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Control of absorption with hyperbolic metamaterials

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We show that absorption of thin dye-doped polymeric films can be tuned and enhanced (nearly threefold) by metallic and lamellar metal-dielectric hyperbolic metamaterial substrates. The effect can be controlled by a combination of the substrate's geometry and composition. As the enhancement of absorption is sustained over large range of incidence angles, the demonstrated phenomenon can lead to a variety of important applications, including solar cell technology. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4703931]

Metamaterials, engineered artificial media composed of subwavelength inclusions ("meta atoms") with rationally designed shapes, sizes, compositions, and mutual orientations, offer the possibility of unprecedented control over electromagnetic properties of matter, such as negative index of refraction,[1] and lead to unparalleled applications, including subwavelength focusing,[2] cloaking,[3] and sensing.[4] Recently, a class of metamaterials with hyperbolic dispersion[5,6] (also known as indefinite media[7]), in which dielectric permittivities in orthogonal directions have opposite signs, has shown promise in enabling far-field imaging with subwavelength resolution,[6,8,9] table-top modeling of cosmologic phenomena,[10] and achieving unprecedented broadband singularity of the density of photonic states.[11] The latter phenomenon makes possible scores of exciting effects and applications ranging from control of spontaneous emission (single photon gun)[11–15] to suppressed reflectance off corrugated hyperbolic metamaterial surfaces (stealth technology and solar energy harvesting).[16]

In dielectric media, high densities of photonic states and, correspondingly, high rates of spontaneous emission are found in materials with large electric permittivities and indices of refraction.[17] Correspondingly, one can infer that metamaterials and simpler metal/dielectric structures can affect a broad range of physical phenomena, which in regular dielectric media depend on the index of refraction. Such phenomena include but are not limited to absorption and stimulated emission,[17] Förster energy transfer,[18] and donor-acceptor charge transfer.[19] Even a larger number of optical and quantum effects are sensitive to electric permittivities if local correction factors are taken into account. Thus, the local density of photonic states is expected to have a particularly strong effect on nonlinear optical responses, such as harmonic generation and two-photon absorption.[20]

In this work, we have studied the effect of hyperbolic metamaterials and metallic films on absorption in adjacent dielectric media. Experimentally, we have deposited thin dye-doped polymeric films on a variety of substrates, including glass, silver, and gold films; Ag/MgF_2 lamellar multilayered hyperbolic metamaterials; and one pair of Ag and MgF_2 layers. Alternating Ag and MgF_2 layers of hyperbolic metamaterials were deposited on glass substrate using thermal evaporation, see inset of Fig. 1(a). The thicknesses of the layers, measured using a DekTak-6 profilometer, were equal to ∼25 nm for Ag and ∼35 nm for MgF_2. One of the metamaterial samples consisted of seven pairs of Ag/MgF_2 (MgF_2 on top), while the other sample had one more layer of silver (Ag on top). The fabricated multilayered metal-dielectric structures were predicted to have hyperbolic dispersion at $\lambda > 360$ nm.[15]

Thin films (∼80 nm) of 3,3′-diethyloxatricarbocyanine iodide (DOTC) dye-doped polymethyl methacrylate (PMMA) were spun onto all samples. The concentration of DOTC dye in a dried polymeric film was equal to 40 g/l (78 mM). At the wavelength corresponding to the maximum of the dye absorption ($\lambda \sim 700$ nm), the calculated values of metamaterials' dielectric permittivities in the directions parallel and perpendicular to the layers were equal to $\varepsilon_{||} = -8.33 + i0.16$ and $\varepsilon_{\perp} = 3.49 + i0.004$, respectively.

The reflectance spectra of all samples studied were recorded at 8° incidence angle in the PerkinElmer Lambda 900 spectrophotometer equipped with an integrating sphere. (In the experiment, a silver mirror was placed on the back of the sample deposited onto a glass substrate.) After proper normalization, these measurements were equivalent to transmission measurements in films of twice the thickness. The obtained experimental absorption spectra are shown in Fig. 1(a). One can see that the absorption is smallest in the dye-doped film deposited onto a glass substrate (we use it as the reference) and is ∼2.8 times larger in the same film deposited onto a hyperbolic metamaterial with MgF_2 layer on the top, Figs. 1(a) and 1(b). The second largest enhancement of absorption (∼1.7-fold) has been observed on the top of one pair of Ag and MgF_2 layers. At the same time, the absorption in dye-doped films deposited on the top of silver and hyperbolic metamaterial with Ag on the top was almost the same as that in the reference glass-based sample. A slightly better result (1.4-fold enhancement of absorption) was observed on the top of a gold film.

