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Polarization-resolved plasmon-modulated emissions of quantum dots coupled to aluminum dimers with sub-20-nm gaps

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Abstract

Aluminum dimer nanoantenna with nanogaps is an ideal platform for enhancing light-matter interaction at the nanoscale for the UV-Vis spectrum, but its realization has been hindered by the surface oxidation of aluminum nanostructures, aluminum interband loss and practical limitations in lithographic patterning. Here, we have overcome these problems and demonstrated the successful fabrication of aluminum dimer antenna with ~ 10 nm gap, which to the best of our knowledge marks the smallest features of Al nanoantenna. We present the first in-depth study of strongly polarization-dependent emissions of colloidal quantum dots coupled with Al dimers, and elucidate the individual contributions of the excitation intensity, quantum yield, and extraction efficiency enhancements from numerical and experimental perspectives. We estimate the Purcell effect corresponding to a single Al-dimer antenna as ~ 104 by taking into account the ensemble averaging effect and the distributions in emitter dipole orientations. This finding brings a step closer towards a cost-effective realization of bright and ultrafast single emitters.

Introduction

The high spatial overlap between highly localized plasmonic fields with nanoscale objects, and the dramatic increase in the local density of states (LDOS) at plasmonic “hot spots” have led to the enhancement of light-matter interaction at the nanoscale ^{1,2}. The enhancements of various

optical processes, such as light absorption ^{3,4}, photoluminescence ⁵⁻⁹, higher harmonics generation ¹⁰⁻¹⁴, and Raman scattering ¹⁵⁻¹⁸ have been observed in plasmonic nanostructures. In particular, polarization-dependent photoluminescence enhancement of colloidal quantum dots or fluorescence molecules in the vicinity of plasmonic nanostructures has been extensively studied for its potential application in bright and ultrafast single emitters ¹⁹⁻²⁶. The integration of quantum emitters with metal nanoantenna is carried out by embedding the quantum emitters into a polymer host and by spin casting quantum emitter thin film on a substrate. Dye molecules may be doped into a polymer matrix ^{25,27-29}, or drop cast on a substrate at diluted concentrations in order to prevent emission quenching resulting from molecular aggregation ³⁰, while colloidal quantum dots can be applied as a thin film ³¹⁻³³, or as individual emitters ³⁴ that can be surface-functionalized onto metal surfaces ³⁵.

All these enhancements employed gold (Au) and silver (Ag) nanoparticles, most of which are synthesized by self-assembly processes. This is attributed to a very small damping loss in synthesized metal nanoparticles due to their crystallinity, in addition to the fact that gold and silver exhibit low damping loss in the visible and infrared range. However, the light-matter interaction with aluminum (Al) nanoantenna has not been explored as extensively as its Au and Ag counterparts. Despite having the highest plasma oscillation frequency among plasmonic metals ^{36,37}, in addition to being inexpensive and corrosive-resistant, Al actually suffers from much higher damping loss compared to Au and Ag due to its interband transition at 800 nm. There are also other challenges associated with Al surface roughness and native oxidation in Al nanostructure fabrication ³⁸. The plasma oscillation frequency in the deep ultraviolet range makes Al plasmonics an interesting platform for studying light-matter interaction in the UV-vis spectrum, particularly when the enhancements can be facilitated from both the excitation and emission aspects. Recently, periodically arranged Al nanodisks have been investigated for enhancing the emissions of dye molecules and colloidal quantum dots ^{39,40}, where the enhancement was achieved through the surface lattice resonance resulting from the interference of in-plane scatterings from individual nanodisks. Stronger light-matter interaction is to be expected in Al nanoantenna with much reduced mode volume. In this work, we present the first in-depth study of polarization-dependent CdSe/CdS colloidal quantum dot emissions coupled with Al dimer nanoantenna of sub-20-nm gaps. Unlike in other reported works that employed self-assembled metal nanoparticles, the Al dimers in this work were defined lithographically where various dimer sizes, gaps, and orientations can be fabricated on a single chip. This enables us to study systematically the individual contributions of excitation intensity,

quantum yield, and extraction efficiencies in the experimentally measured enhancements for different resonance detuning from the quantum dot emission. Specifically, we demonstrate the plasmon-modulated quantum dot emissions in the polarization-resolved PL measurements of quantum dots coupled with Al dimers, where up to ~ 4.84 -fold PL intensity enhancement has been achieved for Al dimer with small detuning from the emission wavelength. Modification of emission rate with average Purcell factors of ~ 1.5 is observed for PL emissions with polarizations parallel to the dimer, corresponding to an estimated Purcell factor of ~ 104 by a single antenna when ensemble averaging and distributions in emitter orientations are taken into account.

