Multifold Enhancement of Quantum Dot Luminescence in Plasmonic Metamaterials

K. Tanaka,[1,2,*] E. Plum,[1,†] J. Y. Ou,[1] T. Uchino,[3] and N. I. Zheludev[1,‡]

[1]*Optoelectronics Research Centre and Centre for Photonic Metamaterials, University of Southampton, Southampton SO17 1BJ, United Kingdom*

[2]*Sony Corporation, Shinagawa-ku, Tokyo, 141-0001, Japan*

[3]*School of Electronics and Computer Science and Centre for Photonic Metamaterials, University of Southampton, Southampton SO17 1BJ, United Kingdom*

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

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Control of Joule losses is a key challenge for plasmonic and metamaterial technologies. Losses hamper the development of negative index media for superresolution 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 application [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], organic dyes embedded into metal nanostructures [4], and metamaterials manufactured on quantum wells [5]. Parametric metamaterial gain systems are also under investigation in theory [6–8]. 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 metamolecules [9]. 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 metamolecules that shall ensure coherent laser action [10,11]. 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 asymmetric split-ring slits, which have been successfully applied to switching, nonlinear, and sensor applications [12]. The metamaterial arrays with a total size of $40 \times 40\ \mu$m were each

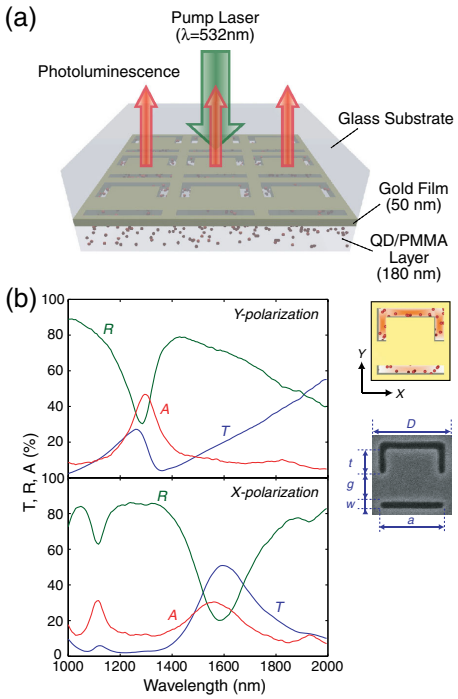

FIG. 1 (color online). (a) Schematic of a plasmonic metamaterial functionalized with QDs. (b) Measured spectra of transmission T, reflection R, and absorption A for a QD-coated metamaterial with a unit cell size of $D = 545$ nm. The insets show a sketch of QDs in the resonant mode volume, as seen from 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.

fabricated by focused ion beam milling in a 50 nm-thick gold film on a glass substrate [see the inset of Fig. 1(b)].

In order to systematically investigate the correlation between the 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, a slit width of $w = 65$ 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 are trapped in the grooves of each metamolecule. Spectra (transmission, reflection, and absorption) and photoluminescence of the metamaterials with QDs were measured using a microspectrophotometer. In the photoluminescence measurements, the QDs were optically pumped by a frequency doubled cw Nd:YAG laser [13] ($\lambda = 532$ nm) from the substrate side through the metamaterial array [see Fig. 1(a)]. The Nd:YAG laser was focused to a $\sim$100 μm spot with intensity 35 W/cm^2 by the microscope objective (N.A. = 0.28). Using a linear polarizer a selected polarization component of QD photoluminescence was collected by the same objective. Figure 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 for y polarization shows a narrow and strong resonance peak around 1300 nm (Q factor $\simeq 11$), which is a collective resonance of the metamaterial array [10,11].

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 the 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 multifold 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 of the photoluminescence peak is decreased to approximately 100 nm compared to 176 nm without the metamaterial. Here the metamaterial's absorption resonance wavelength λ_{abs} almost perfectly matches the QD emission wavelength λ_0 (see the red dashed absorption spectrum). This suggests that the drastic photoluminescence enhancement results from the interaction

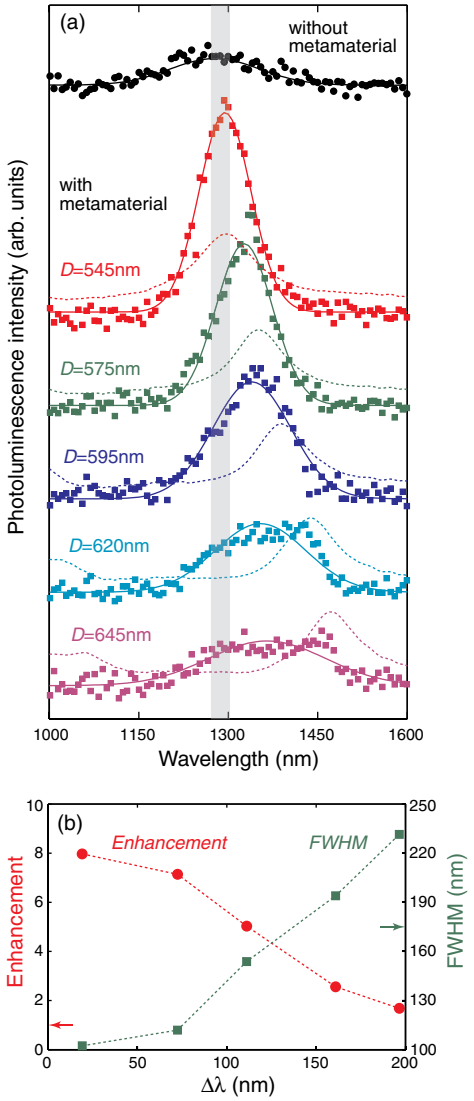

FIG. 2 (color online). Photoluminescence controlled by plasmonic metamaterials. (a) Photoluminescence spectra of the QDs without (top) and with a metamaterial layer accompanied by Gaussian fits (solid lines). Dotted lines indicate metamaterial absorption spectra. (b) Intensity enhancement and FWHM of the QD-metamaterial photoluminescence spectra. Enhancement is normalized to the photoluminescence peak intensity measured without a metamaterial layer. Reference values measured without a metamaterial layer are indicated by arrows.

