Light-Matter Interaction in Disordered Metal-Dielectric Environments

S. Rout[1], M. Biener[2], Zhen Qi[2], C. E. Bonner[1], T. V. Shahbazyan[3], M. A. Noginov[1]
[1]*Center for Material Research, Norfolk State University, Norfolk, VA 23504, USA*
[2]*Lawrence Livermore National Laboratory, P.O. Box 808, L-370, Livermore, CA 94550*
[3]*Department of Physics, Atmospheric Sciences & Geoscience, Jackson State University, Jackson, MS 39217*

Abstract: We studied emission kinetics of HITC dye in disordered metal-dielectric environments and found that the latter, contrary to expectations, can reverse emission kinetics shortening in highly concentrated dyes, caused by a combination of relaxation processes.

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Light and matter can interact in both weak and strong coupling regimes. In the weak coupling regime, the rates of transitions are affected but not the eigenenergies of the corresponding transitions. The well-known example of the light-matter interaction in the weak coupling regime is the shortening of the emission kinetics in vicinity of the metamaterials with hyperbolic dispersion, which is due to the high density of photonic states [1].

On the other hand, in the strong coupling regime, both the energy eigenvalues and the transition rates are affected. Strong coupling can lead to number of intriguing phenomena, such as change of HOMO and LUMO energy bands (by ~ 1eV), change of electrical conductivity, change of surface potentials, and change of pathways of chemical reactions [2,3].

Recently, we have discovered an intriguing light-matter interaction phenomenon taking place in disordered metal-dielectric environments. Thus, we have fabricated two series of samples with smaller or larger degree of disorder: (i) arrays of Ag nanowires grown in nanoscopic pores of alumina membrane, Fig. 1a, and (ii) highly porous Au nanofoams, Fig. 1b. (While Au nanofoams were disordered by design, a disorder in arrays of Au nanowires was, originally, unintentional, determined by the technology of the sample preparation.) Optical characterization has shown that the Ag nanowire arrays have hyperbolic dispersion at $\lambda \geq 600$ nm. Dye-doped polymer (HITC:PMMA) was deposited on top of the fabricated metal-dielectric substrates and the emission kinetics (at $\lambda \geq 850$ nm) were studied and compared to those in control samples (glass substrates).

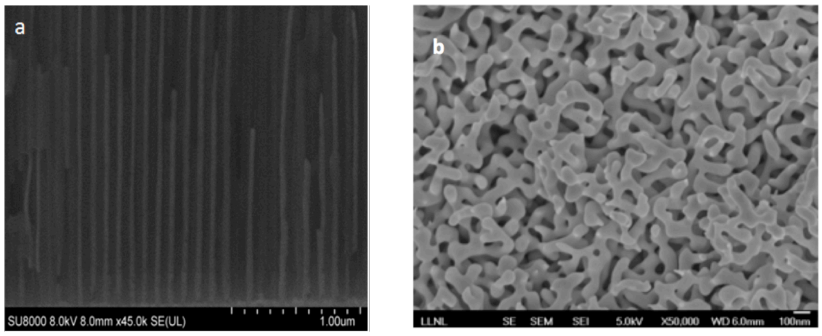

Fig. 1. (a) Cross-sectional Scanning Electron Microscope (SEM) image of the Ag nanowires (bright vertical lines) grown in an alumina membrane with pore diameter 30±5 nm. One can see that nanowires have good regularity at the (bottom) edge of the sample, while their lengths become more irregular in the depth of the sample. (b) SEM image of the Au nanofoam sample.

The emission kinetics of low concentrated HITC dye (1 g/L in solid state) deposited on glass substrate has a relatively long life time of ~1 ns, Figs. 2a and 2b, trace 1. At slightly larger, however, still relatively low dye concentration of 9 g/L, the emission kinetics of dye on glass slightly shortens due to the concentration quenching. Though, this effect is not very significant, Fig. 2a, trace 2. When the same dye (9 g/L) is deposited on the metamaterial with hyperbolic dispersion, such as array of silver nanowires grown in porous alumina membranes, or disordered Au nanofoam, the emission decay rate is getting larger, presumably, due to (i) the Purcell effect and associated with it the high density of photonic states and (ii) energy transfer to plasmons and bound state electron transitions in metal, Fig. 2a trace 3. (Here, we illustrate the phenomenon in an example of array of Ag nanowires. An even more pronounced results have been obtained in Au nanofoams.) On the other hand, when the high-concentrated HITC dye (24 g/L) is deposited on glass, the emission kinetics shortens due to the well-known effect of the

concentration quenching, Fig. 2b trace 2. Therefore, as we deposit the high concentrated dye on top of arrays of Ag nanowires or Au nano-foams, we expect to see an even larger shortening of the emission kinetics, partly because of the high density of photonic states and the energy transfer to metal and partly because of the concentration quenching, Fig. 2b trace 3.