Results

The determining factors for PL enhancement in plasmonic nanoantenna are the local electric fields that signify the local density of photonic states and the radiative efficiency. Square dimer geometry is chosen for its design simplicity and strong local electric fields across the nanogaps. The schematic of a square dimer with dimer size (s) and gap (g) is shown in Figure 1a, with its long axis oriented along the x axis. Despite the known challenges in Al nanoantenna fabrication due to its surface oxidation and dimensional constraints, we have overcome this issue and demonstrated the successful fabrication of Al split ring resonator structures with features as small as ~ 20 nm⁴¹. The transmission electron microscopy (TEM) images of the quantum dot thin film is shown in the inset 1, where the size of the core-shell geometry is deduced as $d \sim 7.51 \pm 0.55$ nm from 120 quantum dots. The determining factors for the PL enhancement are large local E -field enhancement at the plasmonic hotspot and high spatial overlap between the plasmonic field and the quantum emitter. The former is achieved by decreasing the gap size, while the latter by ensuring that the gap sizes are comparable to quantum dot size. For this purpose, we fabricated Al square dimers with 10 nm gaps. The SEM micrograph of this dimer is shown in Inset 2, where the sample was first spin coated with ~ 30 -nm thick conductive polymer to prevent charging during SEM. To minimize the near field coupling between the dimers, the periodicity (p) for these dimer structures was designed as 4x the dimer size ($p = 4s$). This design was verified by our numerical simulations, where the scattering cross section of the dimers is always smaller than the area of the unit cell ($\sigma_{scat} < p^2$). This density is also sufficient for ensuring strong signals in transmission and reflection measurements under bright field geometry. We also exploited the native surface oxidation of Al to form a ~ 3 nm thick Al₂O₃ encapsulation layer for the Al nanostructure, which proves useful for reducing the

emission quenching that normally occurs when quantum emitters are brought to close proximity to metals^{42,43}. The electric field localization across the ~10 nm gap also ensures high quality factor over mode volume (Q/V_{mod}), which translates to high local density of states (LDOS).

The Al nanoantenna were fabricated on quartz substrate, followed by spin coating of 40-nm thick CdSe/CdS quantum dot film (~5 monolayer thick). This film thickness was chosen to ensure a full coverage of the 30-nm thick Al nanostructures. The refractive index of the CdSe/CdS colloidal quantum dot is typically in the range of 1.7-1.95, and it is well known that coating thin film onto metal nanostructure introduces red shift in their resonance wavelengths. In order to take these into account, the Al nanoantenna with smaller dimensions need to be fabricated to compensate such a red shift. The photoluminescence (PL) signals for quantum dots coupled with Al square dimers were characterized by a home-built PL mapping system, where mercury lamp coupled with 434 nm bandpass filter was used as the excitation source (see methods and supplementary information). The quantum yield of CdSe/CdS quantum dot in this work is QY=60%, which is sufficient for compensating the weak excitation intensity of our mercury lamp. In order to increase the PL signal contrast, the dark field geometry is employed in the PL setup to minimize the background excitation signals.

The polarization-resolved PL enhancements from Al square dimers with $g \sim 10$ nm gaps are shown in Figure 1b and 1c for X and Y polarized PL emissions, respectively. The PL signals from the quantum dot film outside of our dimer region are also indicated by the black curves. The strong polarization dependence is indicative of the role of surface plasmons in modulating the PL emission, particularly when the enhancement for the X-polarized PL emission (*PLEX*) is stronger than that of the Y-polarized PL emission (*PLEY*). The stronger PL enhancement for X polarized emission is related to the mode characteristic of a plasmonic dimer, which can be understood in terms of dipolar coupling between the dipole modes of the constituent gold square disks. The extinction cross sections of plasmonic dimer under X and Y polarizations are shown in Fig. S2. When the dimer is excited under X polarization, the dipole modes interact capacitively and give rise to strong *E*-field localization in the dimer gap (Fig. S2, Inset 1). In addition to this field localization, the dipolar coupling also imparts red shift to the resonance. Under Y polarization, however, there is no capacitive coupling since the electric dipoles are parallel to each other. This give rise to a mode characteristic resembling that of the individual

plasmonic disk (Fig. S2, Inset 2). Thus, the stronger field enhancement under X polarization is mainly caused by the capacitive coupling that give rise to strong E -field localization in the dimer gap.

