Supporting Information

Purcell enhancement and wavelength shift emitted light by CsPbI₃ perovskite nanocrystals coupled to hyperbolic metamaterials

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1. HMM structure with 50 % filling factor of metal

**Figure S1:** (a) Angular reflectance measured at $\lambda = 785$ nm (blue diamonds and red circles refer to s and p polarizations, respectively) in a HMM structure with 8 periods 40+40 nm thickness (as measured by HAADF-STEM, see inset) of LiF+Ag multilayer and fitted with $\epsilon_1 = -8.75 + 0.72i$, $\epsilon_2 = +2.86 + 0.01i$ (solid lines). (b) Local Density Of States (LDOS) computed in the near field for this HMM structure terminated with a LiF layer 10 nm thick.

**Figure S2:** Angular reflectance spectra of the HMM structure fabricated with Ag+LiF layers of 40+40 nm thicknesses measured at $\lambda = 632.8$, 785 and 980 nm. The angular dependences for these wavelengths are fitted with (a) $\epsilon_1 = -3.10 + 0.47i$, $\epsilon_2 = +1.54 + 0.03i$ (b) $\epsilon_1 = -8.75 + 0.72i$, $\epsilon_2 = +2.86 + 0.01i$ (c) $\epsilon_1 = -12.81 + 0.99i$, $\epsilon_2 = +3.51 + 0.01i$. Blue diamonds and red circles individually refer to the s and p-polarization in each wavelength and solid lines correspond to simulation.
2. The delayed luminescence in perovskite nanocrystals and its influence on the Purcell Factor

![Figure S3](image)

**Figure S3:** (Color online) PL decay kinetics of CsPbI$_3$ PNCs deposited on top of a reference (purple symbols) and HMM (black symbols) surfaces at room temperature (a) and at $T = 15$ K (b). The reference surface is a 100 nm thick LiF film covering a thick Ag film (100 nm) deposited by thermal evaporation on a Si substrate. For PNCs deposited on top of the HMM surface (8 periods of 40+40 nm LiF+Ag multilayer) the spacer thickness was around 20 nm.

As seen in Fig. S3 in SI (and is also known from the literature [1-5]), the PL decay kinetics of the Perovskite Nanocrystals (PNCs) strongly depends on temperature: as the temperature decreases from 300 to 15 K, the average PL decay time (this is because the PL transient is not monoexponential) of a PNC layer deposited on a dielectric substrate decreases from about 20 to 1.5 ns, respectively. This behavior suggests that, as the temperature rises, the PL decay kinetics becomes a complex process, including the capture of an exciton by shallow traps, which we will further consider as a long-lived non-luminescent (dark) state T (see Fig. S4a in SI), followed by a temperature-dependent process of exciton release from a lower-lying dark traps to a radiative (bright) state. This type of luminescence, which by analogy with Thermally Induced
Delayed Fluorescence (TADF) in molecular spectroscopy [6], can be called “delayed luminescence” and it was considered earlier in application to PNCs [5, 7, 8]. At a sufficiently low temperature, the exciton cannot be released out of the trap into a bright state, so due to absorption of light at cryogenic temperatures all shallow traps become filled by excitons (and therefore de-activated) and no longer take part in formation of the PL decay kinetics. As a result, exciton recombination occurs without delay in shallow traps, with a lifetime $\tau_{PL} = (k_r + k_{nr})^{-1}$. As a rule, at cryogenic temperatures, the rate constant of nonradiative recombination $k_{nr}$ is much lower than the rate constant of radiative recombination $k_r$; therefore, in this case the PL lifetime can be expressed as $\tau_{PL} = (k_r)^{-1}$. Since the Purcell effect affects only the radiative constant $k_r$, it is obvious that the Purcell effect well manifests itself at low temperatures, when the PL decay kinetics is determined only by the radiative constant $k_r$, but not at room temperature, when $k_r$ is comparable in magnitude with $k_{nr}$ (see below, where we consider in more detail the delayed PL model and carry out numerical calculations that confirm the above conclusions).

The phenomenological model illustrated in Figures S4(a) considers two distinct photoexcited states, the “bright” (emitting) excitonic state 1 and the trap state T, which is long-lived non-emitting (“dark”) and non-quenching state (non-radiative recombination is considered for the exciton population, but eventually through different quencher states). The main feature of the model is the presence of the processes of exciton trapping and detrapping (getting back to the emitting excitonic state) occurring with the rate constants $k_{1T}$ and $k_{T1}$, respectively. Here also, $k_r$ and $k_{nr}$ are the rates of the spontaneous radiative and nonradiative recombination of excitons, respectively. When the rate of trapping is much higher than the rates of other photophysical processes (i.e. the condition $k_r, k_{nr} << k_{1T}, k_{T1}$ is fulfilled), the experimentally observed PL decay
kinetics can be much longer than the radiative lifetime $\tau_r = (k_r)^{-1}$ due to the coupling between the two excited states 1 and T by means of the rate constants $k_{IT}$ and $k_{TI}$ [1-3].