The reflectance experiments above were modeled using 2D finite element analysis (COMSOL MULTIPHYSICS). The thicknesses of Ag and MgF_2 layers were kept to be the same as in the experiments; however, the numbers of layers were slightly larger (20 with MgF_2 on the top and 21 with Ag on the top). Dye absorption was modeled as a Lorentzian band

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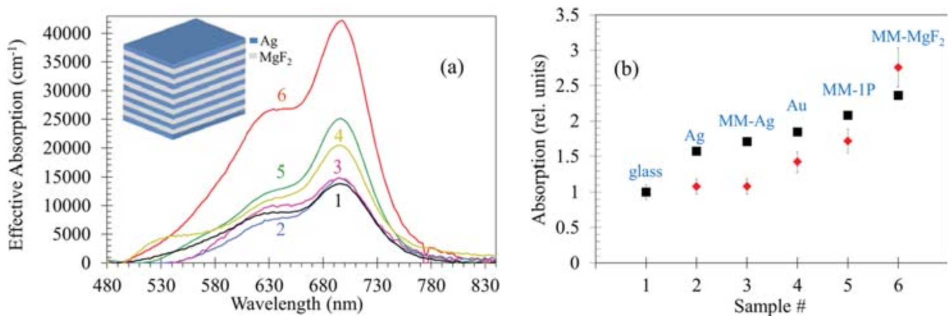

FIG. 1. (a) Spectra of measured absorption coefficients of DOTC-doped polymeric films deposited on glass (1, glass), silver film (2, Ag), Ag/MgF_2 metamaterial with Ag as the top layer (3, MM-Ag), gold film (4, Au), one pair of Ag and MgF_2 layers (5, MM-1P), and Ag/MgF_2 metamaterial with MgF_2 as the top layer (6, MM-MgF_2). Inset: schematic of a lamellar Ag/MgF_2 metamaterial. (b) Maximal absorption coefficients in samples 1-6 of (a) normalized to that in sample 1 (dye-doped film on glass); diamonds—experiment and squares—COMSOL simulation.

with the maximal absorption coefficient (in bulk material) equal to that in the experiment.

The calculated electric field distributions in the samples based on a hyperbolic metamaterial (MgF_2 on top) and 50 nm silver film are shown in Fig. 2(a) and the corresponding electric energy distributions in Fig. 2(b). In order to retrieve effective absorption spectra, we computed reflectance spectra of the samples coated with dye-doped polymeric films and similar samples coated with undoped polymeric films, and used the latter as "100% base lines." The resultant absorption spectra in the two samples depicted in Figs. 2(a) and 2(b) are plotted in Fig. 2(c). The intensities of calculated absorption bands were nearly proportional to electric energy densities integrated over the thickness of corresponding dye-doped films (inset of Fig. 2(c)). (Note that in both experiments and calculations, the "dips" in the reflectance spectra were due to absorption at light propagation through the double thickness of dye-doped polymeric films, and the spectral variations of the reflection coefficients at air-polymer and polymer-substrate interfaces were negligibly small.)

One can see that electric energy density above substrates changes periodically from high to low, determined by constructive and destructive interference of incident and reflected waves, Fig. 2(a). Correspondingly, the absorption strength of a dye-doped film depends on whether the film is placed in bright or dark interference fringe. (Note that the polymeric film influences the fringe positions.) This conclusion is in line with that of Ref. 21, claiming that the performance of a gain medium in a metamaterial critically depends on its location.

The calculated absorption strengths in samples, which have MgF_2 as the top layer, are in reasonably good agreement with the experimental results (Fig. 1(b)). At the same time, the correlation between the experiments and the calculations is worse in samples with silver on top. Silver is a highly reactive material. Therefore, in accordance with Ref. 22, we suspected that the disagreement between the modeling and the experiment could be due to oxidation/etching of silver or reduction of adjacent dye molecules. To exclude the possibility of chemical reaction between the dye-doped film and the metallic substrate, we deposited DOTC:PMMA film onto a much more stable gold substrate. In this case, the discrepancy between the calculation and the experiment was smaller than in the case of silver. However, the agreement was still not perfect (same as in the samples with MgF_2 on the top). This leads to the question whether semi-classical

