**SUPPORTING INFORMATION**

# Luminescence Enhancement Effects on Nanostructured Perovskite Thin Films for Er/Yb-Doped Solar Cells

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## 1) NANOCRYSTAL SYNTHESIS:

Up-converting nanocrystals made of $KY_3F_{10}$ codoped with $Er^{3+}$ (2 mole %) and $Yb^{3+}$ (8 mole %) have been obtained by hydrothermal method at 180°C (filling rate 60%) for two days. It was started from a mixture of solution of potassium, yttrium, erbium and ytterbium nitrates ($K(NO_3)$, $Y(NO_3)_3,6H_2O$, $Er(NO_3)_3,5H_2O$, $Yb(NO_3)_3,5H_2O$) in stoichiometric amount dissolved in a solvent constituted of excess of 40% hydrofluoric acid % and water. The chemical reaction is:

$$K(NO_3) + (3\text{-}x\text{-}y)Y(NO_3)_3,6H_2O + xEr(NO_3)_3,5H_2O + yYb(NO_3)_3,5H_2O + HF_{excess} + H_2O \rightarrow KY_{3-x-y}Er_xYb_yF_{10} + 10HNO_3 + 16H_2O + HF + H_2O \text{ with } x = 0.06 \text{ and } y = 0.24$$

The nanoparticles were then washed by at least four dispersion/centrifugation cycles in water. Afterwards, they were dried at low temperature (60 – 80°C) in a laboratory oven [S1]. As

seen in the scanning electron microscope image (SEM) shown in Figure S.1, the size of the nanocrystal is in the range 50-150 nm.

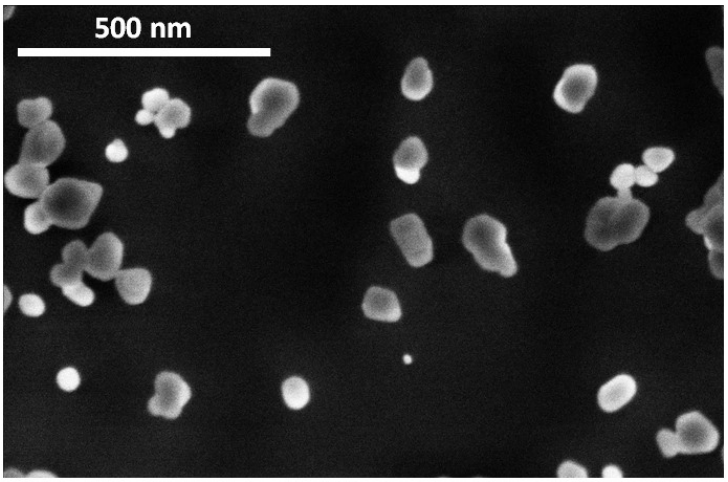


Figure S.1 : SEM picture of the luminescent up-converting nanocrystals. Their diameter is in the [50-150] nm range.

## 2) UP-CONVERTION LUMINESCENCE SPECTRUM OF THE NANOCRYSTALS

$KY_3F_{10}$:Er/Yb nanocrystals were excited in the near-infrared part of the electromagnetic spectrum, at λ = 975 nm [S2]. This excitation scheme is known as up-conversion (see Figure S.2). Two near-infrared photons are absorbed and, after several energy transfers between the ions, fluorescence occurs, in the visible range, at three different wavelengths (λ = 525 nm, λ = 550 nm, and λ = 660 nm).

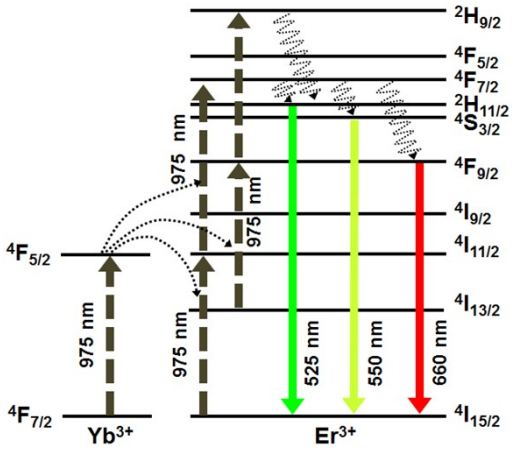


Figure S.2: Energy level diagram of the up-converting nanocrystals, after an excitation at λ = 975 nm.

