Metamaterial enhancement of metal-halide perovskite luminescence

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Supporting Information

Device Fabrication.

The nanoslits metamaterials were fabricated by depositing a 30 nm thin film of gold, via thermal evaporation, over a glass coverslip substrate, followed by focused ion beam (FIB) milling, with a FEI Helios 650 dual FIB/SEM system, of the metamaterial arrays of nanoslits of increasing length and the constant width (nominally ~30 nm), and a second round of thermal evaporation of ~5 nm silica. The substrates were then exposed under UV ozone cleaning for 20 minutes before perovskite deposition. $MAPbI_3$ perovskite film was deposited by spin coating from 0.33M solutions. In a typical example, PbI_2 (89.12 mg, TCI, 99.99%), methylammonium iodide MAI (30.73 mg, Dyesol) and 13.7 µl of dimethyl sulfoxide DMSO (anhydrous, Sigma Aldrich) were dissolved in 580 µl of dimethyl formamide DMF (anhydrous, Sigma Aldrich). The solution was heated at 100 °C for 1h, and then spin-coated on the substrate at 4000 rpm, 15 s. Solvent quenching with 300 µl of toluene (anhydrous, Sigma Aldrich) was performed after 6s of rotation. The films were then annealed for 15 min at 100 °C on a hotplate. All the perovskite deposition procedure was performed in a glove-box under Ar inert atmosphere.

Optical Measurements.

The normal-incidence absorption spectra of the metamaterials were measured, for incident polarizations perpendicular and parallel to the main axis of the nanoslits (TM and TE orientations, respectively), using a microspectrophotometer (Jasco MV2000), through a 36× objective with a circular sampling aperture size of 25 µm × 25 µm.

Steady-state photoluminescence.

Steady-state photoluminescence spectra were measured under a microscope set-up and flow of nitrogen to avoid degradation of the MAPbI film due to moisture absorption. The samples were pumped using a PicoHarp 405 nm diode ps laser, with repetition rate of 40 MHz, focused down to a spot of ~20 µm diameter. The photoluminescence emission was polarized and detected by an ACTON spectrometer with an integration time of 100 ms per wavelength.

Time resolved photoluminescence.

Time resolved PL measurements were done by exciting samples with 405nm wavelength, 100 fs pulse duration and 1000 Hz repetition rate femtosecond laser pulses. Femtosecond laser pulses were generated by Spectra Physics amplified laser system (MaiTai, Spitfire Ace). SHG crystal was used to generate 405nm wavelength. PL signals from perovskite film on metamaterial samples were collected and collimated before focusing in to the Optronics streak camera (SC 10). Temporal resolution of this streak camera is ~50 ps.

Simulations.

Optical spectra and field maps were generated by full-wave electromagnetic simulations using COMSOL Multiphysics. Literature data were used to describe both the silica substrate, the gold film and the 5 nm silica overcoating, while experimental ellipsometric values were used for the perovskite film1. The samples were described as infinitely extended by using periodic boundary conditions and illuminated at normal incidence. The emission spectra were simulated by placing an array of infinitesimally small dipoles within the perovskite film, with spectral distribution mimicking the steady-state photoluminescence spectrum of the flat perovskite film. The total emission power was determined by averaging individual dipole contributions at each wavelength, weighted by the simulated field intensity generated at the dipole position by the pump beam (λ = 405 nm) to account for the absorption[2,3].

$MAPbI_3$ perovskite on nanoslit metamaterials

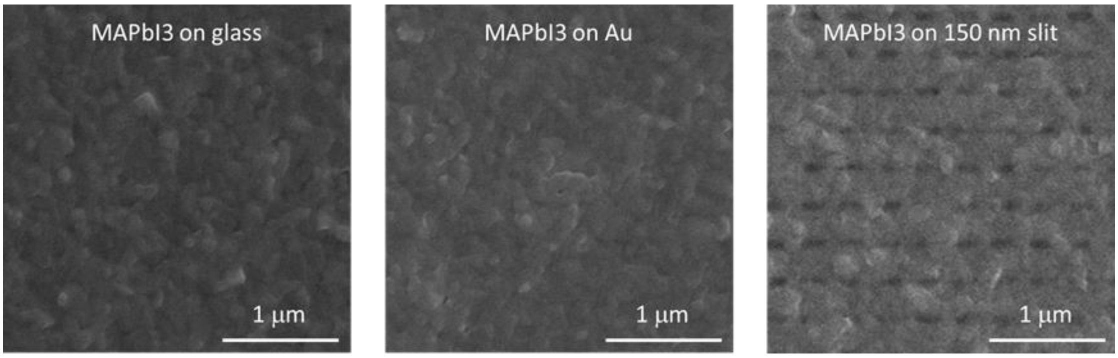

Figure S1: Secondary electron images showing uniform coating conditions of perovskite film on gold, glass and metamaterial arrays

