Planar Double-Epsilon-Near-Zero Cavities for Spontaneous Emission and Purcell Effect Enhancement

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ABSTRACT: The enhancement of the photophysical response of fluorophores is a crucial factor for photonic and optoelectronic technologies that involve fluorophores as gain media. Recent advances in the development of an extreme light propagation regime, called epsilon-near-zero (ENZ), provide a promising approach in this respect. In this work, we design metal/dielectric nanocavities to be resonant with the absorption and emission bands of the employed fluorophores. Using CsPbBr₃ perovskite nanocrystal films as light emitters, we study the spontaneous emission and decay rate enhancement induced by a specifically tailored double-epsilon-near-zero (double ENZ) structure. We experimentally demonstrate the existence of two ENZ wavelengths, by directly measuring their dielectric permittivity via ellipsometric analysis. The double ENZ nature of this plasmonic nanocavity has been exploited to achieve both surface plasmon enhanced absorption (SPEA) and surface plasmon coupled emission (SPCE), inducing a significant enhancement of both the spontaneous emission and the decay rate of the perovskite nanocrystal film that is placed on top of the nanocavity. Finally, we discuss the possibility of tailoring the two ENZ wavelengths of this structure within the visible spectrum simply by finely designing the thickness of the two dielectric layers, which enables resonance matching with a broad variety of dyes. Our device design is appealing for many practical applications, ranging from sensing to low threshold amplified spontaneous emission, since we achieve a strong PL enhancement with structures that allow for straightforward fluorophore deposition on a planar surface that keeps the fluorophores exposed and accessible.

KEYWORDS: Epsilon near zero, spontaneous emission, hyperbolic metamaterials, surface plasmon coupled emission, surface plasmon enhanced absorption, CsPbBr₃, perovskite

Enhancing the spontaneous emission of a fluorophore is of great interest for a plethora of new emerging technologies, such as optical biosensing, low-threshold lasers, and single photon sources. In order to achieve such an enhancement, many approaches have been proposed, most of which utilize an optical cavity to enhance the spontaneous emission rate of a fluorophore, which is positioned either inside or in proximity of it. Such an effect is known as the Purcell effect. One of the most interesting ways to enhance the Purcell effect is to exploit a special propagation regime involving nanometrically confined evanescent waves rising from the plasmonic properties of very thin metallic films. Generally, there are two mechanisms that govern such a phenomenon: surface plasmon enhanced absorption (SPEA) and surface plasmon coupled emission (SPCE). The former is inherent to the enhancement of the absorbance of the fluorophore by means of a plasmonic absorber, while the latter refers to the possibility of improving its emission by exploiting the resonant properties of a plasmonic structure that acts as a cavity. Enhancement of the emission rate and photoluminescence (PL) by several orders of magnitude has been achieved by using specifically designed nanoresonators that embed the fluorophore inside the plasmonic cavity. However, these approaches typically have two drawbacks: (i) the fabrication of such structures is very demanding and (ii) to obtain such record values, the fluorophore has to be inserted at the position of the highest field enhancement, which extends only along a few nanometers. This spatial extent might not be compatible with the size of target biomolecules, and the target molecule might not be exposed to the surface. In this respect, planar plasmonic multilayers could be a very interesting alternative. It has been demonstrated that a planar structure of metallic and dielectric multilayers can behave as an absorber (and as a resonant cavity) if its dielectric permittivity vanishes at a precise wavelength, manifesting a condition known as epsilon-near-zero (ENZ). In this paper, we show how to take advantage of both the SPEA and SPCE effects utilizing a plasmonic system, whose dielectric permittivity has been specifically designed to manifest a double-
**Epsilon-near-zero (double ENZ) behavior.** The first ENZ condition, which occurs at shorter wavelengths, is tuned to match the absorbance band of the fluorophore positioned at the top, thus inducing the enhanced absorption properties. The second ENZ wavelength is tuned on the emission peak of the fluorophore, acting as a resonator to reach the plasmon coupled enhancement of the emission. As a fluorophore, we chose cesium lead halide perovskite (CsPbBr3) nanocrystals that emit in the green spectral region.29 These nanocrystals are a particularly appealing material system to use as emitters for our approach, since their emission and absorption properties can be tuned across the entire visible spectrum both by chemical composition (through anion exchange) and by quantum confinement.29 Furthermore, perovskite emitters manifest excellent optical properties such as high quantum yields that almost reach unity, narrow emission line widths, and negligible influence of self-absorption and Förster resonance energy transfer.55

