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Abstract: Metallic nanoparticle arrays support localized surface plasmon resonances (LSPRs) and propagating surface lattice resonances (SLRs). We study the control of quantum dot (QD) emission coupled to the optical modes of silver nanoparticle arrays, both experimentally and numerically. With a hybrid lithography-functionalization method, the QDs are deposited in the vicinity of the nanoparticles. Directionality and enhancement of the emission are observed in photoluminescence spectra and fluorescence lifetime measurements, respectively. Similar features are also demonstrated in the numerical simulations. The tunable emission of this type of hybrid structures could lead to potential applications in light sources.

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References and links

1. Introduction

Metal nanoparticles support localized surface plasmon resonances (LSPRs) which enable tuning the light-matter interactions at the nanoscale. The mode volume of LSPRs is strongly confined in the near-field region of the nanoparticle interfaces. This sub-wavelength confinement and near-field enhancement contribute to some useful applications such as surface-enhanced...
Raman spectroscopy (SERS) [1], and enhancement of fluorescence [2] and nonlinear processes [3]. However, one of the drawbacks is the intrinsic loss of metals, such that LSPRs typically have poor quality factors (on the order of 10 [4]). Another type of surface plasmon mode, called surface lattice resonance (SLR), is supported by an ensemble of periodically arranged metal nanoparticles [5, 6]. The SLR results from the coupling between the LSPR of single nanoparticles and diffraction orders (DOs) of the lattice determined by the periodicity. The SLR can be also regarded as the consequence of constructive interference between the dipole moments on neighboring nanoparticles. Unlike LSPRs, the collective SLR typically has an improved quality factor (up to \(\sim 700\) [7]).

The dispersive nature and low-losses of the SLRs enable high fluorescence enhancement, tunable over the entire visible spectral range, for emitters placed in the vicinity of metal nanoparticle arrays [8]. Lasing action in plasmonic nanoarrays can be realized in case the enhancement of stimulated emission is able to overcome the losses [9–12]. Furthermore, the coupling between excitons and the collective modes of nanoarrays also offers an approach to exploring quantum and coherence phenomena if the strong coupling regime is achieved [13–15].

In this paper, we investigate the coupling between the emission of silica-coated quantum dots (QDs) [16] and the modes supported by silver nanoparticle arrays. Since the plasmonic modes are strongly confined in the near-field of the nanoparticles, we aim to deposit the QDs only on top of the metal particles. A hybrid lithography-functionalization method has been developed so that the QDs are exclusively attached in the close vicinity of the silver particles. We present the measured angle-resolved extinction and emission spectra of the arrays with different periodicities. The features of the SLRs can be clearly observed in the emission spectra, implying that the emission from the QDs has been coupled sufficiently to the collective modes of the arrays. Lifetime measurements indicate that the spontaneous emission of the QDs has been enhanced by the presence of the plasmonic nanoarrays. Numerical simulations based on the finite-difference time-domain (FDTD) method are also performed, demonstrating the enhancement of spontaneous emission.

2. Sample fabrication

A general approach to deposit colloidal QDs on surfaces is to use a self-assembled monolayer (SAM) of bifunctional molecules to cross-link the QDs to the surface, a technique being called surface modification or functionalization [17–19]. We develop a functionalization process by using (3-Mercaptopropyl)trimethoxysilane (3-MPTS) molecules as linkers between the silver surface and the silica shell of the QDs. The 3-MPTS molecules are first deposited as the SAM on the silver surface with trimethoxysilane tails, through the strong covalent bond between thiol and silver [20]. After hydrolysis and condensation, the silanetriols-terminated SAM can immobilize the silica-coated QDs [21].

The detailed functionalization process is depicted in Fig. 1(a). To form the 3-MPTS SAM on top of the silver surface, the silver-deposited glass substrate is immersed in a solution of 40 mM 3-MPTS in ethanol for 72 hours. The hydrolysis of the 3-MPTS monolayer is accomplished by immersing the substrate into an aqueous solution of 10 mM NaOH for 4 hours. The silanetriols-terminated SAM are condensed on the silica shell of the QDs by immersing the substrate into 0.25 \(\mu\)M silica-coated QD suspension for 48 hours. Note that the \(\sim 10\) nm silica shell prevents total luminescence quenching of the QDs by the silver [22].

