Multi-fold Enhancement of Quantum Dot Luminescence in a Plasmonic Metamaterial

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We report that hybridizing semiconductor quantum dots with plasmonic metamaterial leads to a multi-fold intensity increase and narrowing of their photoluminescence spectrum. The luminescence enhancement is a clear manifestation of the cavity quantum electrodynamics Purcell effect that can be controlled by the metamaterial's design. This observation is an essential step towards understanding loss compensation in metamaterials with gain media and for developing metamaterial-enhanced gain media.

Control of Joule losses is a key challenge for plasmonic and metamaterial technologies. Losses hamper the development of negative index media for super-resolution and optical cloaking devices, and plasmonic data processing circuits. Lowering losses is also crucially important for the performance of spectral filters, delay lines and, in fact, practically any other metamaterial and plasmonic applications [1]. Although using superconducting metamaterials can largely eliminate losses in THz and microwave metamaterials [2], Joule losses at optical frequencies are unavoidable. Recent works report compensation of losses with gain in metamaterials aggregated with semiconductor quantum dots (QDs) [3] and organic dyes [4] embedded into the metal nanostructures. Parametric metamaterials gain systems are also under investigation in theory [5–7]. Another grand goal of active metamaterials research is to improve laser gain media and to develop a 'lasing spaser' device: a 'flat' laser with emission fueled by plasmonic excitations in an array of coherently emitting meta-molecules [8]. An essential part of this development shall be the study of luminescence of active material hybridized with plasmonic nanostructures that could support collective, coherent plasmonic excitations in the lasing spaser. Here we report the first study of photoluminescence of semiconductor QDs hybridized with asymmetric split-ring plasmonic metamaterial. This type of metamaterial supports a closed-mode Fano-type excitation which has the key characteristics required for the lasing spaser application: the mode is formed by collective interactions between individual meta-molecules that shall ensure coherent laser action [9]. In this letter, we experimentally demonstrate that the photoluminescence properties of QDs can be greatly enhanced by the plasmonic metamaterial.

Figure 1(a) schematically illustrates a plasmonic metamaterial combined with QDs. The metamaterials studied here consist of periodic arrays of asymmetrically split ring slits (negative structure), which have been successfully applied to switching, nonlinear and sensor applications [10]. The metamaterial arrays with a total size of 40×40 μm each were fabricated by focused ion beam milling in a 50nm-thick gold film on a glass substrate
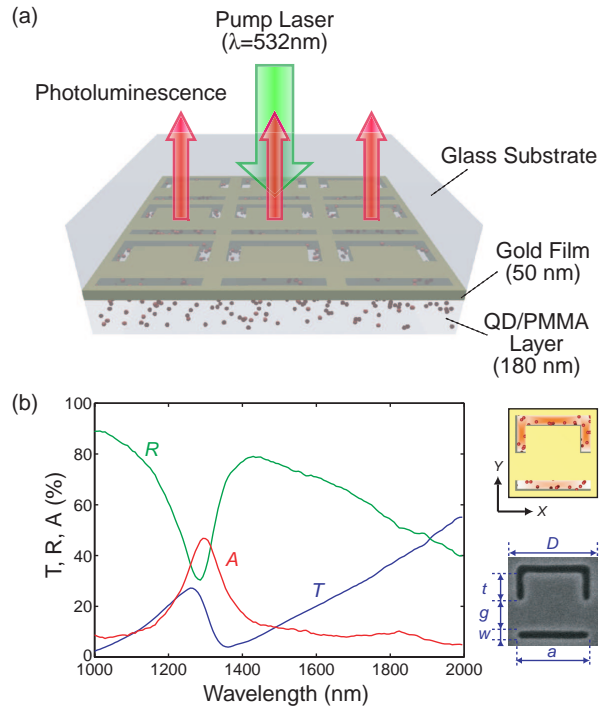

FIG. 1: (color online). (a) Schematic of a plasmonic metamaterial functionalized with quantum dots (QDs). (b) Measured spectra of transmission T, reflection R, and absorption A for a QD-coated metamaterial with a unit cell size of $D = 545$ nm. The incident wave is polarized parallel to the y-axis. The insets show a sketch of QDs in the resonant mode volume as seen from the substrate side and a scanning electron micrograph of the unit cell (without QDs). Feature sizes: unit cell $D = 545$ nm, horizontal slit $a = 470$ nm, top vertical slit and gap $t = g = 170$ nm and slit width $w = 65$ nm.