The effect of plasmonic resonance detuning from the quantum dot emission is exemplified in the PL enhancements for different dimer sizes, where the corresponding $PLEX$ ($PLEY$) of ~ 2.88 (~ 2.72), ~ 4.84 (~ 2.32), and ~ 1.93 (~ 2.1) are observed for dimer sizes of $s = 100$ nm, $s = 80$ nm and $s = 60$ nm, respectively. The plasmonic resonances can be further tuned towards the quantum dot emission by changing the dimer gap and exposure dose during e-beam patterning. Figure 2a and 2b show the transmission responses of Al dimer ($s = 100$ nm) with different gaps, where the plasmonic resonance progressively red shifts at decreasing gap. We observed a slight blue shift as the gap decreases from $g = 30$ nm to $g = 20$ nm. Such a slight inconsistency is mainly caused by the spectral complications arising from the absorption and re-emission of light in the quantum dot film. This is confirmed in the transmission of gold dimers on ITO substrate without quantum dot coating, showing consistent red shift for decreasing gaps (Figure S3, Supplementary Information). A more practical method for tuning resonance is by changing dimer size through exposure dose variation in the nanopatterning. Increasing e-beam dose results in larger dimer size and smaller dimer gap. The tuning range for the X polarization is thus expected to be larger than that for the Y polarization. This is because both the increase in the dimer size and the longitudinal coupling contribute to the red shift of the plasmonic resonance along the X polarization. This is illustrated in Figure 2c, where ~ 80 nm tunability was achieved by increasing the exposure dose by 40% for the resonance along the X polarization. In contrast, for the plasmonic resonance along the Y polarization, the red shift caused by the increase in dimer size is compensated by the blue shift caused by the increase of transverse dipolar coupling. This is illustrated in Figure 2d, where the resonance can be either blue or red shifted depending on which mechanism dominates from the increase of dimer size. We compiled the measured PL intensity enhancements from all set of Al dimers with different gaps and sizes, which were patterned at different exposure doses; and then present their PL enhancements as a function of resonance detuning in Figure 3. The resonance tuning range for X and Y polarizations are ~ 300 nm and ~ 200 nm, respectively. The dimers exposed at different e-beam dose are grouped according to their sizes, i.e., $s = 100$ nm (red), $s = 80$ nm (green), $s = 60$ nm (blue), and nominal gaps, i.e., $g = 30$ nm (squares), $g = 20$ nm (circles), $g = 10$ nm (triangles). Due to the spectral complications arising from the quantum dot absorptions and re-emissions, the resonance positions for the dimer structures were deduced

from the transmission dips instead of reflection peaks. The transmission linewidths of these dimers were found to be in the range of ~ 60 - 180 nm, making the Q factors in the range of ~ 4 - 8 . As evident from Figure 3 (right panel), larger PL enhancements are observed as the resonance is tuned towards the quantum dot emissions. The same trend is observed for the Y polarization, although not as apparent as the X polarization. This result clearly demonstrates the role of plasmonic radiation in shaping the PL emissions.

We then studied the lifetime modification from time-resolved PL signals of the quantum dots (QDs) on Al dimers with 80-nm size and 20-nm gap. The decay rates corresponding to quantum dots with and without Al nanostructures are presented in Figure 4a. Due to the unpolarized nature of the time-resolved PL measurements, we also include the decay rates of QDs on Al film and isotropic Al dimers. The isotropic dimer in this context consists of four Al square nanodisks separated by nanogaps in x and y directions. Based on this design, the E -field localization across the nanogaps occurs not only under X polarization as in the typical dimers but in both X and Y polarizations equally. The corresponding PL intensity enhancements for the dimer structure is presented in the inset, showing $PLEX \sim 3.43$ and $PLEY \sim 2.19$. The smaller intensity enhancements for this dimer (i.e., $s = 80$ nm, $g = 20$ nm) compared to those in Figure 2a-b ($s = 100$ nm, $g = 20$ nm) are attributed to the weaker E -fields across wider dimer gap, and blue-shifted resonances resulting from weaker longitudinal coupling. This is illustrated by the transmission responses of the same dimer (inset of Figure 4a), showing resonance positions at ~ 569 nm and ~ 518 nm for X and Y polarizations, respectively.