Figure 1(b) depicts the fabrication steps of the sample. First, a 200 nm thick resist layer of polymethyl methacrylate (PMMA) is spin-coated on a cleaned fused silica substrate. After evaporating 10 nm of aluminum as the conductive layer, the sample is exposed by e-beam lithography (Vistec, EPBG 5000pES). The aluminium layer is etched in an aqueous NaOH solution and the resist is developed in a MIBK : IPA (1 : 3) solution. The designed pattern,
Fig. 1. (a) Schematic view of the functionalization process that deposits QDs on top of silver surface. (b) The fabrication flow of the silver nanoparticle array functionalized with QDs. The functionalization process is performed before the lift-off, in order to deposit QDs on the silver particles only.

Fig. 2. AFM images of (a) bare silver nanorods on a fused silica substrate and (b) silver nanorods with QDs deposited on top following the functionalization process described in the text. Right panels: AFM cross sections along the white dotted lines.

i.e. the nanoarrays, occur in PMMA as dissolved domains. Subsequently, 2 nm of titanium and 30 nm of silver are evaporated on the substrate. The functionalization process and deposition of the QDs are performed before the lift-off of the excessive metal layer with acetone, such that the QDs remain only on top of the silver nanoparticles.

Figures 2(a) and 2(b) show atomic force microscope (AFM) images of a bare silver nanoarray and a functionalized array with QDs on top, respectively. The fabricated nanoparticles are rod-like. The rod width, $d_y$, and the periodicity along y-axis, $p_y$, are fixed to 65 nm and 200 nm, while the rod length, $d_x$, and the periodicity along x-axis, $p_x$, are varied. The size of each array is $100 \times 100 \mu$m$^2$. The cross-sections in the right panels show that the functionalized particles
are at least 30 nm higher than the bare particles, indicating the presence of QDs on top (the average diameter of the silica-coated QDs is $\sim 35$ nm [16]). Note that the images of some samples show that the QDs occasionally attach beside the nanorods but remain mostly in their vicinity. Therefore, the functionalization method allows to place the emitters in the near-field region of the plasmonic particles and enables optimizing the coupling between the emission of the QDs and the modes supported by the plasmonic nanoarrays.

3. Extinction and emission spectra of plasmonic arrays with and without QD

Angle-resolved spectroscopy measurements are performed to study the dispersion relations of the hybrid structures. To obtain the dispersions, extinction spectra are measured with a Fourier-space measurement setup, developed based on the method in [15]. The basic principle of the setup is to guide the back focal plane image (Fourier image) inside the microscope objective into the entrance slit of a spectrometer. The sample is immersed in index matching oil (Cargille, Type FF, $N_{\text{oil}} = 1.4766$ at 6563 Å) such that the structures are surrounded by a medium with a homogeneous refractive index. The extinction spectrum is given by $1 - T$, where $T$ is the angle- and wavelength-resolved transmission, $T = I_{\text{structure}}/I_{\text{reference}}$, measured with a halogen lamp. The entrance slit of the spectrometer is parallel to the x-axis of the sample, thus the dispersion can be acquired by calculating the in-plane component of the wave vector $k_x = 2\pi \sin \theta / \lambda$.

Similarly, the emission spectrum is obtained by illuminating the sample by a collimated pulsed laser beam with a central wavelength of 508 nm, as shown in Fig. 3(a). The average power of the laser beam is 1.15 mW and its diameter on the sample is approximately 120 µm. A dichroic mirror is placed in the detection path such that the excitation beam is filtered out. A polarizer, oriented along the y-axis of the sample, is placed in front of the entrance slit in order that the spectrometer detects only the TE-polarized emission. The photoluminescence (PL) intensity is given by the emission from the array by subtracting the emission (background signal) from outside of the array, $PL = I_{\text{array}} - I_{\text{outside}}$.

Figures 3(b)-3(d) show the extinction spectra of the arrays without QDs. The spectra show the dispersions of the SLRs supported by the silver nanorods arrays, revealing particularly narrow extinction line shapes and therefore high quality factors and long lifetimes of the modes. We see that the first-order SLRs closely follow the $(+1,0)$ and $(-1,0)$ DOs in Rayleigh condition [23, 24]. The SLRs are coupled at $k_x = 0$, meaning that the modes propagating in opposite directions are scattered back and forth, and they therefore form a standing wave. This particular point in the dispersion is referred as the $\Gamma$-point, the location of which (in frequency) depends on the periodicity of the nanorod array.

