Active hyperbolic metamaterials: enhanced spontaneous emission and light extraction: supplementary materials

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This document provides supplementary information to “Active hyperbolic metamaterials: enhanced spontaneous emission and light extraction,” <http://dx.doi.org/10.1364/optica.2.000062>. In this document we provide detailed information about the quality of the layers composing the HMM, Effective Medium Theory for the anisotropic permittivity of the structure, calculations for photonic density of states and radiative decay rate enhancement, grating design simulations, fabrication method, imaging setup, lifetime calculations. © 2015 Optical Society of America

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1. Quality of Layers

The optical quality of the layers is highly important in order to obtain bulk plasmon-polariton modes and avoid local scattering. A silver layer with thickness of less than 20nm tends to form percolated films when deposited on dielectric materials. It has been shown that a seed layer of Ge that acts as an efficient wetting layer for Ag and results in an optically smooth surface with very low roughness [1,2]. We used a Ge seed layer (<2nm) which allows fabrication of ultra-smooth thin silver films without significantly altering the overall optical properties of the HMM. Fig. S1a shows an Atomic Force Microscope (AFM) image of the top surface of the unit cell in our structure: 10nm Ag layer deposited on top of the Ge seed layer on 15nm of Al₂O₃ with a glass substrate. The top layer Ag film is found to have surface roughness factor $R_{RMS} = 0.1nm$ with maximum peak to valley roughness of 0.5nm. For a single Al₂O₃ layer of similar thickness a surface roughness factor of $R_{RMS} = 0.3nm$ was measured with maximum peak to valley roughness of <2nm. These values were corroborated by Transmission Electron Microscope (TEM) images. Fig. S1b shows a cross-sectional TEM image of the 7P structure showing an Al₂O₃ layer sandwiched between two metallic layers. The individual layers are well defined with minimal variation over distance scales up to 10μm in the direction parallel to the layers. All layers were deposited by electron-beam evaporation in vacuum pressure < 1 · 10⁻⁵ Torr and at a deposition rate of 0.3Å/sec.

Figure S1. (a) AFM image of the top surface of a unit cell consisting of Ag/Ge/Al₂O₃ (top to bottom) on a glass substrate. (b) TEM image of an Al₂O₃ layer sandwiched between two Ag layers. The Ge wetting layer is indistinguishable in the TEM image.

2. Effective medium theory

A metal-dielectric stack can be validly approximated by a homogenous anisotropic medium when the unit cell thickness is smaller than $\lambda/10$ and if it consists of at least 4 periods [3]. In such case the parallel (||) and perpendicular (⊥) permittivities of the medium with respect to the layers are given by

$$\epsilon_{||} = \rho\epsilon_m + (1 - \rho)\epsilon_d, \quad (S1)$$

$$\epsilon_{\perp} = \frac{\epsilon_m\epsilon_d}{\rho\epsilon_d + (1 - \rho)\epsilon_m}, \quad (S2)$$

Where ϵ_m and ϵ_d are the complex permittivities of the metal and dielectric respectively and ρ is the fill fraction of the metal, $\rho = t_m / (t_m + t_d)$. In our 4P and 7P structures $\rho \approx 0.36$ which places the transition point into the hyperbolic regime at wavelength $\lambda = 420\text{nm}$.

3. Local photonic density of states and radiative enhancement

In an ideal structure approximated by EMT, hyperbolic dispersion corresponds to infinite local photonic density of states (LPDOS). However, in a realistic structure that includes finite layers and losses, the LPDOS and corresponding spontaneous emission rate is finite due to the discrete, finite number of plasmonic modes of the multilayer. We use a dyadic Green's function approach [3–5] to calculate the wavelength resolved LPDOS as a function of the normalized wave-vector parallel to the layers (k_x/k_0) for our four period (4P) and seven period (7P) structures with an emitter positioned on top of the 4P structure and at the center of the fifth dielectric layer of the 7P structure.

In the Green's function approach, the weak coupling of the quantum emitter with the plasmon-polaritonic modes of the multilayer structure allows the emitter to be treated as a radiating point dipole whose radiation rate is enhanced through interaction with the electric field of the plasmonic modes. In our experiment, the CdSe/ZnS quantum dots (QDs) are embedded within an alumina (Al₂O₃) layer. Within the absorption and emission spectral bands of the QDs, Al₂O₃ has very low dielectric loss ($\text{Im}(\epsilon) \ll 1$). Therefore, in our calculations, our radiating point dipoles are embedded in a non-absorbing dielectric layer. This assumption helps circumvent the well-known problem of the divergence of the longitudinal part of Green's tensor for dipoles embedded within lossy, absorbing media [5].