Owing to various optical processes, the decay rate of the QDs cannot be modelled by a single exponential model⁴⁴. The lifetime distributions of different scenarios are presented in Figure 4b, where the area under the curve for each distribution is normalized to unity. The progressive reduction in the emission lifetime can be observed clearly as the CdSe/CdS quantum dots ($\tau_{\text{avg}} = 9.13$ ns) are coupled with Al thin film ($\tau_{\text{avg}} = 7.2$ ns), Al dimers ($\tau_{\text{avg}} = 6.56$ ns), and Al isotropic dimers ($\tau_{\text{avg}} = 5.82$ ns). From the lifetime distribution measurements, there exist two processes responsible for the decay rate modification. The first modification originates from the metal itself, as evident from the comparison between the QD film on glass (first panel) and on the Al thin film (second panel). The second modification is caused by plasmonic resonances of the metal nanoantenna. The existence of these two processes is clearly seen in the two peaks of the lifetime distributions in the Al dimers (third panel). The peak around ~ 6 ns is associated with the modification based on plasmonic resonance along the X polarization, while the peak

around ~ 7 ns is associated with the modification based on the metal itself because the plasmonic resonance along the Y polarization is largely detuned from the quantum dot emission. Another agreement is found when the position of the second peak (~ 7 ns) is close to that of the distribution from Al thin film (~ 7.2 ns). In order to ascertain that the second peak does originate from a far-detuned plasmonic resonance along the Y polarization, we measured the lifetime distributions of QDs on isotropic Al dimers which exhibit the same plasmonic resonances along X and Y polarizations. As illustrated in the last panel, the lifetime distribution of the QD film on isotropic dimers does exhibit only a single peak positioned around ~ 6 ns, in a good agreement with the position of the first peak from the Al dimer sample.

Discussions

As the PL intensity depends mainly on the excitation intensity (I_{EXC}), quantum yield (QY) and the extraction efficiency (η) of the measurement setup, the measured PL enhancements are not solely caused by plasmonic resonance. Based on this understanding, the PL enhancement can be expressed as $PLE = PLE(I_{EXC}) \times PLE(QY) \times PLE(\eta)$, where $PLE(I_{EXC})$ is the enhancement of excitation intensity, $PLE(QY)$ is the enhancement of quantum yield, and $PLE(\eta)$ is the enhancement of extraction efficiency. The PL enhancements are dominated by the excitation intensity enhancement when the plasmonic resonance is much shorter than the emission wavelength and close to the excitation wavelength. This is clearly seen in the ~ 2 -fold PL enhancement of QD coupled to 60-nm sized dimers (Figure 3). As the plasmonic resonances are tuned towards emission wavelength, the PL enhancements are mainly determined by $PLE(QY) \times PLE(\eta)$, where the highly localized electric field results in the enhancement of both quantum yield due to the increased local density of states, and antenna radiation due to the strong electric dipole. The role of the local field enhancement in the PLE can be further studied by comparing the PLE_X and PLE_Y of different dimers whose resonances are of the same detuning. In Figure 5, we present the $PLE_X = 4.84$ corresponding to dimers with $s = 80$ nm and $g = 10$ nm (Fig. 1b, $s = 80$ nm) and the $PLE_Y = 2.71$ corresponding to dimers with $s = 100$ nm and $g = 10$ nm (Fig. 1c, $s = 100$ nm), both of which have near zero detuning with the quantum dot emission wavelength. The calculated electric field distributions from the insets reveal that the local electric field is ~ 2 x stronger for the X-polarization than for Y-polarization. From the perspective of the local density of states ($\propto |E|^2$)⁴⁵, the spatially-averaged enhancement per unit area ($\propto (1/p^2) \int_{cell} |E|^2 dx dy$) for X polarization is expected to be ~ 1.44 x higher than that for the Y polarization.

In addition to increasing LDOS, strong local E -fields also reshapes QD emission pattern in the vicinity of Al nanoantenna. The extraction efficiency for each dimer can be estimated from the far-field projection (see methods). Using $NA = 0.55$ for the 50x objective lens, the extraction efficiencies for each dimer can be calculated as $\eta_{dimer}^X \sim 33.7\%$ (for X-polarized emissions of dimer with $s = 80$ nm and $g = 10$ nm) and $\eta_{dimer}^Y \sim 24.2\%$ (for Y-polarized emissions of dimer with $s = 100$ nm and $g = 10$ nm), making the extraction efficiency ~ 1.39 x higher for the X polarization. Combining the increase in LDOS (~ 1.44 x) and extraction efficiency (~ 1.39 x) makes the overall PL intensity to be ~ 2 x stronger for the X polarization compared to the Y polarization. This is in reasonable agreement with the ~ 1.78 x stronger PL intensities shown in Figure 5. The extraction efficiency of a QD film without Al nanoantenna with the same objective lens is estimated as $\eta_{QD} \sim 11.5\%$, making the extraction efficiency enhancements of $PLEX(\eta) = \eta_{dimer}^X / \eta_{QD} \sim 2.94$ (for X-polarized emission) and $PLEY(\eta) = \eta_{dimer}^Y / \eta_{QD} \sim 2.1$ (for Y-polarized emission). By assuming $PLE(I_{EXC}) \sim 1$ for near zero detuning, the quantum yield enhancements for the 10-nm gap dimers can be estimated as $PLEX(QY) = PLEX / PLEX(\eta) \sim 1.65$ and $PLEY(QY) = PLEX / PLEX(\eta) \sim 1.29$.