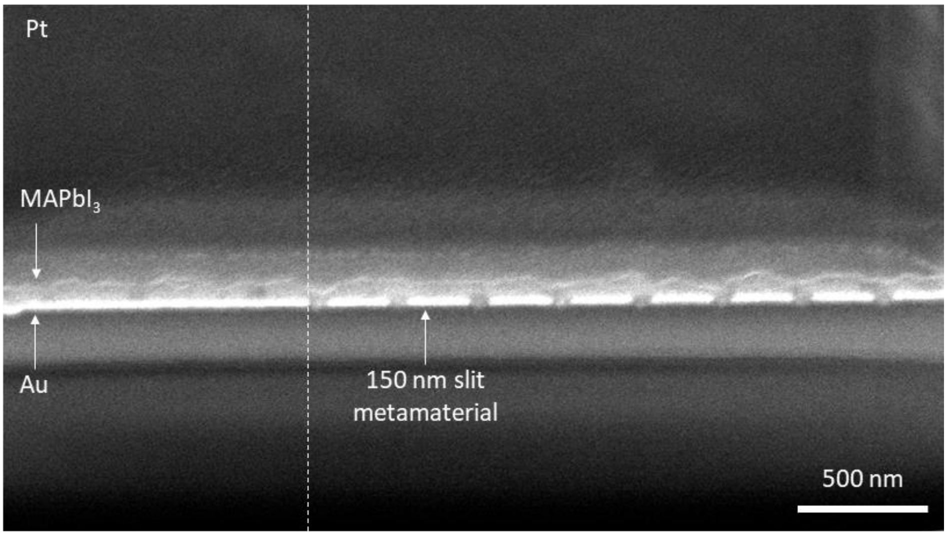

Figure S2: Secondary electron cross-sectional image of a representative sample, showing the hybrid perovskite/metamaterial structure. The dashed line marks the boundary between the unpatterned gold film (on the left) and the 150 nm nanoslit metamaterial array (on the right).

Non-conformal coverage of the nanoslit by the perovskite films.

The perovskite films do not fully penetrate the slits, as shown in the SEM image of Figure S1. This may be the reason in all Full wave COMSOL simulations of photoluminescence enhancement[1] for the perovskite film IN and ON the metamaterial slit, for both TM and TE polarizations. TM polarized emission is much further enhanced when the perovskite film sits inside the slits.

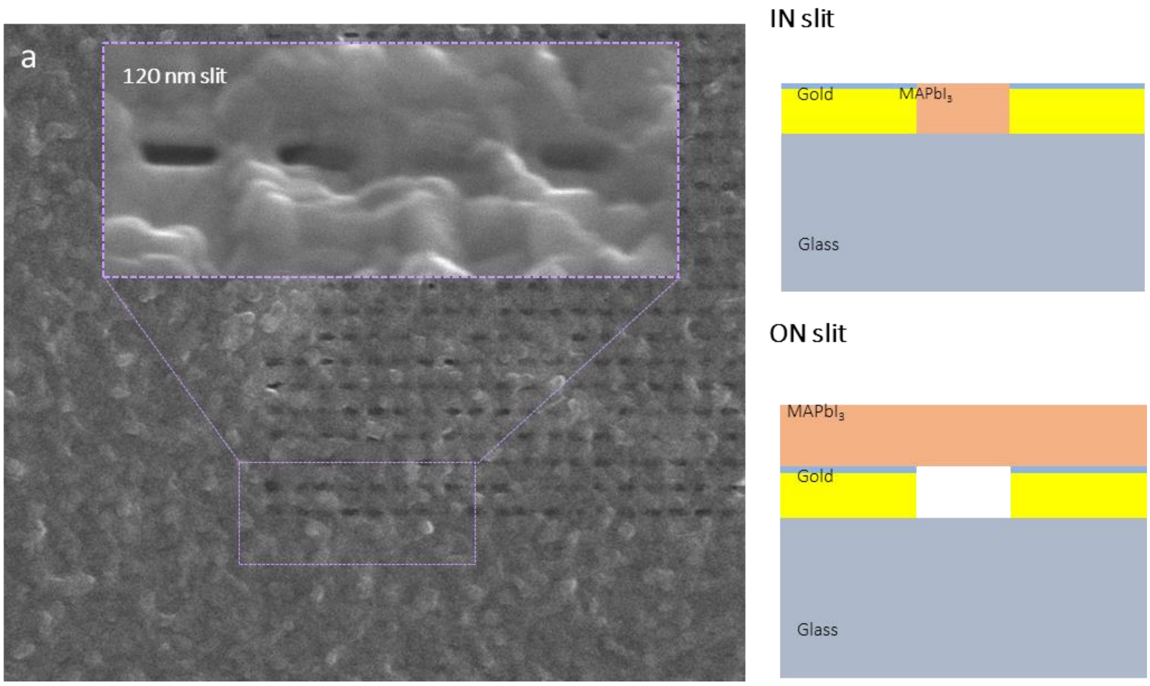

Figure S3: Secondary electrons image (a) of 120nm slit metamaterials carved by FIB milling on a 30nm Au + 5nm SiO_2 film, on glass substrate, and coated with 65nm thick $MAPbI_3$ perovskite film: the perovskite film appears to be partially IN the slit and partially ON the slit, as exemplified by the schematics.

References

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