Our experimental system contains randomly oriented dipoles so we must take into account the contributions of dipole orientations parallel ($\parallel$) and perpendicular ($\perp$) to the layers. Following the work of Ford & Weber [5], we can write the LPDOS for both orientations as following:

$$\rho_{\parallel} = \frac{1}{k_z} \frac{k_{\parallel}}{\sqrt{\epsilon_d} k_0} \left[1 + r_s e^{2ik_z d} + (1 - r_p e^{2ik_z d}) \frac{k_z^2}{\epsilon_d k_0^2} \right], \quad (\text{S3})$$

$$\rho_{\perp} = \frac{1}{k_z} \left(\frac{k_{\parallel}}{\sqrt{\epsilon_d} k_0} \right)^3 (1 + r_p e^{2ik_z d}), \quad (\text{S4})$$

Where $k_z = \sqrt{k_{\parallel}^2 - \epsilon_d k_0^2}$, $k_{\parallel} = \sqrt{k_x^2 + k_y^2}$ is the wave-vector parallel to the layers (x-y plane), k_0 is the wave-vector in free-space, ϵ_d is the permittivity of the layer in which the dipoles are embedded, r_s and r_p are the reflection coefficients for TE and TM polarized light calculated by transfer matrix method. In the ensemble approximation we can write the total LPDOS as

$$\rho(\lambda, k_{\parallel}) = \frac{1}{3} \rho_{\perp} + \frac{2}{3} \rho_{\parallel}, \quad (\text{S5})$$

And the decay rate enhancement as

$$\beta = \frac{\Gamma}{\Gamma_0} = (1 - \eta) + \eta \text{Re} \left[\int_0^{\infty} \rho(\lambda, k_{\parallel}) dk_{\parallel} \right], \quad (\text{S6})$$

Where η is the quantum yield of the emitter ($\eta \sim 0.45$), Γ is the radiative decay rate of the QDs in the medium, and Γ_0 is the radiative decay rate of the dipole in vacuum. Fig. S2a and S2b show the calculated LPDOS for the dipoles in the 4P and 7P structures where high- k modes are distinguished bright bands with normalized wave-vectors $k_x/k_0 > 2$. These modes provide a radiative decay channel for the dipoles. Fig. S2c and S2d show the calculated radiative decay rate enhancement for a perpendicular dipole ($\beta_{\perp}$) and parallel dipole ($\beta_{\parallel}$) as a function of wavelength for the two structures.

Figure S2. Top Panel: Local Photonic Density of States as a function of wavelength and wave-vector parallel to the layers. Middle Panel: Radiative decay enhancement as a function of wavelength calculated for vertical (Ver) and horizontal (Hor) dipoles. Bottom Panel: Electric Far-field pattern emitted by a vertical and horizontal dipole (marked by arrows). 4P structure in (a) (c) and (e); 7P structure in (b) (d) and (f).

The total enhancement, β , is composed of the weighted contribution of each dipole orientation in the ensemble approximation and represents the decay rate enhancement for a dipole ensemble in or on top a HMM. However, when it comes to experimentally measuring the decay rate enhancement we must take into account how much light reaches the far field from each dipole orientation since the measured lifetime is a mixture of the lifetimes of the two dipole types [6]. Therefore we define the far-field Purcell factor as

$$F = A \cdot \beta_{\perp} + B \cdot \beta_{\parallel} \quad (\text{S7})$$

$$A = \frac{I_{\perp}}{I_{\perp} + 2I_{\parallel}}, \quad B = \frac{2I_{\parallel}}{I_{\perp} + 2I_{\parallel}} \quad (\text{S8})$$

A and B are the weight functions for the two dipole types. $I_{\parallel}$ and $I_{\perp}$ are the intensities of propagating waves incident on the imaging lens of the horizontal and parallel dipoles respectively. In Fig. S2e and S2f we graph the far field radiation pattern emitted by the two dipole orientations as calculated by FEM simulations and from which we calculate the incident intensity factors $I_{\parallel}$ and $I_{\perp}$.