Similarly, the extraction efficiencies for the 20-nm gap dimers (in Figure 4) are $\eta_{dimer}^X \sim 34.9\%$ and $\eta_{dimer}^Y \sim 12.1\%$, giving extraction efficiency enhancements of $PLEX(\eta) = 3.04$ and $PLEY(\eta) = 1.06$. The smaller enhancements in the 20-nm gap dimers are expected as their resonances are more detuned from the emission wavelength, particularly for the Y polarization where the extraction efficiency is not much different than that of the uncoupled QDs. For the X-polarized emission, owing to the large detuning from the excitation wavelength ($\Delta\lambda_{EXC} \sim 135$ nm) and small detuning from the emission wavelength ($\Delta\lambda_{QD} \sim 49$ nm), we can still assume $PLEX(I_{EXC}) \sim 1$ and estimate the quantum yield enhancement as $PLEX(QY) = PLEX / PLEX(\eta) \sim 1.13$. This is consistent with the much larger quantum yield enhancement for the 10-nm gap dimer, which results from stronger local E -fields across the gap and smaller mode volume. For the Y-polarized emission, the contribution from the excitation enhancement cannot be ignored as the detuning from the emission ($\Delta\lambda_{QD} \sim 100$ nm) is larger than that from the excitation ($\Delta\lambda_{EXC} \sim 84$ nm). Thus, the contribution from the excitation and quantum yield enhancements for the Y-polarization are estimated as $PLEY / PLEY(\eta) = PLEY(I_{EXC}) \times PLEY(QY) = 2.07$.

It is also possible to decouple $PLE(QY)$ and $PLE(\eta)$ based on the relation between $PLE(QY)$ and the decay rate modification. From the perspective of decay rate, quantum yield is defined as $QY = k_{rad}/(k_{rad} + k_{nrad})$, where k_{rad} and k_{nrad} are the radiative and non-radiative recombination rates of the quantum dots, respectively. In the vicinity of metal nanoantenna, the emission rate of the quantum dots is enhanced by a Purcell factor defined by $F_p = (k_{na} + k_{rad})/k_{rad}$, where k_{na} is the radiative decay rate caused by the nanoantenna. The modified quantum yield in the presence of metal nanoantenna is expressed as $QY' = (k_{na} + k_{rad})/(k_{na} + k_{rad} + k_{nrad})$, and the quantum yield enhancement is $PLE(QY) = QY'/QY$. The Purcell factor is thus related to the quantum yield by $F_p = (1 - QY)/(1 - QY')$,⁴⁶ indicating that both the emission rate modification and PL intensities occur simultaneously. However, large Purcell factor does not necessarily mean large PL intensity enhancements as the maximum PL intensity enhancement depends on the initial quantum yield of the emitter. Based on the CdSe/CdS quantum dot used in this work ($QY \sim 0.6$), the maximum quantum yield enhancement (corresponding $F_p = \infty$) is thus limited to $PLE(QY)_{MAX} \sim 1.67$.

From the PL traces in Figure 4, the average Purcell factor of the 20-nm gap dimers can be directly measured as $F_{p,X} \sim 1.5$ (for X-polarized emission) and $F_{p,Y} \sim 1.28$ (for the Y-polarized emission). To ensure the reproducibility of these Purcell factors, the same sample was characterized by another time-resolved micro-PL setup based on free-space excitation technique, where comparable Purcell factors of $F_{p,X} \sim 1.4$ and $F_{p,Y} \sim 1.29$ were measured (Figure S4, Supplementary Information). Referring to the Purcell factor for the X-polarized emission (Fig. 4), $F_{p,X} \sim 1.5$ corresponds to a modified average quantum yield of $QY' = 0.73$ and a quantum yield enhancement of $PLEX(QY) \sim 1.2$. This is again in agreement with $PLEX(QY) \sim 1.13$ that was estimated previously. The extraction efficiency enhancement for X-polarized emission is deduced as $PLEX(\eta) = PLEX/PLEX(QY) \sim 2.85$. For the Y-polarized emission, $F_{p,Y} \sim 1.28$ corresponds to a modified quantum yield of $QY' \sim 0.69$ and a quantum yield enhancement of $PLEY(QY) \sim 1.15$. As the plasmonic resonance is close to the excitation wavelength ($\Delta\lambda_{EXC} \sim 84\text{nm}$), we expect the PL enhancement for Y-polarized emission to be contributed mostly by the excitation intensity enhancement. This is supported by the fact that the detuning ($\Delta\lambda_{QD} \sim 100\text{nm}$) is larger than the linewidth of the PL response ($\Delta\lambda_{PL} = 60\text{nm}$). Using $PLEY(\eta) = 1.06$ from the previous calculation, we can deduce the excitation intensity enhancement of $PLEY(I_X) \sim 1.8$ for 20-nm gap dimer. This is in agreement with the ~ 2 -fold