We demonstrate that, by exploiting the SPEA and SPCE effects, the spontaneous emission of the perovskite nanocrystal layer is enhanced by a factor of 4 with respect to the emission from a layer on the bare dielectric substrate. In order to highlight the contribution of both ENZ conditions, we present a comparison with a plasmonic structure that manifests only one ENZ regime in the absorption band of the fluorophore. For such a system, only the SPEA effect is present, which enables us to clearly separate the SPEA and SPCE contributions from the fluorophore emission. In the case of the single ENZ, we observe a small increase in the emission (by about a factor of 1.5) and only a slightly reduced decay time, while a 4-fold enhancement of the emission, accompanied by a significantly shortened decay time is observed for the double ENZ one. We demonstrate experimentally and theoretically that tuning the thickness of the dielectric spacer layer to some tens of nanometers maximizes the PL enhancement and quantum yield. Finally, we show how, by simply acting on the thickness of each single dielectric layer, the two ENZ wavelengths can be tuned within the whole visible range, which makes the proposed structure a widely versatile planar plasmonic platform for the enhancement of the spontaneous emission and decay rate of a broad variety of fluorophores.

Recently, ENZ behavior has been demonstrated in metal/dielectric multilayers known as hyperbolic metamaterials, which consist of a large number of periodically stacked subwavelength metal (M)/insulator (I) pairs.36−50 Usually, the design of the ENZ wavelength in these systems is carried out in the framework of the effective medium theory (EMT). Although the EMT is found to be useful for a high number of layers, it fails to predict the salient features that occur in plasmonic systems made of a low number (1, 2, 3, etc.) of metal/insulator cavities (see Supporting Information), as is the case for the MIM and MIMIM structures discussed here and illustrated in Figure 1a,b.

Figure 1b shows the double ENZ system, which consists of a double metal/insulator (MIMIM) plasmonic cavity, in comparison with a single ENZ (MIM) one (Figure 1a). Ag has been chosen as the metal due to its excellent plasmonic properties and low losses in the band of interest (with a wavelength of about 500 nm), while Al2O3 has been used as a dielectric due to both its suitable refractive index and high transparency in the visible range. Scattering matrix method calculations allowed the thickness of the layers that were optimized to 20 nm for Ag and 80 nm for Al2O3 to be precisely designed. An exhaustive description of the propagation of the light inside MIM and MIMIM structures has been given by Meier and by Avrutsky et al.52 The MIM double cavity system supports four modes, where only two with symmetrical field distribution persist.52 These modes are denominated gap plasmon polaritons (GPP) and are extremely confined inside the structure. When the number of adjacent nanocavities (intended as the number of dielectric layers sandwiched between two silver ones) increases, a mutual repulsion of these modal indices occurs. This interaction between these cavity plasmon modes induces their hybridization,53−55 giving rise to strongly confined bulk modes called bulk plasmon polaritons (BPPs).52