The angle resolved far-field is truncated at 60° as this is the largest angle that can be resolved by the 0.85NA air objective used in the experiment. By integrating F over the photoluminescence (PL) spectrum of our QDs the total far-field Purcell factor for the 4P structure is calculated to be $F_{4P} = 4.82$ and for the 7P structure $F_{7P} = 9.38$ which corresponds well with the experimentally obtained values of $F_{4P, \text{exp}} = 4.84$ and $F_{7P, \text{exp}} = 9.5$.

4. Grating design

FEM numerical simulations to determine the out-coupling efficiency were performed using COMSOL Multiphysics™ software. In the simulations, a double-parameter sweep of the grating half-period and height are performed to determine the maximum power in the upwards ($\hat{z}$) direction within an emission half-angle of 45° . The grating optimization simulations are done for a dipole located directly under the grating, emitting at the center wavelength of our QDs, $\lambda_{em} = 635\text{nm}$. We take into account the isotropic distribution of dipole moments of the QDs by solving for both perpendicular ($\perp$) and horizontal ($\parallel$) dipole orientations with respect to the layers and averaging the out-coupled power according to the ensemble approximation

$$P_{ens} = (P_{\parallel} + 2P_{\perp}) / 3, \quad (\text{S9})$$

We examined the out-coupling efficiency of several available materials for the grating such as PMMA, Al_2O_3 , Ag, and Ge. Fig. S3 shows a comparison the out-coupling parameter space for an Al_2O_3 grating (Fig. S3a) and a Ge grating (Fig. S3b). The maximum out-coupled power from the Ge grating at height of 60nm and half-period 125nm is more than double the maximum out-coupled power from the Al_2O_3 grating at height of 120nm and half-period 200nm . Due to its large real part of the refraction index (~ 4) Ge acts as a high contrast grating (HCG) assisting in translating the high- k modes into propagating waves in the far-field.

Figure S3. Out-coupled power in the z direction with a 45° half-angle. (a) Al_2O_3 grating. (b) Ge grating. The Ge grating provides more than double of the maximum efficiency of the Al_2O_3 grating.

Fig. S4 plots the full wavelength response for the maximum output parameters of a Ge grating, $\Delta=125\text{nm}$ and 60nm grating height.

The out-coupled power reaching the far-field within half-angle of 45° is normalized by the total power emitted by a dipole in air with a flat frequency spectrum (the same intensity at every wavelength). It is seen that even with the poor output of horizontally oriented dipoles it is possible to achieve directional output that exceeds the total power of an emitter in free space. The output peak has a FWHM of 50nm which is suitable for out-coupling of emitters such as QDs with a similar FWHM spectral width of $\sim 40\text{nm}$. For emitters with a broader spectrum, such as nitrogen vacancy centers in diamond, a chirped grating design can be applied.

Figure S4. Grating wavelength response. Ver, Hor, and Ens denote the response for a vertical dipole, horizontal dipole, and an ensemble.

5. Materials and Methods

Al_2O_3 , Ge, and Ag layers were deposited on pre-cleaned glass cover slips by e-beam evaporation using a Leksar PVD 75 Thin Film System while keeping the pressure $< 1 \cdot 10^{-5}$ Torr. After growing four periods of $\text{Al}_2\text{O}_3/\text{Ge}/\text{Ag}$ terminating with a 6nm thick Al_2O_3 spacer. CdSe/ZnS core/shell quantum dots in Toluene purchased from NN Labs were diluted to a concentration of 25% by volume and spin-coated on top of the structure forming a layer of thickness $\sim 25 \pm 5\text{nm}$ then covered by another 6nm of Al_2O_3 and the remaining three periods, again terminating with a thin ($\sim 3\text{nm}$) Al_2O_3 capping layer. At this point PMMA A2 was spin coated on the top layer at 7000RPM and patterned using JEOL JBX6300-FS e-beam lithography system. The pattern was developed in 3:1 MIBK and Isopropanol for 60 seconds. Ge was deposited on top and the PMMA film was lifted-off in acetone leaving behind the inverse grating in Ge. Although the optimal grating design called for 60nm high grating, our fabrication resulted in a thinner grating of $30 \pm 10\text{nm}$ as determined by DekTak 150 stylus surface profiler. Although non-optimal, this grating height is still within the maximum out-coupling design of the $\Delta=125\text{nm}$ grating (see Fig. S3b) since the amount of out-coupled power is relatively insensitive to the grating height.

