Supporting Information

Efficient photoluminescent thin films consisting of anchored hybrid perovskite nanoparticles

Laura Martínez-Sarti, Teck Ming Koh, Maria-Grazia La-Placa, Pablo P. Boix, Michele Sessolo, Subodh G. Mhaisalkar and Henk J. Bolink

[a] Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Catedrático José Beltrán, 2, 46980 Paterna, Spain.
[b] Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, 637553 Singapore.
[c] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798 Singapore.

Synthesis of the $MAPbBr_3$ NPs and sensitized ZnO films

For the $MAPbBr_3$ NPs fabrication, the 11-aminoundecanoic acid was initially converted into its ammonium salt with an excess of HBr, to enhance its solubility in DMF. $PbBr_2$ (0.04 M) and 474 µL of oleic acid were dissolved in 2.5 mL of DMF (solution A). Subsequently, 596 µL of this solution were added into 0.5 mL of another DMF solution B containing MABr (0.04 M) and varying amounts of $Br^-NH_3^+$-C_{10}-COOH. 0.5 mL of this precursor solution (A+B) was quickly injected into toluene (5 mL) under vigorous stirring at room temperature (RT) or previously heated at 60 ºC. A yellow-green solution was immediately observed, consequence of the formation of the NPs. The solution was centrifuged at 12.5 krpm for 10 minutes to remove larger aggregates, and a bright luminescent supernatant solution was obtained.

For coating the ZnO films, 0.5 mL of a solution of 40 wt% in ethanol from Sigma-Aldrich (average particle size of 35 nm) were diluted in 3 mL of ethanol, and then spin-coated using a GYRSET® (closed cover coating technology). The layers were then annealed at 450 ºC during 30 min.

For the ZnO/$MAPbBr_3$ NPs films preparation, the ZnO coated substrates were immersed into the NPs suspension for 12 hours and subsequently rinsed with toluene.

Characterization

The photoluminescence (PL) characteristics were studied using a Xe lamp coupled to a monochromator as the excitation source and an integrated sphere coupled to a spectrometer (Hamamatsu C9920-02 with a Hamamatsu PMA-11 optical detector) in order to quantitatively determine the PLQY. UV-visible absorption spectra of the films were collected using a fiber-optics based Avantes Avaspec2048 spectrophotometer. UV-visible spectra of the dispersions were recorded using a quartz cuvettes spectrometer in a UV-visible spectrophotometer Agilent 8453E. TEM and high resolution TEM (HR-TEM) were performed with a Field Emission Gun (FEG) TECNAI G2 F20 microscope operated at 200 kV. LEDs were characterized under inert conditions inside a glovebox. The current density and luminance versus voltage characteristics were measured using a Keithley 2400 Source-Meter and a photodiode coupled to a Keithley 6485 pico-ammeter, using a Minolta LS100 camera to calibrate the photocurrent. The AFM images were collected with a Digital Instrument Veeco Nanoscope IVa AFM microscope in tapping mode, using silicon tips with natural resonance frequency of 320 kHz and with an equivalent constant force of 42 N m^{-1}.

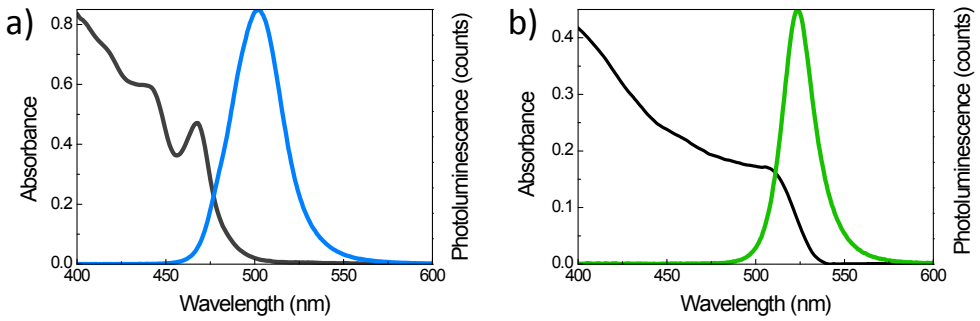

Fig. S1 Absorption (gray) and PL spectra (blue and green) of $MAPbBr_3$ NPs colloidal solutions in toluene at 60 ºC for $Br^-NH_3^+$-C_{10}-COOH/MA molar ratio of (a) 2 and (b) 0.5.