Figure 2a,b shows the p-polarized reflectance (R) and transmittance (T), which are measured with an ellipsometer at a grazing angle of 40° for the MIM and MIMIM nanocavities. The absorbance (A) was then calculated by A = 1 − (T + R). As expected, a maximum in absorbance is detected very close to
the dip in reflection for the MIM structure (see Figure 2a), which corresponds to the BPP mode at 425 nm. For the MIMIM system, as predicted, two BPP modes are observed as maxima in absorbance, the first one at 373 nm and the second one at 510 nm. Both the MIM and MIMIM structures manifest a peak in absorbance at $\lambda = 327$ nm due to the well-known Ferrel–Berreman mode. The Ferrel–Berreman mode represents a particular case of very low-loss BPP resonance, whose ENZ nature has been extensively investigated theoretically.\textsuperscript{56,57} Even though the SPEA process does not take the contribution of the Ferrel–Berreman mode into account, its presence is crucial for validating our experimental investigations. As previously mentioned, the optical constants of metal/dielectric multilayers are usually approximated in the framework of the EMT. For structures with only a small number of layers (like in our case), this method does not yield zero crossings in the effective permittivity dispersions at the frequencies of the BPPs; therefore it completely neglects their occurrence, as we show in detail in Figure S3 and the related discussion in the Supporting Information. Consequently, a direct measurement of the dielectric permittivities of both the MIM and MIMIM system is required. For this purpose, ellipsometry is a powerful tool, and Figure 2c,d shows the ellipsometrically measured real and imaginary dielectric permittivities of the MIM and MIMIM multilayers, respectively. The ellipsometric investigation (see details in Figure S1 and the related discussion in the SI) of the optical response of the MIM and MIMIM structures allows for the homogenization of their dielectric permittivities, that is, the optical properties of the plasmonic multilayer structures can be fully described by a homogenized permittivity function. This approach elucidates the ENZ nature of the BPPs originating from the plasmonic multilayers and is corroborated by accurately reproducing the experimental transmission and reflection spectra (see Figure S2 in the SI). Ellipsometric measurements confirm that the Ferrel–Berreman mode occurs in both the structures at about 327 nm, highlighting its low loss ENZ nature. For the MIM structure, one other low-loss ENZ wavelength is detected at $\lambda = 425$ nm, the BPP$_1$ that corresponds to a maximum in absorbance. For the MIMIM structure, two low-loss ENZ modes are detected, in addition to the Ferrel–Berreman mode, and these BPP$_1$ and BPP$_2$ modes are found at 373 and 510 nm, respectively, which correspond precisely to the two peaks measured in absorbance. In order to confirm the plasmonic nature and the nanometric confinement of the electric field inside the dielectric layers that are sandwiched between the silver ones, finite element method based simulations have been performed by using COMSOL Multiphysics. Figure 3a shows a comparison between the experimentally derived absorbance and the COMSOL simulation (red curve), calculated by integrating the electric field inside the two dielectric layers. The very good agreement in spectral position and amplitude between the experiments and the simulations confirms the ENZ nature of the two absorbance peaks. The difference in the full-widths at half-maximum (fwhm) can be ascribed to spectral broadening in the experimental case caused by nonideal film thickness and morphology. Figure 3b,c shows the electric field inside and around the MIMIM multilayer, which was induced by illumination at an angle of 40° incidence for wavelengths at 384 and 510 nm (the ENZ wavelengths). Clearly, the electric field is strongly enhanced in the dielectric layers of the MIMIM structure at the BPP frequencies, which is due to the ENZ condition. Although the BPPs are excited with impinging light at an oblique angle (40°), the wave vector $\mathbf{k}$ inside the dielectric layers of the cavity is close to zero as expected by the dispersion relation of $k(\varepsilon_{\text{eff}})$. This also affects the wave fronts that are almost parallel to the layers in the plasmonic cavity. To give more insight into this phenomenon, we plot the dependence of the BPP frequencies on the angle of incidence in Figure S4. We note that the simulated absorbance peak is found at 384 nm, slightly red-shifted with respect to the experimental one at 373 nm.

Recently, it has been demonstrated that the weak coupling based interaction between a fluorophore and an adjacent plasmonic absorber induces the SPEA phenomenon.\textsuperscript{17} Moreover, the possibility of reaching an extremely high photonic density of states (PDOS) in the proximity of the ENZ wavelength has been extensively demonstrated.\textsuperscript{26,58,59} The hyperbolic (or indefinite) isofrequency surfaces that appear in the ENZ regimes allow wave vectors up to infinitely high values to propagate inside the metamaterial, which are usually known as "high-k modes".\textsuperscript{37,39,40,44} This effect results in an extremely high PDOS at the ENZ frequency. Due to the high PDOS, a fluorophore in the proximity of an ENZ medium experiences a high Purcell effect, and as a consequence, its decay time is strongly reduced.\textsuperscript{37,39,40,44} Eventually, such a high PDOS can lead to the enhancement of the spontaneous emission of a fluorophore, an effect known as SPCE. The MIMIM plasmonic multilayer allows us to take advantage of both the SPEA and SPCE effects at the same time, thanks to its double ENZ resonating nature. In order to evaluate the SPEA and SPCE contributions to the PL and decay time, we compare the results of the MIMIM and MIM structures. Due to its single ENZ behavior, the MIM system can solely exploit one resonance effect, which in the case of CsPbBr$_3$ nanocubes as a dye is the SPEA. For CsPbBr$_3$ nanocubes, the absorption band falls within the single plasmon band of the MIM system and the first plasmon band of the MIMIM structure, and their emission matches the second ENZ wavelength of the MIMIM system.