Imaging. Fluorescence lifetime imaging microscopy measurements were performed on an inverted confocal microscope (Oxford X71) coupled to a diode pumped solid state laser delivering 440nm , 90psec pulses, at 8MHz repetition rate. The sample's luminescence was spectrally separated from the

laser by a Semrock RazorEdge 532 long pass filter (LPF) and detected by an MPD Picoquant Avalanche Photodiode (APD) coupled to a PicoHarp 300 time analyzer. See Fig. S4 for a schematic of the setup. The laser spot size on the sample is $0.5\mu\text{m} \times 0.5\mu\text{m} \times 2\mu\text{m}$ and the pinhole placed before the APD has a diameter of $75\mu\text{m}$. We used a 60X air objective with NA of 0.85 for all measurements. Piezo-controlled stage (PI) allows for a scan area of up to $80\mu\text{m} \times 80\mu\text{m}$. Integrated SymPhoTime 64 software is used to analyze the images and obtain lifetime distribution curves for the scan area.

Figure S5. Schematic of fluorescence lifetime imaging setup.

6. Beam curving effect in the near field

Figure S6. FEM simulation of dipole emission from a $\Delta=125\text{nm}$ grating. The beam curves above the center of the grating. When light is collected in the far-field the origin of the beam appears to be shifted. The inset shows the confocal image of the emission pattern having a dark center.

A feature of the emission which is observed most clearly in the $\Delta=125\text{nm}$ grating is the dark circle at the center. In order to explain this feature we turn our attention to the simulation of the electric field shown in Fig. S6. In this simulation of a vertical dipole placed below the center of the grating it can be seen that the light emitted follows a cone-like emission pattern (the horizontal dipole exhibits the same emission pattern with lesser out-coupling

efficiency). If a straight line is traced from the final far-field direction it appears as if the beam originated from a spot with a radius of $\sim 1\mu\text{m}$ around the grating center which approximately corresponds to the radius of the dark center in the image (Fig. S6 inset).

7. Lifetime kinetics and Purcell enhancement of vertical and horizontal dipoles in the grating region

Lifetime kinetics of the QDs inside and outside are presented in Fig. S7. The decay curves were fitted with a three exponents decay and the average lifetime was determined by the respective weights of the components.

$$y = y_0 + Ae^{-(x-x_0)/t_1} + Be^{-(x-x_0)/t_2} + Ce^{-(x-x_0)/t_3} \quad (\text{S10})$$

$$t_{\text{avg}} = (A \cdot t_1 + B \cdot t_2 + C \cdot t_3) / (A + B + C) \quad (\text{S11})$$

We find that the measured average lifetime of the quantum dots outside the grating region (Fig. S6b) is $\sim 0.7\text{ns}$ longer than the lifetime of QDs in the patterned region (Fig. S6a). See Table 1 for exact numerical values of the fitting parameters.

	Inside grating		Outside grating	
Parameter	value	Std Error	value	Std Error
y0	25.00	-	71.55	-
x0	10.80	-	10.78	-
A1	6839.60	168.90	4491.33	108.81
t1	0.86	0.01	0.88	0.02
A2	6152.14	118.78	3285.79	107.68
t2	2.57	0.07	3.22	0.08
A3	406.66	83.60	241.64	14.94
t3	8.11	0.70	25.48	1.28
Avg Lifetime	1.86ns		2.58ns	

Table 1. Parameters for calculation of average lifetime inside and outside of the grating area.

The reason for the apparent shortening of the lifetime is due to the grating's preferential out-coupling for vertical dipoles as seen in Fig. S4. The ratio between the weight functions A and B used in eq. S7 is shifted from A:B=1:2 to A:B=2:1.

To calculate the Purcell factor from simulation we measure the total power emitted by a dipole with a given orientation and divide by the total power emitted by a dipole in air (calculated in the same way). The Purcell factors for both dipoles in the presence of a grating are nearly the same as for the 7P structure without the grating ($<3\%$ change).

Figure S7. Lifetime kinetics of QDs (a) within the grating region (b) outside the grating region. Measured data (black curve) and 3 exponents decay (smooth curve).

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