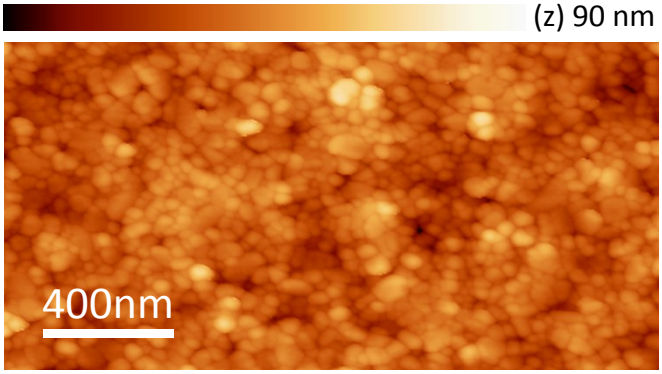

Fig. S2 AFM topography of a solution-processed ZnO film.

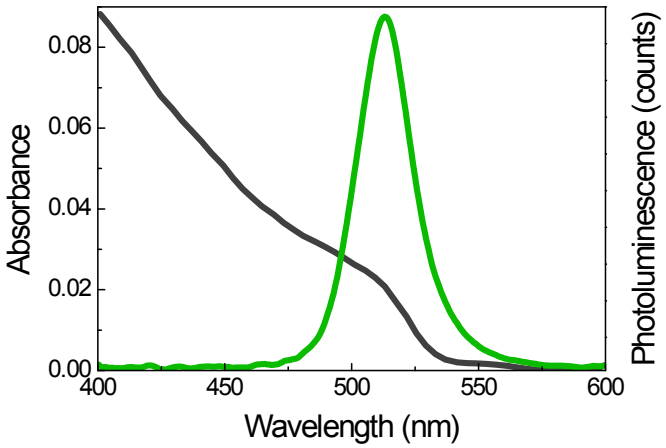

Fig. S3 Absorbance (gray) and photoluminescence (green) spectra of the $MAPbBr_3$ NPs anchored to a PEDOT:PSS substrate.

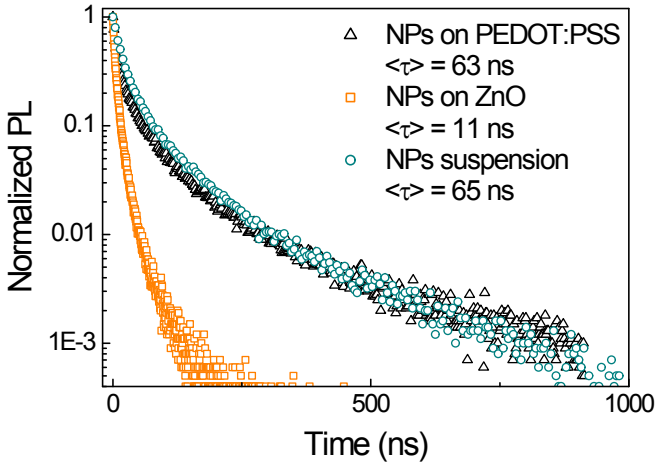

Fig. S4 Time-resolved PL measurements taken at the peak emission wavelength (521 nm) of the $MAPbBr_3$ NPs colloidal solution and the NPs anchored on ZnO and PEDOT:PSS thin films, with a pump wavelength of 405 nm.

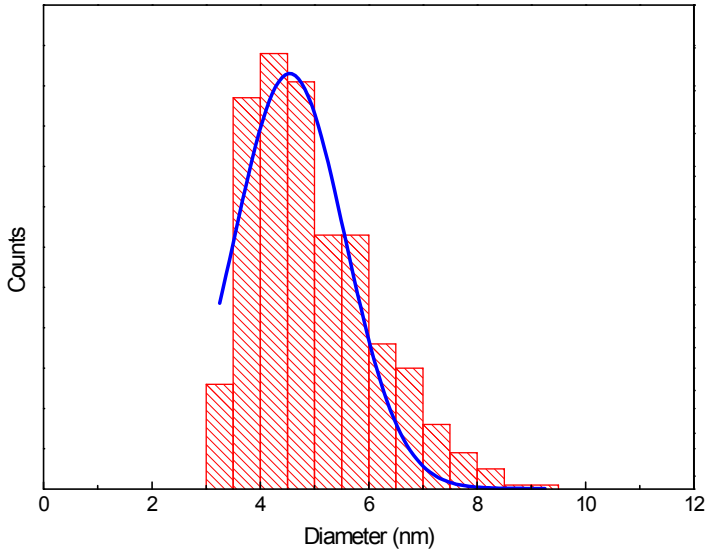

Fig. S5 Particle size histograms calculated from the TEM image in Fig. 2a, plotted from analysis of >500 particles. Mean and standard deviation for the distribution are 4.6 and 2.4 nm, respectively.