Figures 3(e)-3(g) demonstrate the emission spectra of the arrays of the same geometrical parameters but with the QDs on top. Remarkably, the emission spectra follow the SLR dispersions, i.e. the narrow peaks in the extinction spectra. Furthermore, we note that the emission is greatly enhanced in the regime where the QD emission overlaps with the dispersions of the SLRs, as shown in the inset of Fig. 3(g). Thus, by placing the QDs in the near-field regions of the nanoparticles, the collective modes of the nanoarrays are coupled efficiently with the QD emission.

In order to find the origin of the SLR features in emission spectra, we measure the emission from both bare silver arrays and functionalized arrays with the QDs on top. Figures 4(a)-4(c) present the angle-resolved emission spectra from bare silver nanoarrays. The samples show silver PL [25, 26] which is spread within the spectral window of detection. The spectra follow closely the dispersions depicted in Fig. 3. This illustrates the coupling between the emission and the SLRs. Meanwhile, Figs. 4(d)-4(f) show the emission spectra from the nanoparticle arrays with QDs on top. Compared with the bare silver arrays, the spectra have dramatic enhancements in the frequency regime of the QD emission. This feature demonstrates that the QD emission is
Fig. 3. (a) Schematic view of the setup used for the characterization of the light emitted by the sample. The light is collected in the Fourier space, allowing to obtain angle-resolved emission spectra from the nanoparticle arrays. Angle-resolved extinction spectra from three bare arrays: (b) $p_x = 365$ nm, $d_x = 180$ nm; (c) $p_x = 415$ nm, $d_x = 210$ nm; (d) $p_x = 435$ nm, $d_x = 220$ nm; and emission spectra from the functionalized arrays with QDs on top of the same geometrical parameters (e)-(g). The inset of (g) shows the normalized emission spectrum of the colloidal QDs.

Fig. 4. Angle-resolved emission spectra from bare plasmonic nanoarrays: (a) $p_x = 365$ nm, $d_x = 219$ nm, (b) $p_x = 415$ nm, $d_x = 249$ nm, (c) $p_x = 470$ nm, $d_x = 282$ nm; and from functionalized samples with QDs on top of arrays with the same geometrical parameters (d-f).
Fig. 5. (a) Schematic view of the setup used for the lifetime measurement of the QD emission. Light is collected in the image plane with a photodetector which is connected to a TCSPC card. (b) Normalized fluorescence decay histograms for QDs embedded in index matching oil (black curve) and for QDs coupled with the plasmonic nanoarrays with the periodicity $p_x = 400$ nm (blue curve) and $p_x = 415$ nm (red curve).

coupled to the SLR modes. The QD emission radiates mostly normal to the sample plane when it is coupled to the nanoarray with a periodicity $p_x = 415$ nm, corresponding to the case that the QD emission peak matches the $\Gamma$-point of the nanoarray. These results show that the plasmonic nanoarrays enable shaping of the directionality of the QD emission, and the coupled emission thereby occurs with a higher level of coherence.

4. Decay rate of QDs coupled to plasmonic nanoarrays

To quantify the spontaneous emission enhancement of the QDs, when coupled to the plasmonic nanoarrays, we measure the fluorescence lifetime of the QDs deposited on top of the arrays using a time-correlated single-photon counting (TCSPC) setup. Figure 5(a) depicts the setup we use. Emission from the sample is passed through a band-pass filter (617/73 nm) and focused into an avalanche photodetector (Micro Photon Devices). A polarizer oriented along y-axis is placed in front of the detector. Both the laser driver and the detector are plugged into a TCSPC acquisition card (PicoHarp 300, PicoQuant GmbH). The repetition frequency of the pulsed laser is set to 5 MHz and the average power of the beam is 123 $\mu$W. The decay histogram is obtained for a 200-second acquisition time.