intensity enhancements for 60-nm sized dimers that have small detuning from the excitation source ($\Delta\lambda_{EXC} < 40 \text{ nm}$).

The ideal Purcell factor is calculated based on the assumptions that the emitter is located at the spatial maximum with its dipole orientation perfectly aligned with the nanoantenna local E -fields. Based on the calculated $V_{mod}^X = 2.1 \times 10^{-3}(\lambda/n)^3$ and measured $Q_{meas}^X \sim 6.05$, the ideal Purcell factors for a single dimer antenna with 20 nm gap is $F_{P,X} \sim 104.9$ for X-polarized emission. This is ~ 70 x higher than the measured Purcell factor in Figure 4 ($F_{P,X} \sim 1.5$). This is indicative of the ensemble averaging effect where only quantum dots located within the plasmonic hot spots are significantly modified. By assuming quantum dots to be uniformly distributed within the thin film, the fraction of quantum dots in the plasmonic hot spot can be estimated as $f = V_{mod}/(t_{na}p^2) \sim 0.031$, giving the spatially averaged Purcell factor of $F_{P,AVG} = fF_P + (1 - f) \sim 4.18$. Another equally important factor is the distribution of emitter dipole orientations in the QD thin film. While the dipole orientations are likely to be random in all directions (isotropic) for quantum dots suspended in a solution or when the quantum dot film is very thick, the same property may not hold for quantum dot films with a few monolayers thickness. By assuming $\cos^2 \theta$ dependence in the emission rate for a dipole at angle θ from the local E -field²³, the average dipole orientation for 5-monolayer thick quantum dot film can be estimated as $\theta \sim 53^\circ$ from the XY plane. Better alignment between the emitter and the nanoantenna is to be expected when the QD film thickness is reduced to only a monolayer thick. This may be achieved through surface functionalization for ensuring good adhesion between quantum dots and the substrate.

Conclusion

Photoluminescence emissions of CdSe/CdS colloidal quantum dots coupled with Al plasmonic dimer nanoantenna of sub-20-nm gaps have been experimentally demonstrated together with numerical simulation. The role of plasmonic radiation in shaping the PL responses is evidenced by the strong polarization dependences in the PL emissions. The enhancements of the excitation intensity, the quantum yield, and the extraction efficiency have been investigated in Al dimers with different plasmonic resonances over $\sim 300 \text{ nm}$ of wavelength detuning, and PL intensity enhancements up to ~ 4.84 x and ~ 2.72 x have been measured for emissions along the X and Y polarizations. By tuning the size of Al dimers, we can increase the PL by enhancing either the excitation intensity or emission extraction efficiency. We have shown that the ~ 2 x

PL enhancements for the 60-nm sized dimers are dominated by the excitation intensity enhancement. Based on this understanding, it is possible to design Al nanoantenna with resonance modes matching the excitation and emission wavelengths. In addition to further improvement in the PL emission efficiency, plasmonic nanostructures with multi-resonance modes could be useful for enhancing other process, such as frequency upconversion^{47,48} and photodetection⁴⁹. By comparing the X-polarized and Y-polarized PL emissions of two different dimers with the same near zero detuning, the role of the local E -field in increasing LDOS and reshaping QD emission pattern have been discussed. The faster decay rates and PL intensity enhancements of quantum dots coupled with Al dimer nanoantenna indicate that the rate modification is indeed caused by antenna radiation instead of by non-radiative quenching. Spatially averaged Purcell factors of ~ 1.5 and ~ 1.28 have been measured for X-polarized and Y-polarized emissions from Al dimers with 20 nm gap. By relating the Purcell factor with the quantum yield, we have deduced the enhancement in the quantum yield that results from the higher LDOS, where quantum yields increase from 60% in the QD films to $\sim 73\%$ and $\sim 69\%$ for X-polarized and Y-polarized emissions of QDs on dimers, respectively. Finally, nonidealities associated with spatial averaging and dipole orientation distributions have been identified for causing $\sim 70\times$ smaller Purcell factor in the experimental measurements.