[see inset of Fig. 1(b)].

In order to systematically investigate the correlation between QD photoluminescence spectrum and the spectral position of the Fano plasmonic metamaterial resonance, we manufactured five metamaterial arrays with different unit cell sizes ranging from $D = 545$ nm to 645 nm, slit width $w = 65$ nm and a fixed ratio of $t/g = 1$. We used lead sulfide (PbS) semiconductor

quantum dots from Evident Technologies with a luminescence peak around 1300 nm and mean core diameter of 4.6 nm. These QDs were dispersed in polymethylmethacrylate (PMMA) and the QD/PMMA solution was then spin-coated onto the metamaterial arrays forming a 180 nm thick layer. We estimate the QD area density on the array to be 1.6×10^5 μm^{-2} and thus approximately 4000 quantum dots per meta-molecule are trapped in the groves of the structure. Spectra (transmission, reflection, and absorption) and photoluminescence characteristics of the metamaterials with QDs were measured using a microspectrophotometer. In the photoluminescence measurements, the QDs were optically pumped by a frequency doubled CW YAG laser ($\lambda = 532$ nm) from the substrate side through the metamaterial array [see Fig. 1(a)]. The YAG laser was focused to a (~ 100 μm) spot with intensity 35 W/cm^2 by the microscope objective (N.A.= 0.28). Photoluminescence emitted from the QDs was collected by the same objective with a polarizer so that only a selected polarization component of photoluminescence could be detected. Fig. 1(b) shows the spectral characteristics of the QD/PMMA-coated metamaterial with $D = 545$ nm in the absence of the pump. The absorption spectrum shows a narrow resonance peak around 1300 nm (Q-factor $\simeq 11$).

The photoluminescence of the metamaterial functionalized with QDs is presented in Fig. 2. Here we measure the y-polarization, for which the metamaterial's Fano-mode can be excited, see Fig. 1(b). The photoluminescence spectrum of the QD/PMMA layer on the glass substrate (i.e. without metamaterial) is shown at the top of Fig. 2(a) and peaks at $\lambda_0 = 1280$ nm which is indicated by the shaded area.