Figure 5(b) shows the measured decay histograms. The black curve is measured from an ensemble of QDs deposited on a fused silica substrate and embedded in index matching oil, which obeys well a single exponential decay curve. The presence of plasmonic nanoarray in the vicinity of QDs drastically changes the decay curve, as demonstrated in the blue and red histograms, which correspond to the QDs on top of the arrays with a periodicity of 400 nm and 415 nm, respectively. We fit the measured decay curves with a summation of three exponential components $I(t) = \text{IRF} \otimes [\sum_{i=1}^{3} A_i \exp(-t/\tau_i)]$, where IRF is the instrument response function. Among them one component refers to the silver PL, which has quite a short lifetime (below 1 ns). The other two components are related to the hybrid QD-nanoarray system from which we define the average emission decay time $\bar{\tau} = \Sigma A_i \tau_i / \Sigma A_i$ [27, 28]. The obtained decay time for uncoupled QDs is $\bar{\tau}_0 = 14.51$ ns and for the QDs on top of the plasmonic arrays $\bar{\tau} = 4.43$ ns and $\bar{\tau} = 4.19$ ns, for $p_x = 400$ nm and $p_x = 415$ nm, respectively. Thus, the decay rate enhancements $\bar{\tau}_0 / \bar{\tau}$ are 3.28 for $p_x = 400$ nm, and 3.46 for $p_x = 415$ nm. We attribute the faster spontaneous
emission decay to the Purcell effect, i.e., the change in the local density of photonic states (LDOS) near the QDs [29]. The fluorescence lifetime amounts to the spontaneous emission decay rate $\Gamma = 1/\tau$, which is proportional to the LDOS and includes both radiative and non-radiative decays [30, 31]. LDOS describing the local electromagnetic environment is modified by the plasmonic modes supported by the silver nanorod arrays. The values we obtain here are averaged over the possible locations of QDs and over the spectral range of the measurement. This interpretation of the results is supported by the simulations presented below.

5. Numerical simulations

We also perform numerical simulations to study the coupling process between the emitters and the modes related to the plasmonic nanoarrays. For this purpose, FDTD simulations are performed with a commercial software (FDTD Solutions, Lumerical) for the structures introduced above. We first investigate the coupling between an emitter and a single particle. Figure 6(a) depicts the configuration used for the calculation of the decay rate enhancement for an emitter coupled with a single silver nanorod hosted by a homogeneous medium. The geometrical parameters are $d_x = 200$ nm and $d_y = 65$ nm. The particle has a height of 30 nm and it is on top of a 2 nm thick titanium layer. Perfectly matched layers (PMLs) surround the simulation zone. A dipole source is placed 10 nm above the metal surface.

Figure 6(b) shows the calculated spontaneous emission decay rate enhancement for three dipole orientations with respect to the emission wavelength $\lambda_{em}$. We observe that each orientation reveals the coupling with a specific mode supported by the nanorod. There is a 40-fold enhancement at $\lambda_{em} = 660$ nm for a dipole normal to the metal surface ($z$-oriented). The $x$-oriented dipole (oriented along the long axis of the nanorod) shows a decay rate enhancement of 13 at $\lambda_{em} = 520$ nm. Figure 6(c) displays calculated extinction spectra of the nanorod, which

Fig. 6. (a) Schematic view of the simulation configuration for the calculation of a dipole coupled with a single nanorod. (b) Calculated decay rate enhancement of an emitter (dipole) placed on top of a silver nanorod for three dipole orientations. (c) The calculated extinction spectra of the same nanorod for two angles of incidence. The incident light is polarized along the x-axis.
is illuminated with an x-polarized plane wave. The curves indicate that the decay rate enhancements result from the coupling with the 2\textsuperscript{nd} and the 3\textsuperscript{rd} order longitudinal LSPRs \cite{32, 33} at which the resonances appear at $\lambda = 660$ nm and $\lambda = 520$ nm, respectively. For a dipole oriented along the nanorod short axis (y-oriented), a decay rate enhancement of 10 is observed at $\lambda_{em} = 500$ nm, corresponding to the transverse LSPR mode (not shown in the figure). The region where the decay rate enhancement at a single nanorod has a maximum (see Fig. 6) does not coincide with the QD emission spectrum or the spectral region detected in our experiment. Therefore the observed enhancement is largely due to the coupling with the SLRs (see below), supported additionally by the fact that we observe the directional emission in the angle-resolved measurements.