Figure 4a shows the absorption and emission of the CsPbBr$_3$ nanocubes together with the absorption bands of the MIM and
MIMIM structures, which confirms the aforementioned overlap. The size and shape of the CsPbBr$_3$ nanocubes are evident in the transmission electron microscopy (TEM) image displayed in Figure 4b, and scanning electron microscopy images of the nanocrystal films are shown in Figure S5.

The position of the fluorophore with respect to the plasmonic cavity is crucial to the emission enhancement. One of the best ways to maximize their interaction is to embed the fluorophore inside the plasmonic cavity. However, this requires technologically challenging processes in order to prevent the fluorophore’s degradation and to simultaneously ensure a suitable spacing from the plasmonic metallic elements. A more facile approach consists of placing the fluorophore outside the cavity. In this case, the distance to the cavity determines the emission properties. In our experiments, we use an alumina layer as a spacer between the MIMIM cavity and the nanocrystal emitter layer, and we investigate the PL enhancement while tuning the spacer’s thickness from 5 to 100 nm. We find a maximum in PL for a layer thickness of 50 nm, as shown in the inset in Figure 4c. Since the dielectric spacer layer is made of the same material as the dielectric layers in the MIMIM structure, which can be attributed to the SPEA effect. For the MIMIM multilayer, the PL experiences a noticeable 4-fold enhancement, indicating that both SPEA and SPCE take place. The time correlated single photon counting (TCSPC) measurements displayed in Figure 4d allow the spontaneous decay rate to be accessed, and the fitting results for the lifetimes with a three-exponential decay are reported in Table 1.

In the proximity of the MIM structure, the lifetimes are shorter than those of the bare Al$_2$O$_3$. It is noteworthy that the MIM structure in this spectral range is extremely reflective, manifesting a strong metallic behavior. This is well-known to occur in MIM structures above the ENZ wavelength since they start approaching the features of a so-called type II anisotropy.

The PL spectra of the CsPbBr$_3$ nanocubes are reported in Figure 4c for the three different cases, with the CsPbBr$_3$ nanocube film being on top of (i) a simple 80 nm Al$_2$O$_3$ layer, (ii) the MIM covered with a 50 nm thick Al$_2$O$_3$ spacer layer, and (iii) the MIMIM structure covered with a 50 nm thick Al$_2$O$_3$ spacer layer (see the SI for data with a 5 nm thick spacer layer). A small increase in the PL is found in the MIM system, which can be attributed to the SPEA effect. For the MIMIM multilayer, the PL experiences a noticeable 4-fold enhancement, indicating that both SPEA and SPCE take place. The time correlated single photon counting (TCSPC) measurements displayed in Figure 4d allow the spontaneous decay rate to be accessed, and the fitting results for the lifetimes with a three-exponential decay are reported in Table 1.

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Table 1. Lifetimes for the Three Systems Consisting of Simple Al$_2$O$_3$ and MIM and MIMIM Structures with a 50 nm thick Al$_2$O$_3$ Layer on the Top Obtained from Fitting the Decay Traces with a Three-Exponential Function

| System     | $\tau_1$ (ns) | $\tau_2$ (ns) | $\tau_3$ (ns) | $\tau_{AVG}$ (ns) | QY (%) | $\Gamma_{rad}$ ($\mu$s$^{-1}$) | $\Gamma_{nonrad}$ ($\mu$s$^{-1}$) |
|------------|---------------|---------------|---------------|-------------------|-------|-----------------|------------------|
| Al$_2$O$_3$| 2.14          | 5.74          | 23.26         | 9.77              | 50    | 51.16           | 51.16            |
| MIM        | 1.27          | 4.23          | 20.5          | 6.32              | 35    | 55.33           | 102.76           |
| MIMIM      | 1.34          | 3.58          | 15.67         | 4.59              | 75    | 163.09          | 54.36            |

