

Exciton–Plasmon Interactions in Quantum Dot–Gold Nanoparticle Structures

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Supporting Information

ABSTRACT: We present a self-assembly method to construct CdSe/ZnS quantum dot-gold nanoparticle complexes. This method allows us to form complexes with relatively good control of the composition and structure that can be used for detailed study of the exciton-plasmon interactions. We determine the contribution of the polarization-dependent near-field enhancement, which may enhance the absorption by nearly two orders of magnitude and that of the exciton coupling to plasmon modes, which modifies the exciton decay rate.



KEYWORDS: Quantum dot, nanocrystal, gold nanoparticle, plasmon, exciton, self-assembly, CdSe/ZnS, DNA

The controlled coupling of a quantum emitter (QE) to a metal nanoparticle (NP) is one of the most challenging yet promising goals in plasmonics. This coupling profoundly affects the QE absorption and emission rates, and, hence, by controlling the design of a QE-NP structure one can tailor the optical properties of the system. The mechanisms through which these rates are affected by the QE-NP coupling are different. The QE absorption changes due to the local field enhancement near the NP,^{1,2} while its emission is modified due to the interaction between the QE dipole and the plasmons in the NP. This interaction may lead to an enhanced radiative rate when dipole modes are excited in the metal and to emission quenching when higher multipoles are excited.^{1,3}

Many studies of QE-NP interactions were conducted with organic molecules as the emitter. The ease of attaching these molecules to metal surfaces, by direct bonding or through an intermediate ligand, has triggered a wealth of studies of this system.^{4–7} However, organic molecules are characterized by a large overlap between the absorption and emission spectra, and it is therefore difficult to isolate the changes which are due to absorption enhancement from those related to emission changes.⁴ This gives rise to a large scatter in the reported results^{3–6,8–10} and limits our insight into the behavior of the system.

[']Semiconductor quantum dots (QDs) offer several advantages in this context.^{10–14} Their absorption spectrum extends over a broad range, and it is simple to overlap it with the spectrum of NP plasmon of various sizes and material systems. The emission spectrum, on the other hand, is narrow and wellseparated from the absorption. In fact, it is typically narrower than that of the plasmon, and therefore by selecting QDs of different sizes one can tune the exciton emission across the plasmon resonance. Finally, the strong oscillator strength associated with the QD exciton allows performing single object experiments easily. Indeed, the formation of a QD-NP system has been a subject of growing interest in the past decade. The straightforward approach to realize this system is based on using a scanning probe. In this approach the QD-NP distance was controlled either by moving a NP on a substrate with QDs using an atomic force microscopy (AFM) tip¹⁵ or by using the metallic AFM tip itself as the plasmonic structures.¹⁶ Other approaches have used patterned metallic substrates to define the plasmonic structure. The QDs are either distributed uniformly¹⁷ or positioned in prepatterned locations.^{13,18}

In this work we present a method to construct QD-NP complexes, which is based on the self-assembly of gold NPs and CdSe/ZnS QDs.^{19–21} The QD-NP distance in these complexes is defined by an intermediate DNA molecule, through the number of DNA basepairs.²² This method allows us to form complexes with relatively good control of the composition and structure that can be used for a detailed study of the QE-NP coupling. We determine the plasmonic effect on the QDs absorption and separate it from the changes in the emission. We find that when the incident polarization is changed from

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        Received:
        May 22, 2012

        Revised:
        June 26, 2012

        Published:
        June 27, 2012
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being aligned along with to being perpendicular to the QD-NP axis the QD absorption may change dramatically, by nearly 2 orders of magnitude in NP-QD-NP structures, thus offering an effective tool for controlling the emission of these objects.

The schematic structure of the QD-NP complexes that we study is illustrated in Figure 1. We start with commercially



Figure 1. QD-NP complexes studied in this work. The QDs (blue spheres) are surrounded by streptavidin molecules and are connected by an intermediate biotin-dsDNA-thiol molecule to 80 nm gold NPs (yellow spheres). (a) Multiple QDs attached to a single gold NP, (b) a single QD attached to a single gold NP, and (c) a single QD having two DNA strands in between two gold NP (all scale bars are 50 nm.).

available CdSe/ZnS QDs covered with streptavidin (Invitrogen) and suspended in aqueous solution. The gold NPs are prepared in a two-stage process: 17 nm gold nanoparticles are prepared by citrate reduction of gold precursors in the presence of tannic acid.²¹ These NPs are used as seeds for the growth of larger spherical NP in three steps, using hydroxyl amine as the reducing agent (see Supporting Information for this letter). The NP diameter is selected to be 80 nm throughout this work. This relatively large size gives rise to strong plasmonic effects, which are typically proportional to the NP volume and hence facilitate the measurements. To link the QDs to the gold NPs we use thiol-DNA-biotin molecules: the thiol end of the molecule covalently binds to the surface of the gold NP, while the biotin end binds to the streptavidin on the QD. By controlling the QD to NP ratio we can form structures that consist of one or multiple QDs that are attached to a single NP (Figure 1a,b). When a few DNA molecules are attached to a single QD we can obtain structures where several NPs are connected to a single QD, in particular NP-QD-NP structure (Figure 1c). We select the desired complex from the solution using gel electrophoresis separation.¹⁹ The full description of all of the synthesis processes is available in the Supporting Information for this letter.