The presence of the plasmonic metamaterial drastically changes the QD photoluminescence characteristics: it leads to a multi-fold intensity enhancement as well as spectral narrowing of the photoluminescence peak. For instance, for $D = 545$ nm the photoluminescence peak intensity is enhanced by a factor of 8, while the full width at half maximum (FWHM) of the photoluminescence peak is decreased to approximately 100 nm compared to 176 nm without metamaterial. Here the metamaterial's absorption resonance wavelength λ_{abs} almost perfectly matches the QD emission wavelength λ_0 (see red dashed absorption spectrum). This suggests that the drastic photoluminescence enhancement results from interaction between the excited-state gain medium (QDs) and the surface plasmon resonance [11–14], and, in particular, can be understood in terms of the cavity quantum electrodynamics (QED) Purcell effect [15, 16] as discussed later. Such coupling between QD-excitons and metamaterial surface plasmons must be sensitive to a mismatch $\Delta\lambda = \lambda_{abs} - \lambda_0$. Indeed, when the metamaterial resonance is red-shifted, by increasing the unit cell size from $D = 545$ nm to 645 nm, the photoluminescence spectrum is weakened, broadened and distorted.
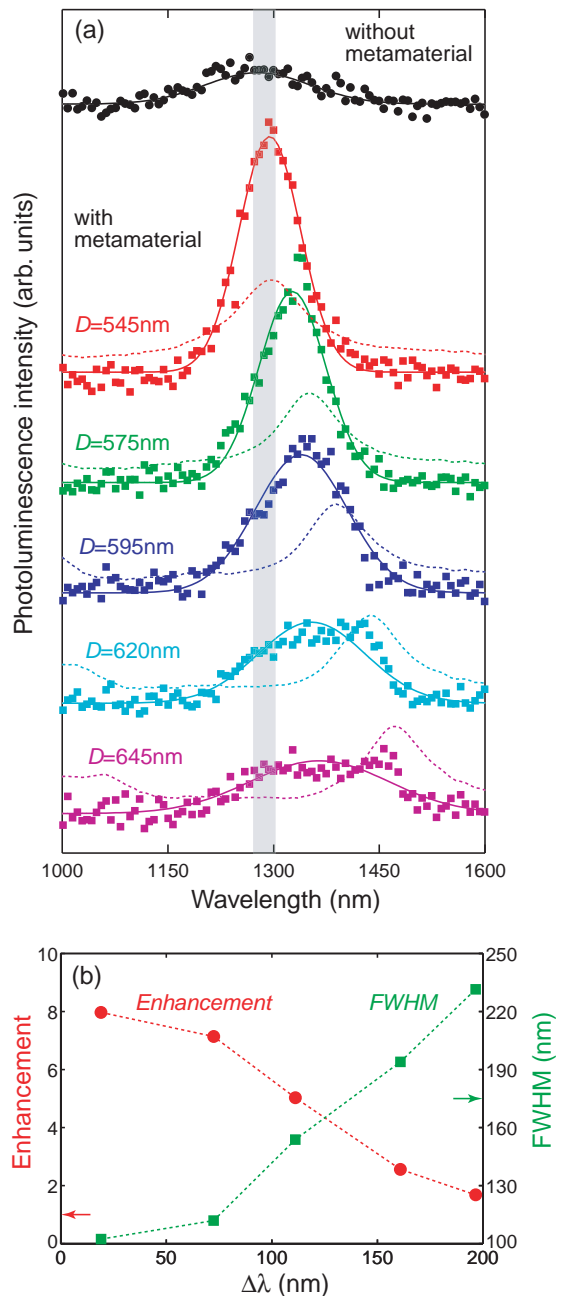

FIG. 2: (color online). Photoluminescence controlled by plasmonic metamaterials. (a) Photoluminescence spectra of the QDs without (top) and with metamaterial layer. A best-fit Gaussian curve is plotted with each spectrum (solid line). The dotted line indicates the metamaterial absorption spectrum. (b) Intensity enhancement and full width at half maximum (FWHM) of the QD-metamaterial photoluminescence spectra. Enhancement is normalized to the photoluminescence peak intensity measured without a metamaterial layer. For comparison, reference values measured without a metamaterial layer are indicated by arrows.

In all cases the photoluminescence peak is shifted from its original position λ_0 towards the respective metama-

terial's absorption resonance λ_{abs}. For a large mismatch $\Delta\lambda > 150$ nm (i.e. $D \geq 620$ nm), the photoluminescence spectrum becomes non-Gaussian and appears to develop two peaks close to λ_0 and λ_{abs}, respectively. Intriguingly, the observed photoluminescence red-shift becomes quite large, reaching almost 200 nm. The intensity enhancement and FWHM of the photoluminescence spectra are summarized in Fig. 2(b) as a function of the mismatch $\Delta\lambda$. Narrow photoluminescence spectra with greatly enhanced intensity are observed when the QD-luminescence matches the metamaterial resonance wavelength (i.e. small $\Delta\lambda$). On the other hand, for a large mismatch ($\Delta\lambda > 150$ nm) the photoluminescence spectrum becomes even broader than it is without the metamaterial layer. Here we note that all metamaterial samples had almost identical transmission levels at the pump wavelength (532 nm), and therefore there was no significant difference in pump power reaching the active layer.