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Contributions

D.H.Z. initiated and supervised the project. L.Y.M.T conceived the idea, fabricated and characterized the transmission and photoluminescence mapping properties of the plasmonic nanostructures. K.E.F. synthesized the CdSe/CdS quantum dots, while L.Y.M.T. built the photoluminescence mapping setup. M.D.B, Y.G, C.D., H.V.D facilitated and characterized time-resolved photoluminescence, where M.D.B and D.C. contributed technical discussions on photoluminescence and Purcell factor. L.Y.M.T. wrote the manuscript, with the inputs from all the authors. All the authors read and approved the manuscript.

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METHODS

Nanofabrication of Al nanoantenna with CdSe/CdS quantum dots. The Al nanostructures were fabricated on quartz glass substrate by sonicated cold development processes⁴¹, where the patterning was done by electron beam lithography system (Raith e_LiNE) with 20keV beam energy and 30pA beam current. The patterned samples were evaporated by 30-nm thick Aluminium at 0.05nm/s rate, followed by lift-off in *n*-methylpyrrolidone for 10 minutes. Different types of Al nanoantenna were fabricated on the same chip, where each nanostructure occupies 100 x 100 μm² footprint. CdSe/CdS quantum dot film (30 mg/ml concentration) was then spin coated at 2000 RPM speed, giving 40-nm film thickness as verified by surface profilometer.

Photoluminescence and optical characterization. Both the photoluminescence (PL) and transmission measurements were carried out by the same microscope system. In the transmission measurements, the halogen lamp was focused by a condenser into the sample and the transmission signals were collected by 10x objective lens (NA 0.3) under bright field geometry. The signals were directed to the transmission grating and CCD sensor, and the piezo stage was scanned in order to get the transmission image. The transmission for a particular nanoantenna array was obtained from the pixels corresponding to the structure, followed by normalization with respect to the signals from the substrate (on which the quantum dot film was spin coated). The image based on 10x objective lens consists of 1024 lines, where the scanning time for each line is 0.05 s. All the signals are averaged within 20 by 20 pixels area. In the photoluminescence measurement, we used mercury lamp coupled (with 434nm bandpass filter) focused by 50x objective lens (NA 0.55). Although PL-measurements can be done in

both dark or bright field geometries, the measurements based on dark field setting exhibit higher signal-to-noise ratio due to the much smaller background excitation. As the excitation source (434 nm) is sufficiently far from quantum dot emission (618 nm), long pass filter (LPF) is not required. The PL measurements in our experiment were done with and without LPF (with onset wavelength at 500 nm), showing good consistency in the PL enhancements. The PL intensity enhancement is obtained by normalizing the pixels corresponding to Al nanoantenna with the pixels corresponding to the quantum dot substrate. The image based on 50x objective lens consist of 720 lines, where the scanning time for each line is 0.5s (with gain ON). As in transmission measurements, the signals are averaged within 20x20 pixels area.

Time-resolved Photoluminescence. The time-resolved PL measurements were obtained by confocal scanning fluorescence lifetime imaging microscopy (FLIM). The sample was excited by a pulsed laser with a wavelength of 375 nm, repetition rate of 20 MHz, and pulse duration of 100 ps. The instrument response is 200 ps. The lifetime mapping area is 900x900 μm^2 . The lifetime of each pixel within the mapping area was recorded, and their distribution was obtained from an area that corresponds to a certain nanostructure.

Numerical simulations. We performed finite difference time domain simulations (FDTD solutions, *Lumerical Inc*) to calculate the optical responses of aluminium square dimer antenna. The scattering properties were calculated using total-field-scattered-field module, where the inward and outward power flows were calculated to deduce absorption (σ_{abs}) and scattering (σ_{scat}) cross sections. The extinction cross section (σ_{ext}) is $\sigma_{ext} = \sigma_{abs} + \sigma_{scat}$. The radiation efficiency of Al nanoantenna was calculated as $\eta_{rad} = \sigma_{scat}/\sigma_{ext}$. The periodic boundary condition was enforced in the simulation in order to take into account the effect of periodicity. The permittivity of aluminium and quartz glass was based on Palik model. The quantum dot film is assumed as dielectric layer with refractive index of $n_{qd} \sim 1.75$, which was obtained from fitting the red-shifted resonances of the Al nanoantenna after quantum dot film is spin coated. The extraction efficiencies were calculated as the fraction of the radiation collected by the objective lens. The radiated power was calculated by integrating the forward and backward far-field projections over all the direction cosines, i.e., $-1 \leq u_{x,y,z} \leq 1$, while the collected power was calculated by integrating the far-field projection over a circular area that represents the numerical aperture of the lens, i.e., $u_x^2 + u_y^2 < NA^2$. The direction cosines are defined as $u_x = \sin\theta\cos\phi$, $u_y = \sin\theta\sin\phi$, and $u_z = \sqrt{1 - u_x^2 - u_y^2}$. The extraction efficiency for the