What we have observed experimentally was highly surprising and completely opposite to the heuristic predictions: The emission decay rate strongly decreased and became comparable to (or smaller than) that of the low-concentrated dye on top of glass Fig. 2b trace 4. Thus, Ag nanowires and Au nano-foam environments seem to reverse both the effect of the photonic density of states and the concentration quenching – a surprising and intriguing phenomenon, which calls for a detailed theoretical study. (Even stronger effect was observed in Au nanofoams).

Note that the emission kinetics on top of arrays of Ag nanowires or Au nanofoams had a very large spread of emission rates (see multiple data points in Figs. 2a and 2b, where each color and each type of characters corresponds to a particular emission kinetics). Thus, the emission kinetics measured in different spots on the sample were strongly different from each other. This spread of decay rates, which was never observed in our previous studies of dye on top of thin-film metallic or multilayered metal-dielectric substrates, is another unusual phenomenon requiring thorough investigation. In this study, we analyze the emission kinetics corresponding to the ensembles of dye molecules characterized by the strongest coupling with nonlocal metal-dielectric environments.

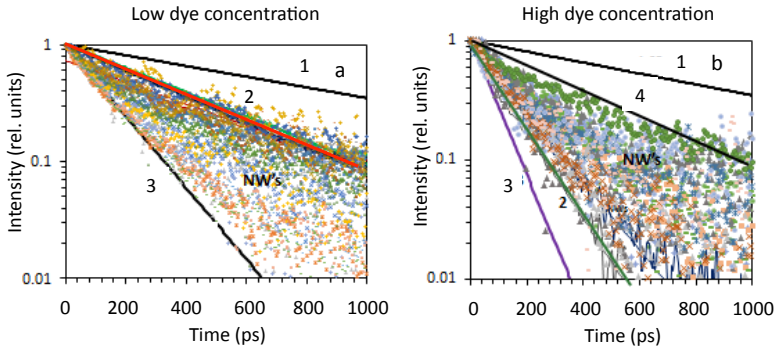

Fig. 2. (a) Emission kinetics of HITC:PMMA film at short-pulsed laser pumping (t_{pulse}≈150 fs, λ=795 nm) at low dye concentration of 1 g/L (trace 1) and 9 g/L (trace 2) on top of glass substrate. Emission kinetics of 9 g/L HITC:PMMA film on top of array of Ag nanowires (trace 3). (b) Trace 1 is the same as trace 1 in Fig. 2a. Emission kinetics of HITC:PMMA films at high dye concentration (24 g/L) on top of glass (trace 2). Naively expected emission kinetics on top of array of Ag nanowires, partly due to the concentration quenching and partly due to the Purcell enhancement and energy transfer to metal (trace 3). Emission kinetics of highly concentrated dye (24 g/L) deposited onto array of Ag nanowires (trace 4).

Our preliminary studies reported above have been made using a limited number of metal-dielectric substrates (arrays of Ag nanowires and Au nano-foams) and limiting number of dye concentrations. We are currently in a process of full-scale investigation of this intriguing phenomenon, using large series of metal-dielectric samples (with different size parameters) and large number of dye concentrations. As the result of this study, we anticipate to uncover a complex interplay between the effects of metal-dielectric environments on spontaneous emission and Förster energy transfer, which is the primary reason for concentration quenching. In disordered metal-dielectric environment, Förster transfer between dyes is shunted by energy exchange with localized plasmon modes resulting in faster kinetics. Slower kinetics for high dye concentrations could be attributed to a reduction of metal quenching for strongly-coupled dyes as their spatial distribution becomes more homogeneous. This discovery, leading to ultimate control of excited molecular states with non-local metal dielectric environments, will be important both in terms of fundamental science and applications of quantum emitters. The details of the experiments and analysis will be presented at the conference.

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