Strong coupling in the novel dye / alumina membrane metamaterial

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Abstract: We present the novel metamaterial based on a nanoporous alumina membrane impregnated with R6G dye molecules. The splitting of the reflectance and emission bands at large dye concentration is discussed in terms of strong coupling.
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Strong coupling of plasmonic resonances in metallic nanoparticles or the strong coupling of excitons (in *e.g.* organic dyes or semiconductors) with surface plasmons and resonant cavities has attracted, in recent years, the interest of many research groups working in the areas of photonics, (meta) materials and nanotechnology. The intriguing underlying physics and unparalleled applications of the strongly coupled systems span from quantum communication [1] and Fano resonances [2] to control of the energy transfer [3] and chemical reactions [4, 5]. On the other hand, formation of molecular aggregates and their spectroscopic properties have been extensively studied at the quantum chemistry level [6, 7]. In this work, we apply the strong coupling approach to interaction of excitons in a novel composite (meta)material based on R6G dye infiltrated into nano-pores of the anodic alumina membrane.

The metamaterial samples in our studies were self-standing nanoporous anodic aluminum oxide membranes impregnated with rhodamine 6G (R6G) laser dye *via* electroplating. The ~100 nm diameter pores (voids) were oriented perpendicular to the membrane's surfaces and penetrated through the ~ 100 μm thick samples wall-to-wall. The center-to-center distance between the voids was ~ 110 nm. In different ethanol-based electroplating solutions used in our experiments, the concentration of R6G varied from 0.01 g/L to 9 g/L, resulting in strongly different concentrations of the dye molecules in the membranes' pores. The x-ray diffraction spectra of the dye-impregnated membranes (at high concentration of R6G) suggested crystalline ordering of the tightly packed dye molecules.
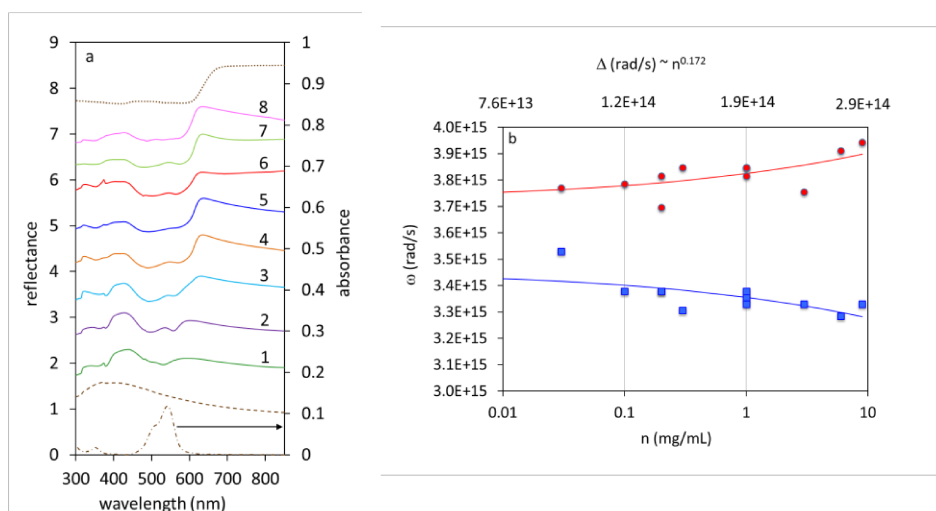

Fig. 1. (a) Reflectance spectra of the alumina membranes filled with R6G at different dye concentrations in the ethanol electroplating solution. (1) 0.03 mg/mL, (2) 0.1 mg/mL, (3) 0.2 mg/mL, (4) 0.3 mg/mL), (5) 1 mg/mL, (6) 3 mg/mL, (7) 6 mg/mL and (8) 9 mg/mL. Dotted line: Reflectance spectrum of polycrystalline R6G powder. Dashed line: Reflectance spectrum of the undoped membrane. Dashed-dotted line: Absorption spectrum of R6G in the PMMA polymer (in concentration 425 g/L). (b) The dispersion curves obtained from plotting the positions of the dips in Fig. 1a as the function of concentration *n* (low axis). Solid lines: the best fit dispersion curves calculated from the Hamiltonian model, plotted versus the coupling energy *Δ* (upper axis).

