE spectrum.

Extraction of f_1, f_2 and f_3 by manipulation of measured EQE spectra

f_2 and f_3 can also be computed from analysis of the EQE, assuming as the only geometrical consideration the thickness of ZnSe (200 nm for the case analyzed in the manuscript).

By analysis of measured EQE spectra it is possible to estimate the volume fraction of absorber layer contributing to the collection of photogenerated carriers underneath ZnSe (f_2) as well as the volume fraction of potentially active absorber layer where carrier collection is impossible due to the ZnSe surface coverage (f_3).

f_3 can be expressed as a function of the difference Δ_1 between the ZnSe-free reference EQE spectrum EQE_R and the measured EQE spectra, computed at the plateau (i.e. $h\upsilon \sim$ 2.25 eV, where $T_{ZnSe} \sim 1$).

(8) $$f_3 = \frac{\Delta_1}{EQE_{R(2.25eV)}}$$

Likewise, f_2 can be expressed as a function of the difference Δ_2 between the ZnSe-free reference EQE spectrum EQE_R and the measured EQE spectra both normalized against their highest photocurrent values (i.e. $h\upsilon \sim$ 2.25 eV, where $T_{ZnSe} \sim 1$), computed at 3.0 eV photon energy (corresponding to the maximum filtering effect).

(9) $$f_2 = \frac{\Delta_2}{EQE_{R(3eV)} \cdot (1 - T_{ZnSe\,(3eV)})}$$

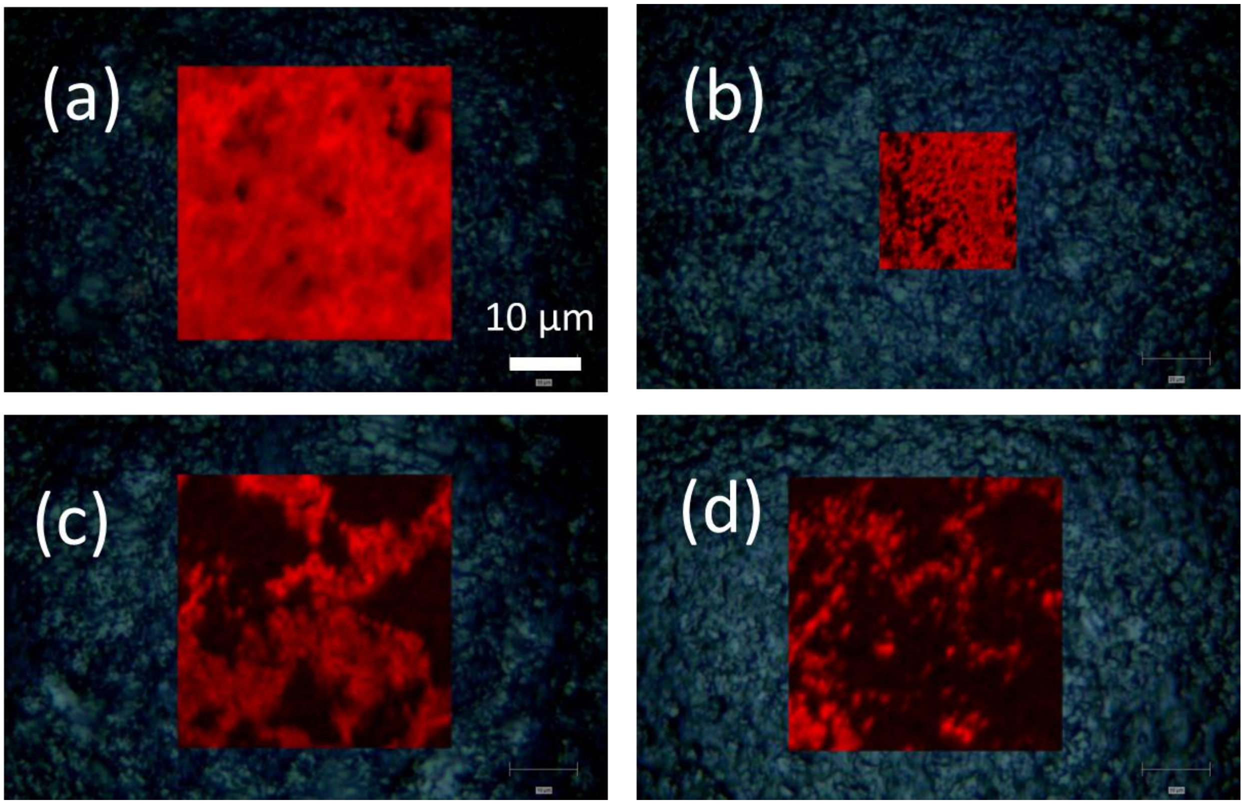

Fig. SI6 Raman maps acquired with an excitation wavelength of 442 nm of absorber films with ZnSe mole fractions of 0.53 (a), 0.43 (b), 0.34 (c) and 0.25 (d). ZnSe is shown as red.