We simulate also the case of silver nanorod arrays with dipoles on top. As depicted in Fig. 7(a), we perform FDTD simulations by setting periodic boundary conditions along the x-axis and y-axis, which effectively creates an infinite periodic array. The lattice periodicity along the y-axis is fixed to $p_y = 200$ nm. Figure 7(b) shows the calculated decay rate enhancements for two lattice periodicities $p_x = 400$ nm and $p_x = 415$ nm. Here, the normalized decay rate enhancement is defined as an average rate over all three dipole orientations, $\Gamma / \Gamma_0 = (\Gamma_x + \Gamma_y + \Gamma_z) / (3\Gamma_0)$. We observe maximum decay rate enhancement of 75 at $\lambda_{em} = 585$ nm for $p_x = 400$ nm, and maximum enhancement of 60 at $\lambda_{em} = 608$ nm for $p_x = 415$ nm ($\lambda_{em} = 608$ nm corresponding to the QD emission peak). In the experiments, the observed decay rate enhancements are one order of magnitude lower than the maximum enhancements in the simulated ideal case. However, it must be remarked here that the lifetime is experimentally measured over a broad spectral region (617 ± 37 nm). Furthermore, the simulations are performed for the QDs in fixed positions with respect to the nanoparticles, while in the experiments the locations of the QDs on/around the nanoparticles vary. Therefore, the measured enhancement is an average value over the whole spectral region and different positions. For $p_x = 400$ nm, e.g., the simulated decay rate enhancement at $\lambda_{em} = 608$ nm is only 7.2, which is the same order of magnitude as obtained in the experiments.

Fig. 7. (a) Schematic view of the simulation configuration for the calculation of the decay rate enhancement of dipoles coupled with an array of silver nanorods. (b) Calculated decay rate enhancements of the dipoles coupled with nanoparticle arrays for two lattice periodicities $p_x$.

In the simulations, we place an electric dipole, which models the dipolar transition moment of the QD, on top of a single nanorod or nanorod with periodic boundary conditions. The intrinsic quantum yield of the QD is assumed to be unity. Thus, the quantum yield of the QDs on top of the structure can be calculated by integrating the power propagating into the far-field divided by the total dissipated power from the dipole(s): $\eta = \Gamma_{\text{Radiative}} / \Gamma_{\text{Total}} = P_{\text{Radiative}} / P_{\text{Total}}$. By doing this, a quantum yield of 28% is obtained at $\lambda_{em} = 608$ nm for an isotropic dipole on top of a single nanorod, as schematically shown in Fig. 6(a). In contrast, the calculated
quantum yield for dipoles on top of nanoparticle arrays with periodicities $p_x = 415$ nm and $400$ nm, as schematically shown in Fig. 7(a), are $50\%$ and $10\%$ at $\lambda_{em} = 608$ nm, respectively. For instance, for the array with $p_x = 415$ nm at QD emission peak wavelength, the spontaneous emission decay rate enhancement of $60$ and quantum yield of $50\%$ are obtained. Therefore, as the intrinsic quantum yield is assumed to equal $1$, also the radiative decay rate of the hybrid QD-SLR system is enhanced by a factor of $30$. This simulation result indicates that also in the experiments the radiative decay rate is enhanced.

6. Conclusion

In conclusion, we have demonstrated that the functionalization method provides a useful tool for assembling and fabricating hybrid structures of QDs and metal nanoparticle arrays. We have shown that the presence of plasmonic nanoarrays in the vicinity of QDs strongly affects their emission properties. The emission from the randomly-oriented QDs couples with the collective SLR modes of the plasmonic lattice, resulting in a directional light emission. Coupling with the plasmonic modes was also found to enhance the spontaneous emission decay rate of QDs. The ability of the nanostructures to enhance emission is supported by numerical simulations. While the simulations predict enhancement on the order of $50 - 100$, in the actual structures we observe enhancement on the order of $2 - 10$.

Enhancement of the decay rate and shaping of the emission direction have been shown before for other types of plasmonic nanostructures and QDs, see for instance [22, 34, 35]. However, for the particular type of plasmonic nanoparticle arrays considered here, only one study exists [8]. Our work goes beyond that by considering QDs instead of quantum rods, by the lifetime measurements and simulations, and notably, by the functionalization method developed here. Our results are of interest considering the potential of this type of nanoparticle arrays with respect to lasing [9–12], strong coupling studies [13–15], and even prospects of phenomena such as photon condensation [36].

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