One might attempt to explain such broadening as a result of filtering the QD luminescence spectrum through the metamaterial, thus assuming no plasmon-exciton interaction. However, such a simple explanation can be ruled out, as it does not explain any photoluminescence enhancement resulting from the presence of the metamaterial. Furthermore, the convoluted spectrum of QD luminescence and metamaterial transmission does not agree well with the photoluminescence measurements.

The metamaterials studied here have profound polarization-dependent properties. While a strong plasmonic Fano-resonance is excited by y-polarization [see Fig. 1(b)], this resonance vanishes for the orthogonal polarization [3]. This polarization dependence may be expected to affect the interaction with the isotropic QDs, and hence the polarization dependence of the photoluminescence was measured as illustrated by Fig. 3 for the metamaterial with $D = 545$ nm. By changing the polarization state from y to x, the absorption spectrum becomes featureless around λ_0 [Fig. 3(b)]. The corresponding photoluminescence drastically degrades [Fig. 3(a)], providing additional evidence that the photoluminescence spectrum is controlled by the plasmonic resonance.

We argue that the observed enhancement of photoluminescence can be understood in terms of the cavity QED Purcell effect [15, 16]. Indeed, the spontaneous emission decay rate is proportional to the density of photon states that the photonic environment offers for spontaneous decay. Thus the internal dynamics of a quantum system are controlled by a photonic environment that is resonant with radiative transitions of the source. Enhancement of the radiation rates has been seen in various systems including QDs in nanocavities and photonic crystals. In our experiments the ensemble of QDs with its exciton emission line is placed at a resonant plasmonic metamaterial. The metamaterial creates an environment equivalent to a microcavity with a quality factor Q, and a mode confined in an ultrasmall volume V that enhances
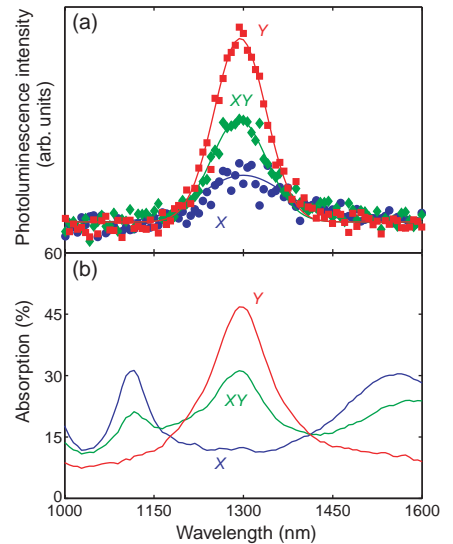

FIG. 3: (color online). Polarization dependence of (a) photoluminescence and (b) absorption, measured for the metamaterial with $D = 545$ nm. Polarizations x and y are introduced in Fig. 1, while xy is the intermediate polarization.

the density of photon states leading to the Purcell factor enhancement of luminescence: $F_p = \frac{3}{4\pi^2}\left(\frac{\lambda}{n}\right)^3\frac{Q}{V}$. Here n is the refractive index of the medium and λ is the wavelength.

For the sake of rough estimate, the mode volume is calculated by $V = 2(a+t)wh$ (where $a = 470$ nm, $t = 170$ nm, $w = 65$ nm, and $h = 50$ nm), i.e. the mode is assumed to be confined in the slits of the metamaterial metal film of thickness h. With $\lambda = 1300$ nm, $Q = 11$, and $n = 1.48$, this gives the following value for the Purcell factor $F_p = 136$. This is of the same order of magnitude as the experimentally observed enhancement of overall luminescence $\mu = 8$, corrected for the fraction of QDs in the slits $f = V/(D^2p)$, where $p = 180$ nm is the thickness of the QD/PMMA layer: $F_{p,exp} = \mu/f = 103$. Here we note that the general Purcell enhancement formula used in our calculations only gives approximate values for luminescence enhancement in plasmonic systems [17].