Assuming that the electron detrapping to the excitonic state is phonon-assisted and therefore the population distribution between the trap state T and the excitonic state 1 obeys the Maxwell–Boltzmann distribution, the relation between the rate constants $k_{TI}$ and $k_{IT}$ is described by the expression

$$k_{T1} = k_{1T} \exp(-\Delta E / k_B T)$$

(1)

From this equation, it appears that thermal detrapping can be important at room temperature (Figure S4(a)), but practically negligible at 15 K, as depicted in Figure S4(b). The excitonic and trap state populations, $N_1(t)$ and $N_T(t)$, satisfy the following rate equations:

$$\frac{dN_1}{dt} = -k_r N_1 - k_{nr} N_1 - k_{1T} N_1 + k_{T1} N_T$$

(2)

$$\frac{dN_T}{dt} = +k_{1T} N_1 - k_{r1} N_T$$

(3)

The system of the differential equations (1)-(2) was solved numerically for the initial conditions $N_1(t = 0) = 1$ and $N_T(t = 0) = 0$, which means that at $t = 0$ only the excitonic state 1 is populated after absorption of an excitation photon. We suggest that at room temperature the condition $k_r, k_{nr} \ll k_{IT}, k_{TI}$ is fulfilled so that the delayed PL kinetics is observed with a PL lifetime $\tau_{pl} >> \tau_r = (k_r)^{-1}$. With the use of calculated PL decay kinetics in Figure S4(c,d) we explain why the effect of the HMM surface (which influences only the radiative rate constant $k_r$) on the measured PL decay kinetics is quite low at room temperature, whereas it is maximum at cryogenic temperatures where radiative recombination of excitons dominates. First of all, on the basis of numerical solution of the rate equations 2 and 3 with parameters similar to those used in ref. [1] ($k_r = 10^9$ s$^{-1}$, $\Delta E = 100$ meV, $T = 300$ K) we calculated a delayed PL decay kinetics of the PNCs
at 300 K. We have also used $k_{nr} = 4.10^9$ s$^{-1}$ to take into account the measured PL Quantum Yield (PLQY) = 0.20 in our PNCs. The model of delayed PL kinetics yields $\tau_{PL} = 10$ ns (blue solid line in Figure S4(c)). When at these conditions we model the influence of the HMM surface by a two-fold increase of $k_r$, this results in only a minor decrease of $\tau_{PL}$ from 10 to 8.3 ns (black dotted line in Figure S4(c)).

Figure S4: (Color online) (a, b) Energy diagrams describing the delayed luminescence at room temperature, when thermally activated detrapping is possible (a) and at low temperature, when detrapping is blocked (b). The state 1 is the excitonic state, and T is the shallow trap state. The rate constant $k_e$ corresponds to the spontaneous radiative recombination of the excitons and $k_{1T}$ and $k_{T1}$ describe the trapping and detrapping rates. The nonradiative channel is described by its rate constant $k_{nr}$. The circle symbolizes the cyclic process of the population exchange between the bright excitonic and the dark trap states. (c),(d) present the sensitivity of the calculated PL decay kinetics to 2-fold increase of the radiative emission rate in case of 300 and 15 K, respectively (see the main text for details). (e) Experimental PL kinetics of CsPbI$_3$ PNCs deposited on top of HMMs structures (40+40 nm of Ag + LiF layers and spacer d = 20 nm) measured at different temperatures between 15 and 250 K. (f) Evaluation of the $\tau_x$(ref)/$\tau_x$(d) ratio as a function of temperature for PNCs on top of HMM structure consisting of alternating layers of Ag (40 nm) and LiF (40 nm) with a spacer thickness d = 20 nm.

Contrarily, at 15 K, the following modifications occur in the mechanism of the PL kinetics formation: (i) since $k_{nr}$ is strongly thermally activated, it diminishes drastically and becomes negligible as compared to $k_e$; as a result, PLQY = 1.0; (ii) $k_{T1}$ dramatically decreases in the case
of \( \Delta E = 100 \) meV, so that trapped excitons stay in the traps very long time at the timescale of the experiment. This implies that traps become filled and cannot longer participate in the exciton recombination (no more delayed PL decay). In absence of detrapping process, equation 2 reduces to:

\[
\frac{dN_1}{dt} = -k_i N_i
\]  

which results in a PL decay kinetics \( N_1(t) = A_0 \exp(-t/\tau_r) \), (see Figure S4(d)). In this case modeling the influence of HMM surface by doubling the radiative decay rate will result in two-fold shortening of the observed PL lifetime, from 1 to 0.5 ns (solid and dotted lines, respectively).

3. Additional experimental results in the HMM structure with 42% filling factor of metal

![Figure S5: PL spectra of CsPbI₃ PNCs deposited on top of HMM substrates as a function of the thickness of spacer.](image)

Figure S5: PL spectra of CsPbI₃ PNCs deposited on top of HMM substrates as a function of the thickness of spacer.
Figure S6: (Color online) PL decay kinetics of CsPbI$_3$ PNCs at 15K deposited on top of the HMM structure Ag+LiF of thickness 25+35 nm with (a) d=10 nm (b) d=20 nm (c) d = 50 nm (d) d = 250 nm spacer. In each frame several kinetics are measured in different points throughout the sample surface.

4. Purcell factor of the HMM structures as a function of wavelength and spacer thickness
**Figure S7**: Dependence of the Purcell factor calculated as a function of wavelength with dipole at position C for a spacer thickness $d = 10$ nm (a) and calculated as function of the spacer thickness at the experimental PL peak wavelength ($\approx 700$ nm) with dipole at different positions (b), for the HMM structure fabricated with Ag+LiF layers of 40+40 nm.

![Graph](image)

**Figure S8**: Dependence of the Purcell factor calculated as a function of wavelength with dipole at position C for a spacer thickness $d=20$ nm (a) and calculated as function of the spacer thickness at the experimental PL peak wavelength ($\approx 700$ nm) with dipole at different positions (b), for the HMM structure fabricated with Ag+LiF layers of 25+35 nm.

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