A key aspect of our studies is the use of photoluminescence excitation (PLE) measurements as the method to obtain the QD absorption: We scan the exciting wavelength continuously over a broad range and measure the emission spectrum (Figure 2a). The changes in the integrated emission intensity as a function of excitation wavelength is proportional to the absorption spectrum. This method allows us to isolate the absorption spectrum of the QD from other processes that occur in parallel in the solution, primarily resonant scattering. We perform these measurements using a Jobin Yvon Fluorolog-3 spectrofluorometer system. Figure 2b shows a comparison between the PLE spectrum of a solution of NPs connected to multiple QDs (Figure 1a) and a solution of bare QDs. To be able to compare the two, we normalize the spectra such that the emission intensity of the two solutions under excitation at 350 nm coincides. It is seen that the two spectra lie precisely on each other over a broad spectral range (350–480 nm) and separate as the excitation energy approaches the plasmon resonance wavelength at 560 nm. The absorption enhancement at the plasmon resonance is clearly visible.

To determine the enhancement factor we simply divide the QD-NP spectrum by that of the bare QD, and the results are shown in Figure 2c. We perform this measurement on different QDs, with emission wavelengths ranging between 565 nm and 655 nm, and observed very similar enhancement factors, ranging between 3 and 4. To compare our results with theory we calculate the local field enhancement factor as a function of the excitation wavelength for this geometry, averaging over the different incident light polarization. We use the boundary element method 23 to perform fully retarded electromagnetic calculations of QD-NP and NP-QD-NP structures. Near-field intensities, dependence on excitation polarization, ensemble averages, and decay rates of a dipole embedded in the dot are determined. It is seen that the calculated wavelength dependence of the enhancement is in a very good agreement with our measurement. In particular, the measured 4-fold enhancement agrees nicely with a 10 nm gap (Figure 2d). This length is the expected gap in our structure, which consists of 20 base-pairs of double-stranded DNA (6 nm) and a streptavidin tetramer (4 nm), and is verified in transmission electron microscopy (TEM) imaging. We have conducted experiments with smaller NPs, with 40 and 60 nm diameters, and observed a smaller enhancement, as expected from theory. Previously published measurements of plasmon enhancement have given enhance-ment factors that span a large range.^{3-6,8-10} Our experiment resolves this ambiguity and gives a quantitative value for the enhancement factor.

To obtain a complete picture of the QD-NP interaction, we conduct time-resolved measurements of the QD exciton emission. Figure 2e compares the emission lifetime of bare QD and QD-NP solutions, with peak emission at 605 nm. The bare QD lifetime could be easily resolved within our time resolution and is found to be 17 ns. It is seen that the QD-NP lifetime is much shorter and is comparable to our time resolution. Using an iterative fitting process, in which the measured system response is convolved with exponential decay rates, the QD-NP data could best be fit to two exponential decay rates of 0.3 and 1.4 ns. Figure 2f shows the calculated enhancement of the decay rates for a 10 nm gap QD-NP structure. It is seen that the total decay rate, which is the sum of the radiative and nonradiative rates, increases by more than an order of magnitude at 605 nm, in good agreement with the observed result. We note that both rates should be enhanced in the QD-NP structure relative to the bare QD, and the quantum efficiency, which is the fraction of the radiative rate from the total, becomes approximately 0.5 at 600 nm, and may go down to 0.05 at 520 nm.

The solution measurements described above are insensitive to the incident polarization. To study this aspect we conduct measurements of single objects, consisting of a gold NP attached to a single CdSe/ZnS QD (Figure 1b). This experiment is performed using an inverted Nikon TI-E microscope in an epifluorescence configuration. The objects



Figure 2. Photoluminescence excitation (PLE) and lifetime measurements of aqueous solutions containing complexes of multiple QDs attached to single gold NPs. (a) The emission intensity as a function of excitation and emission wavelengths. (b) A comparison between the PLE spectra of QD-NP structures and bare QDs (the PL intensity is measured at 655 nm). The plasmon enhancement of the QD absorption around 560 nm is clearly visible. (c) The enhancement spectrum of various QD-NP structures emitting at 565, 585, 605, 655, and 705 nm. (d) A calculation of the average near field enhancement spectrum for a QD-NP structure (5 nm QD, 80 nm NP, 10 nm spacing). (e) The decay time of bare QDs (blue) and QD-NP structures (green; the system response is shown in red). The large decrease of the decay time in the QD-NP structures is clearly visible. (f) The radiative and nonradiatiative decay rate of QD-NP (relative to a bare QD) and the quantum efficiency as function of the emission wavelength.

are dispersed on a microscope coverslip and are immersed in water. They are illuminated by a 532 nm laser (1 μ W) focused to a tight spot (2 μ m diameter), and the collected light intensity is measured by an imaging spectrometer (Andor SR-303i) and an EM-CCD (Andor Ixon^{EM}+ 897). We verified by SEM imaging that the objects are well-dispersed, and the typical distance between them is much larger than the excitation spot. Figure 3a shows a typical emission spectrum of a single QD measured in this system (red line). It is clearly seen that the spectrum of this single object is significantly narrower than that obtained in a solution measurement (gray line), reflecting the size distribution of the QDs in a solution.