The luminescence spectrum of the nanocrystals is shown in Figure S.3. In the experiments described in the core of the article, we are detecting the green and yellow fluorescence lines, in the range [525-550] nm that correspond to the two transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$. The luminescence spectrum of the nanocrystals is shown in Figure S.3.

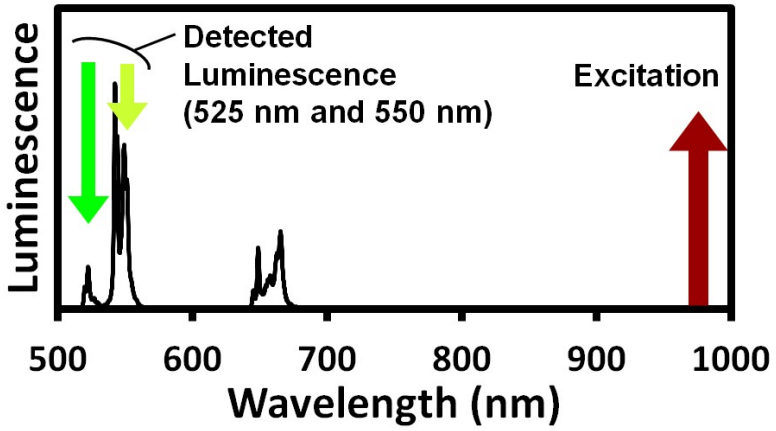


Figure S.3: Luminescence spectrum of the nanocrystals after an excitation at 975 nm.

### 3) TIP FABRICATION PROCEDURE

A single up-converting nanocrystal was glued at the end of a sharp tungsten tip using a homemade nanomanipulation system. The set-up for performing this operation is described in reference S3. An SEM picture of an example of nanocrystal glued at the end of a sharp tip is shown in Figure. S.4.

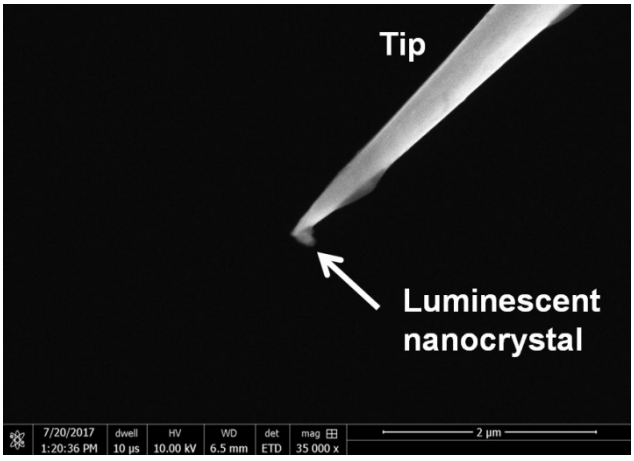


Figure S.4: SEM picture of an example of tip with a nanocrystal attached at its end.

[S1] A. Assy, H.-J. Lin, M. Schoenauer-Sebag, P. Gredin, M. Mortier, L. Billot, Z. Chen, and L. Aigouy, Sens. Actuators A **2016**, 250, 71.

[S2] L. Aigouy, M.-U. González, H.-J. Lin, M. Schoenauer-Sebag, L. Billot, P. Gredin, M. Mortier, Z. Chen, and A. García-Martín, Nanoscale **2019**, 11, 10365.

[S3] L. Aigouy, Y. De Wilde, M. Mortier, J. Giérak, and E. Bourhis, Applied Optics **2004**, 43(19), 3829.