The reflection spectra of the fabricated material changed dramatically with increase of the R6G dye concentration in the electroplating solution, Fig 1. Thus, at small dye concentrations, the reflectance spectra featured only one dip (Fig. 1a, trace 1), corresponding to the absorption band of the dye. However, with increase of the dye concentration in the solution, the reflection dip split in two and the energy gap between the two minima increased with increase of the dye concentration (Fig. 1a). This behavior is consistent with the splitting of the energy eigenstates commonly observed at strong coupling of *e.g.* excitons and surface plasmons. However, since only one type of dye molecules was present in our experiment and the alumina membrane did not have any pronounced spectral features in the visible range of the spectra, we tentatively explain the splitting in terms of the strong coupling of the main peak and the shoulder of the absorption band of the R6G dye.

The corresponding dispersion curve was fitted with the Hamiltonian model taking into account the energies of the unperturbed states (absorption maximum and shoulder, E_1 and E_2) and the coupling energy Δ (Fig.1 b):

$$\det\left(\hat{H}\right)=\begin{vmatrix} E_1-E & \Delta \\ \Delta & E_2-E \end{vmatrix}=0.$$ The reasonably good agreement between the theory and the experiment was obtained

when the coupling energy was proportional to $n^{0.17}$, where *n* was the dye concentration. This empirical power dependence requires the explanation to be published elsewhere.

The spontaneous emission band had one maximum at small dye concentrations and developed the shoulder and the second band at the increased dye concentrations, Fig. 2a. Furthermore, the main and the secondary emission bands demonstrated the tendency of repulsion, Fig 2b. At the same time, the excitation spectra featured only one maximum, whose spectral position practically did not change with the increase of the dye concentration, Figs. 2a and 2b.
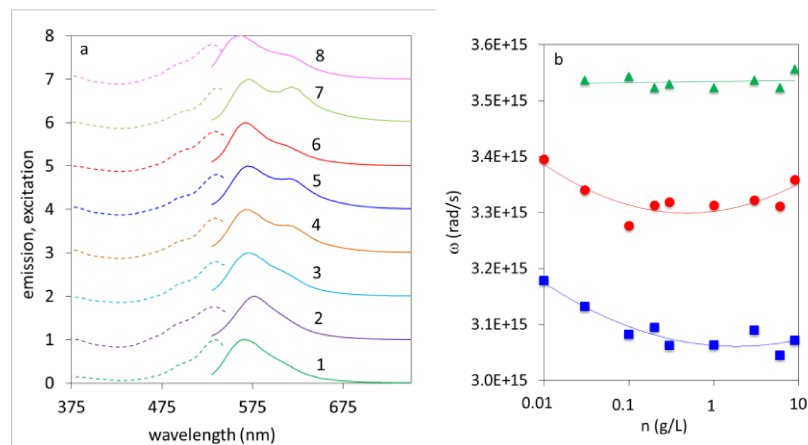

Fig. 2. (a) Emission spectra (solid lines) and the excitation spectra (dashed lines) of the alumina membranes filled with R6G at different dye concentrations in the ethanol electroplating solution. (1) 0.03 mg/mL, (2) 0.1 mg/mL, (3) 0.2 mg/mL, (4) 0.3 mg/ml), (5) 1 mg/mL, (6) 3 mg/mL, (7) 6 mg/mL and (8) 9 mg/mL. (b) The dispersion curves obtained from plotting the positions of the spectral maxima and shoulders in Fig. 2a as the function of concentration *n*. Circles and squares: Positions of the two bands forming the emission spectrum. Triangles: Maxima of the excitation spectra.

The reflectance spectra of the dye-doped membrane sample (electroplated at *n*=6 g/L), taken at different incidence angles *θ*, demonstrated a weak but noticeable dependence of the 486 nm reflection dip on *θ*. This behavior, frequently observed at strong coupling of *e.g.* dye molecules and resonant cavities, is consistent with the collective response of multiple dye-doped channels and constitutes the development of the coherent all-dielectric metamaterial.

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