Peculiarity of our experimental conditions in comparison with numerous reports on the Purcell factor enhancement of luminescence of individual QDs is in a large number of QDs located within the mode volume (~ 4000): the exciton line is inhomogeneously broadened due to a natural variation of the QD sizes [Fig. 4(a)]. Here, detuning of the plasmon resonance from the centre of the exciton emission line leads to the Purcell enhancement being applied to the wing of the emission line as it is clearly manifested by the transformation of the photoluminescence spectrum presented in Fig. 2. The photoluminescence spectra resulting from this Purcell enhancement may be expected to be proportional
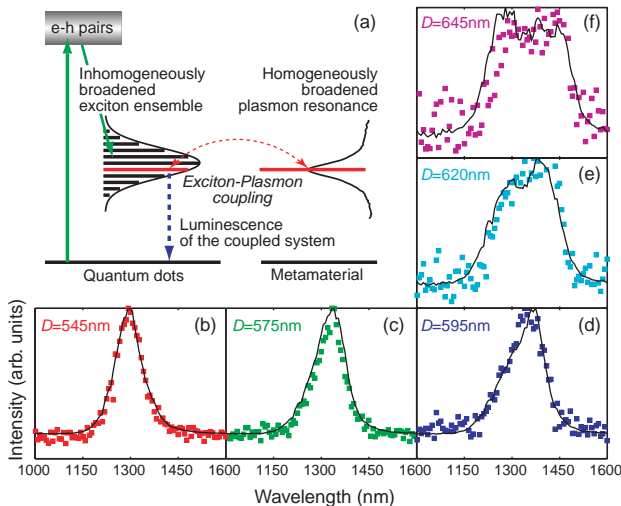
FIG. 4: (color online). Nature of photoluminescence change in the plasmonic metamaterial. (a) Energy diagram of the QD-metamaterial coupled system. (b)-(f) Comparison of the measured photoluminescence (data points) with $\chi_A(\lambda) = PL_0(\lambda) \times A(\lambda)$ (lines) for metamaterials with different unit cell sizes ranging from $D = 545$ nm to 645 nm. Here, $PL_0(\lambda)$ is normal QD photoluminescence without metamaterial structure, and $A(\lambda)$ is the metamaterial's absorption spectrum.

to $\chi_A(\lambda) = PL_0(\lambda) \times A(\lambda)$, where $PL_0(\lambda)$ is the normal QD photoluminescence spectrum without metamaterial structure and $A(\lambda)$ is the absorption spectrum of the metamaterial array (a measure of the local density of states). As illustrated by Fig. 4(b)-(f), $\chi_A(\lambda)$ (lines) is in excellent agreement with the measured photoluminescence (data points) in all cases, providing further evidence for the Purcell effect and plasmon-exciton coupling in the QD-metamaterial system.

We argue that in a coupled QD-plasmonic metamaterial system the resonant enhancement of luminescence can be exploited for increasing optical gain and thus for the development of compact, low-threshold lasing devices. At the same time it is not clear yet what effect the profound Purcell enhancement of luminescence has on the metamaterial's Joule losses as it reduces the fraction of energy that is transferred to the plasmonic system.

In summary, we have experimentally demonstrated multi-fold enhancement and substantial spectral narrowing of photoluminescence from semiconductor quantum dots resulting from resonant coupling to a plasmonic metamaterial. We have shown that the intensity enhancement and spectral width of the photoluminescence

in the combined system are controlled by the spectral overlap of the emission peak of free QDs and the metamaterial's plasmonic resonance, and thus this effect is linked to exciton-plasmon coupling between QDs and metamaterial. The observed photoluminescence enhancement provides the first and clear demonstration of the cavity QED Purcell effect in metamaterials.

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