We measure 50 bare QDs and compare their emission intensity to that of a similar number of QD-NP. We find that the QD-NP ensemble exhibits a significantly broader distribution of intensities. The uniformity of our reaction products, NP and QD size as well as the QD to NP separation, suggests that the large variability in emission intensity does not originate from inhomogeneity of the objects but is rather fundamental. We show below that the reason for this variability is the random orientation of the symmetry axis of the various QD-NP objects relative to the laser polarization.

Figure 3b shows the emission intensity of a single QD-NP object as the excitation polarization angle is varied. It is seen that the intensity exhibits a clear and reproducible sinusoidal dependence on the polarization angle. We took special care to verify that this dependence does not originate from a measurement artifact, such as slight movement of the excitation spot with the rotation of the polarization. Indeed, the maximum for different objects appears at different angles. This proves that



Figure 3. Single object measurements. (a) A comparison of the measured emission spectrum of a single QD and of a solution of QDs. (b) Two consecutive measurements (blue and pink) of the emission intensity of a single QD while continuously varying the excitation polarization. (c) The emission intensity as a function of laser polarization for a single QD-NP and a bare QD. The data are taken by performing five consecutive measurements as in b and taking the "high" values. (d) The calculated near field enhancement factor for a QD-NP structure (5 nm QD, 80 nm NP,10 nm spacing) as a function of the excitation polarization angle with respect to the axis connecting the QD and the NP.

the observed dependence is due to the relative orientation of the QD-NP axis relative to the laser polarization. It is seen that the sample shows emission intermittency, which is a characteristic of a single QD measurement, and in the following we consider the highly emitting state only.

Figure 3c compares the polarization dependence of a bare QD and a single QD-NP. We present the curve of a QD-NP object, which exhibits the largest contrast, presumably because its axis is parallel to the coverslip plane. Objects that are oriented at an angle to this plane would have lower polarization dependence. We note that there is a weak polarization dependence also in the bare QDs measurement. This is probably related to an asymmetry in the QD shape.^{24,25} The sinusoidal dependence of the QD-NP objects agrees well with the expected plasmonic behavior: the near field around the metal sphere is maximal along the laser polarization axis, and minimal perpendicular to it. As we rotate the laser polarization we move the maxima and minima around the NP, and consequently modify the local field experienced by the QD. At the peak of the curve we find that the emission intensity of the QD-NP is enhanced relative to the bare QD, by approximately a factor of 4, while the intensity at the minimum is suppressed. Figure 3d shows the calculated polarization dependence of the enhancement factor for a 10 nm gap. It is seen that the contrast

ratio between minimum and maximum values, which is approximately 7, agrees very well with that found experimentally. This calculation describes only the enhancement of the local field at the QD. The measured emission intensity is a product of this enhancement curve and the modified quantum efficiency, which is \sim 0.5 at this wavelength (Figure 2f).

The strong polarization sensitivity is further enhanced in the NP-QD-NP structure (Figure 1c). Figure 4a shows the polarization dependence of the emission intensity for a single NP-QD-NP object and compares it to a bare QD (its average is taken to be 1). Again, a sinusoidal dependence is observed, but this time with a contrast ratio, which is close to 100. Figure 4b shows a calculation of the near field intensity for this structure. We find that the contrast ratio is maximal when the QD is located on the axis between the spheres and drops as the QD shifts away from this axis. This maximum is close to 100 for the parameters of our sample, in a very good agreement with our findings. This observation demonstrates the strength of plasmonic structure design in tailoring the optical properties of a quantum emitter.

In conclusion, our measurements provide quantitative insight into the various mechanisms affecting the plasmon coupled QD emission. In particular, we separate the contribution of the near field enhancement near the NP, which gives rise to an increase



Figure 4. NP-QD-NP structure measurements. (a) Emission intensity of a single NP-QD-NP structure as a function of the polarization angle. We obtain up to 20-fold enhancement with respect to a typical bare QD, and there is 85:1 contrast between the maximal intensity to the minimal intensity. (b) Calculated near field enhancement for a NP-QD-NP structure (5 nm QD, 80 nm NP, 5 nm spacings).

of the absorbed power in the QD, and that of the excitonplasmon interaction, which modifies the decay rates and the corresponding quantum efficiency. We show that the selfassembly of QD-NP complexes by the highly specific biotin– avidin interaction and the use of DNA molecules as a spacer provide us with a useful tool for controlling quantum emitter– plasmon interaction.

ASSOCIATED CONTENT

S Supporting Information

Further details of the experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Israel Science Foundation. All mention of product names is done to provide a complete description of this work. This does not imply a validation or endorsement of these products by NIST.

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