between the excited-state gain medium (QDs) and the surface plasmon resonance [14–17] and can be understood in terms of the cavity quantum electrodynamics Purcell effect [18,19] as discussed later. Such coupling between QD excitons and metamaterial surface plasmons must be sensitive to a mismatch $\Delta\lambda = \lambda_{\text{abs}} - \lambda_0$. Indeed, when the metamaterial resonance is redshifted, by increasing the unit cell size from $D = 545$ nm to 645 nm, the photoluminescence spectrum is weakened, broadened, and distorted. In all cases the photoluminescence peak is shifted from its original position λ_0 towards the respective

metamaterial'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 redshift 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 have almost identical transmission levels at the pump wavelength (532 nm), and therefore there is no significant difference in the 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. 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, this resonance vanishes for x polarization [see Fig. 1(b)]. 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 [18,19]. 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 the density of photon

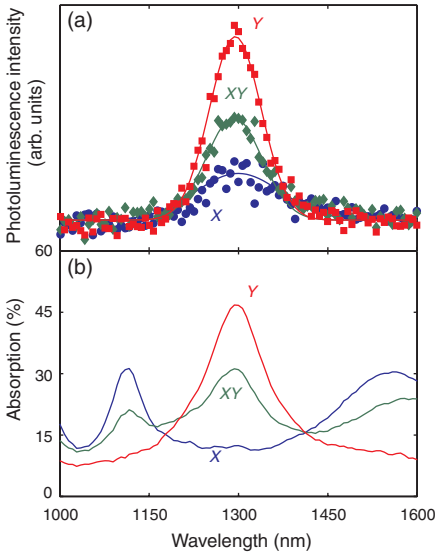

FIG. 3 (color online). Polarization dependence of (a) photoluminescence and (b) absorption, measured for the metamaterial with $D = 545$ nm. Linear polarizations x and y are introduced in Fig. 1(b), while xy is the intermediate polarization at 45° to x.

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

For the sake of a 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 $f = V/(D^2 p)$, where $p = 180$ nm is the thickness of the QD/PMMA layer: $F_{p,\mathrm{exp}} = \mu/f = 103$. Here we note that the general Purcell enhancement formula used in our calculations only gives approximate values for luminescence enhancement in plasmonic systems [20] and does not account for the collective nature of the mode.

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 center 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. We may expect the photoluminescence spectra resulting from this Purcell enhancement to be proportional to $\chi_A(\lambda) = PL_0(\lambda) \times A(\lambda)$, where $PL_0(\lambda)$ is the normal QD

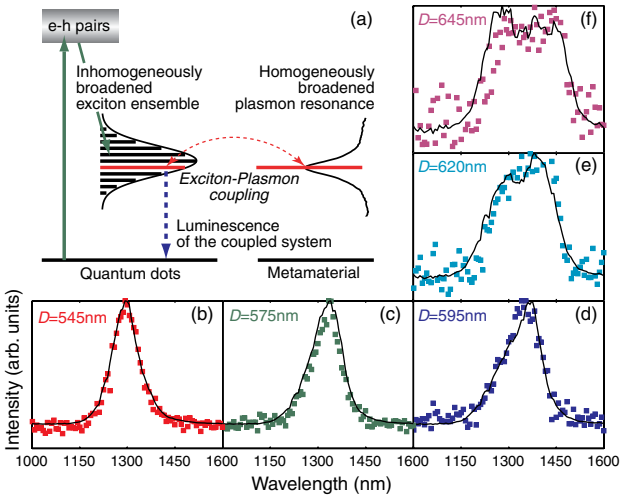

FIG. 4 (color online). Nature of the photoluminescence change in the plasmonic metamaterial. (a) Energy diagram of the QD-metamaterial coupled system. (b–f) Comparison of the measured photoluminescence (data points) with $\chi_A(\lambda) = PL_0(\lambda) \times A(\lambda)$ (lines) for metamaterials with different unit cell sizes ranging from $D = 545$ nm to 645 nm. Here, $PL_0(\lambda)$ is normal QD photoluminescence without a metamaterial structure, and $A(\lambda)$ is the metamaterial's absorption spectrum.

photoluminescence spectrum without a metamaterial structure and $A(\lambda)$ is the absorption spectrum of the metamaterial array (a measure of the local density of states). As illustrated by Figs. 4(b)–4(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 may reduce the fraction of energy that is transferred to the plasmonic system.

In summary, we have experimentally demonstrated multifold 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 the metamaterial. The observed photoluminescence enhancement provides the first, clear demonstration of the cavity QED Purcell effect in metamaterials.

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*KenjiD.Tanaka@jp.sony.com
†erp@orc.soton.ac.uk
‡niz@orc.soton.ac.uk; www.metamaterials.org.uk

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