*The resulting decay time components $\tau_1$, $\tau_2$, and $\tau_3$ of the average lifetimes, and the measured quantum yields (QYs) are reported, as well as the calculated average radiative and non-radiative decay rates that were obtained using eqs 1 and 2.
which is typical of a hyperbolic metamaterial in the hyperbolic region.\textsuperscript{37,39,40,44} This increases the PDOS, which, in turn, enhances the spontaneous decay rate.\textsuperscript{37—41,44,45,60,61} Comparing the MIM and MIMIM structures, we find that their fastest lifetime components $\tau_1$ are very similar (their difference of 70 ps is below the time resolution of our setup), while we observe significantly reduced lifetime components $\tau_2$ and $\tau_3$ in the MIMIM system. We assign this reduction in lifetime to the increased PDOS, which is provided by the SPCE effect, that is, by the coupling of the spontaneous emission with the ENZ regime of the MIMIM system at a wavelength of 510 nm.

We have measured the quantum yield (QY) obtained from the perovskite film on the Al$_2$O$_3$, MIM, and MIMIM substrates, taking the absorbance of each noncoated substrate into account. We obtained a QY of 50\% from the perovskite film on Al$_2$O$_3$, 35\% QY on the MIM, and a high QY of at least 75\% on the MIMIM, as reported in Table 1. The decrease in QY from the Al$_2$O$_3$ to the MIM confirms the low efficiency of the SPEA effect, which is still able to provide a slight increase in the PL, but at the cost of a much higher absorption. The strong increase to a QY of 75\% or higher for the MIMIM structure can be attributed to the plasmonic enhancement by the SPCE process, highlighting the much better performance of the double ENZ configuration with respect to the single ENZ one.

With the QY and average lifetime values, we can calculate the average radiative and nonradiative decay rates, using the following two equations:\textsuperscript{64,65}

\begin{equation}
QY = \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{rad}} + \Gamma_{\text{nonrad}}} \tag{1}
\end{equation}

\begin{equation}
\tau_{\text{avg}} = \frac{1}{\Gamma_{\text{rad}} + \Gamma_{\text{nonrad}}} \tag{2}
\end{equation}

in which $\tau_{\text{avg}}$ is the average lifetime, and $\Gamma_{\text{rad}}$ and $\Gamma_{\text{nonrad}}$ are the average radiative and nonradiative decay rates, respectively. We obtain a strongly enhanced radiative decay rate for the MIMIM structure and an enhanced nonradiative decay in the MIM system that reflects the losses due to the vicinity of the metallic layers. Since the PL and QY are strongly enhanced in the MIMIM structure, we can conclude that the double ENZ condition leads to an enhanced PDOS that acts on the radiative decay of the nanocrystals, manifesting the Purcell effect.

One interesting aspect of the MIMIM double ENZ system is that the separation between the two absorbance peaks can be tuned by carefully designing the thickness of the two dielectric layers in the cavity. With the aim of demonstrating this concept, we calculated, by means of the scattering matrix method, the absorbance spectra of the MIMIM structure while varying the thickness of the top and bottom dielectric layer separately, while the other one remained fixed at 80 nm. In both the cases, as illustrated in Figure 5a,c, a noticeable red shift in the higher wavelength absorbance peak is found, which can be tuned throughout the visible range (see also Figure 5b,d, which shows the shift of the first and second absorbance peak in the two configurations). The possibility of tailoring the two ENZ wavelengths in the visible range makes the MIMIM system extremely flexible and suitable for coupling with a large range of emitter materials, from organic dyes to inorganic nanocrystals.