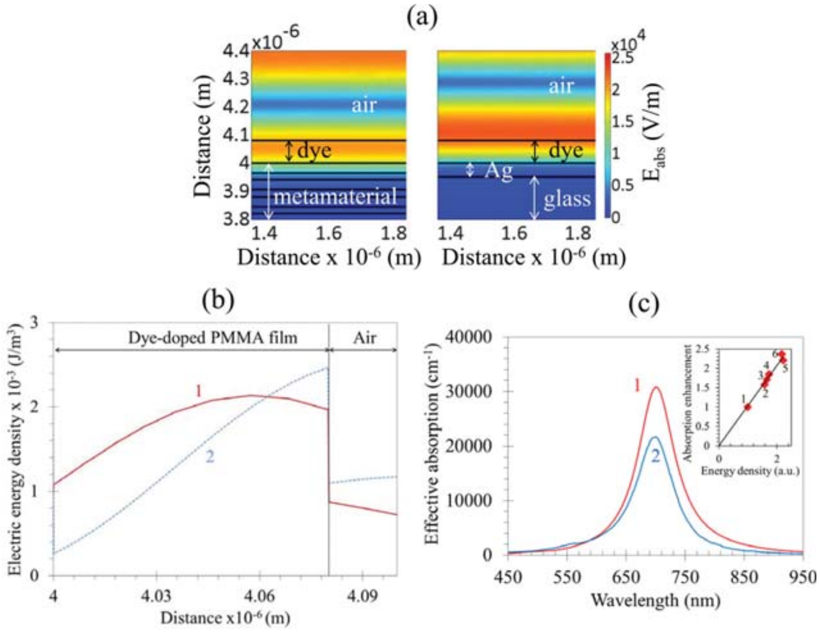

FIG. 2. (a) Calculated values of electric field (defined as $E_{abs} = \sqrt{|E_x|^2 + |E_y|^2}$) in the dye-doped polymeric film deposited on the top of a lamellar Ag/MgF_2 metamaterial with MgF_2 on the top (left) and 50 nm silver film on glass (right). (b) Electric energy density profiles in samples of (a); 1—dye on the top of hyprepolic metamaterial and 2—on the top of Ag film; (c) corresponding effective absoption bands (retrieved from the calculated reflectance spectra); 1—on the top of hyperbolic metamaterial (with MgF_2 as the top layer), 2—on the top of Ag film. Inset: electric energy density integrated over the thickness of the 80 nm dye-doped film in samples 1-6 of Fig. 1(a) plotted vs. corresponding enhancements of effective absorption coefficients.

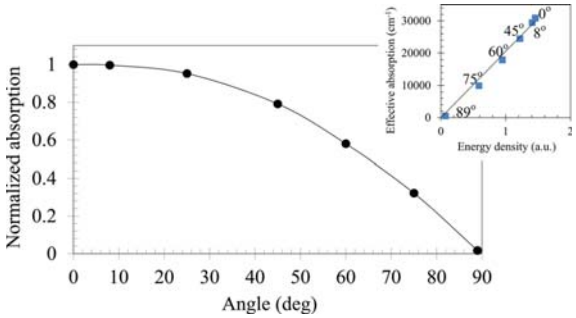

FIG. 3. Angular-dependent absorption (normalized to unity at normal incidence) in the 80 nm dye-doped film deposited onto a hyperbolic metamaterial with MgF_2 on top. Inset: dependence of absorption on electric energy density integrated over the film thickness.

electro-dynamics analysis[23] can adequately describe the phenomenon of light absorption in its entirety or, as claimed in Ref. 24, a quantum mechanical treatment of absorbing centers is required. This is a subject of further studies, to be published elsewhere.

Practical applications of thin absorbing films, e.g., in solar cell technology, may require enhanced absorption to sustain in a broad range of incidence angles. Correspondingly, we have calculated the angular dependence of absorption in a dye-doped PMMA film deposited onto a Ag/MgF_2 metamaterial (MgF_2 on top) and found that although the absorption efficiency decreases with an increase of the incidence angle θ, it remains reasonably high over broad range of angles, dropping to 50% of its maximal value at $\theta = 65°$, Fig. 3. (Note that in the case of inclined illumination, good correlation still exists between the calculated effective absorption coefficient and the electric energy density integrated over the thickness of the dye-doped dielectric film, inset of Fig. 3).

To summarize, we have shown that the absorption of a thin dye-doped polymeric film can be enhanced nearly threefold in the presence of optimized metamaterial substrate. The value of effective absorption can be controlled by a combination of the substrate's geometry and composition. This demonstration paves the way for a variety of important applications, including solar cell technology. Similar control should be possible for a stimulated emission, which will be the subject of further studies.

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