In conclusion, we demonstrated the possibility of exploiting the dual resonant nature of a specifically designed double ENZ MIMIM multilayer in order to enhance both the absorbance and the photoluminescence together with the decay rate of a film of CsPbBr$_3$ perovskite nanocrystals deposited on top of the layer structure. Thanks to the special plasmonic features of the MIMIM system, two ENZ wavelengths at 373 and 510 nm, which represent the BPP modes of this structure, could be theoretically designed and experimentally measured by means...
of spectroscopic ellipsometry. In the MIMIM system, the PDOS is greatly enhanced in the absorption and emission bands of the dye, and therefore both SPEA and SPCE phenomena take place. This leads to a noticeable enhancement of the spontaneously emitted photons and of their decay rates from a fluorophore layer at the surface, with respect to the MIM system, in which only the SPEA effect is present. We demonstrate the possibility of enhancing the Purcell effect without metallic grating couplers and sophisticated lithography processes. The double ENZ MIMIM multilayer shows wide design flexibility, since the two ENZ wavelengths can be tuned across the whole visible range, making it compatible with all large variety dyes. The system we propose here represents a versatile platform for engineering the PL and decay rate enhancement of a desired fluorophore and allows for the facile design and fabrication of the plasmonic cavity as well as for the deposition of the fluorophores. Furthermore, the ease of fabrication is suitable for large surfaces and is compatible with requirements for biomedical sensing and low threshold lasers.

### MATERIALS AND METHODS

Ag and Al2O3 multilayers have been fabricated by means of electron-beam evaporation. The thickness and evaporation rates have been checked in situ with a quartz balance. The optical constants and thickness of the Ag and Al2O3 single layers, as well as those of the MIM and MIMIM structures, were obtained by spectroscopic ellipsometry and carried out by a V-VASE ellipsometer (Woollam). Reflectance (R) and transmittance (T) spectra were ellipsometrically measured, while the absorbance (A) of the MIM and MIMIM structures was calculated with the relation $A = 1 - (T + R)$ by using the measured transmittance and reflectance data. Such an approach gives precise results for multilayers of smooth films. PL and TCSPC measures were obtained with an Edinburgh Instruments spectrophotometer. Finite element method based simulations were performed with the commercial software COMSOL Multiphysics. Simulations are full-field, and a monochromatic plane wave impinging at an angle of 40° was used as an excitation source.

CsPbBr3 nanocrystals were synthesized by following the procedure of Protescu et al. with some minor modifications.29 Lead(II) bromide (PbBr2, 99.999% trace metals basis), cesium carbonate (Cs2CO3, regentPlus, 99%), octadecane (ODE, technical grade, 90%), oleylamine (OLAM, 90%), oleic acid (OA, 90%), ethyl acetate (90%), and toluene (TOL, anhydrous, 99.8%) were purchased from Sigma-Aldrich. PbBr2 (0.3 mmol) and 10 mL of octadecane (ODE) were loaded into a 25 mL 3-neck flask and dried under vacuum for 30 min at 120 °C. Degassed OA (oleic acid, 0.8 mL) and OLAM (oleylamine, 0.8 mL) were injected under nitrogen flow. After the complete dissolution of the PbBr2, the temperature was raised to 170 °C, and 0.6 mL of previously synthesized Cs-oleate (0.125 M in ODE) was swiftly injected. Immediately after the injection, the NC solution was quickly cooled down to room temperature with an ice water bath, and the NCs were collected via high-speed centrifugation (at 12000 rpm for 10 min), followed by redispersion in 3 mL of toluene. The purification process was repeated again by adding 1 mL of ethyl acetate, and finally, the NCs were dispersed into 2 mL of toluene. The deposition of CsPbBr3 NCs was carried out by spin-coating at 2000 rpm for 60 s. SEM analysis, which is reported in the Supporting Information (see Figure S3), confirms the good homogeneity of the deposited films.

PL QY measurements were performed on the NC films deposited on the different substrates using a calibrated integrating sphere.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphoto.8b00121.

Details on ellipsometry analysis, a comparison between effective medium theory and experimental effective dielectric permittivity, SEM analysis of NC films, influence of incident angle of impinging light on the BPP frequency, and details on the fitting of PL decay traces (PDF)

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The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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