quantum dot under specific polarization was calculated by representing the quantum dot as dipole source with the same polarization, followed by the same routine as for the Al dimers. The Purcell factor for slightly detuned case was calculated as $F_p(\omega) = (3/8\pi)(\lambda/n)^3(\omega/V_{mod})\rho_{cav}(\omega)$, where $V_{mod} = t_{na} \int_{cell} \epsilon |E|^2 dx dy / \max(\epsilon |E|^2)$ is the mode volume, and $\rho_{cav}(\omega) = (2/\pi)\Delta\omega_{cav}[4(\omega - \omega_{cav})^2 + \Delta\omega_{cav}^2]^{-1}$ is the total density of states of the resonance mode ⁹. The case of $\omega = \omega_{cav}$ leads to the ideal Purcell factor $F_p = (3/4\pi^2)(\lambda/n)^3(Q/V_{mod})$.

FIGURES AND CAPTIONS

Figure 1. Polarization resolved PL-enhancements of CdSe/CdS colloidal quantum dots by aluminum square dimer structures. (a) Schematic of the Al square dimer. The square disk size is varied from $s = 60$ nm to $s = 100$ nm, while the gap spacing is varied from $g = 10$ nm to $g = 30$ nm. The thickness of all Al nanoantenna is $t_{na} = 30$ nm. Insets: (1) TEM image of the CdSe/CdS colloidal quantum dots. (2) SEM micrograph of the fabricated Al square dimers with $s = 100$ nm and $g = 10$ nm. The scale bar represents 100 nm. The black shades are the conductive polymer spin coated prior to SEM. (b)-(c) PL enhancements by Al square dimers for fixed gap spacing ($g \sim 10$ nm) with different size. The PL signals are normalized to the maximum PL signal from the same QD film outside the dimer regions (i.e. bare QDs on substrate). The PL signals from the bare QD films are presented for both polarizations as reference.

Figure 2. Tuning plasmonic resonance towards quantum dot emission. (a)-(b) The role of gap spacing in resonance mode positions under X and Y polarizations in Al square dimers with $s = 100$ nm (exposed at 256 pC/cm) and gaps of 30 nm (black), 20 nm (blue), and 10 nm (red). (c)-(d) The role of exposure dose in tuning the resonances for Al square dimers with $s = 80$ nm and $g = 30$ nm, where the antenna were patterned at 320 pC/cm with dose variation of $\pm 20\%$.

Figure 3. Polarization resolved PL enhancement for different resonance detuning. For each combination of dimer size (s) and gap (g), $\pm 20\%$ exposure dose variation is introduced for the purpose of geometrical tuning. The dimers are grouped in terms of sizes (s) and gaps (g). The sizes of $s = 100$ nm, 80 nm, and 60 nm are indicated by (1), (2), and (3), respectively. For each size, the dimers were fabricated with three gaps, i.e., $g = 30$ nm (square), $g = 20$ nm (circle), and $g = 10$ nm (triangle).

Figure 4. Fluorescence lifetime modification by Al nanostructures. (a) Time resolved PL signals, and (b) Lifetime distributions of the quantum dot substrate (top panel), Al film (second panel), Al dimer (third panel), and Al isotropic dimer structures (bottom panel). Impulse Response Function (IRF) of the equipment is indicated by the dashed line. The average lifetime for each scenario is $\tau_{\text{avg}} = 9.13$ ns (substrate), $\tau_{\text{avg}} = 7.2$ ns (Al thin film), $\tau_{\text{avg}} = 6.56$ ns (Al dimer), $\tau_{\text{avg}} = 5.82$ ns (isotropic Al dimer). The nanoantenna for this measurement is Al dimer with $s = 80$ nm and $g = 20$ nm, and the associated PL intensity enhancements and transmissions for X and Y polarizations are shown in the inset of (a).

Figure 5. The role of local electric field enhancement in PL enhancements. Two Al dimers were chosen such that the X-polarized and Y-polarized emissions occur at near-zero detuning from the QD emission: (1) $s = 80$ nm, $g = 10$ nm, X-polarization, (2) $s = 100$ nm, $g = 10$ nm, Y-polarization. The inset shows the $|E|$ -field distributions for both resonances.

Supplementary Information

Polarization-resolved plasmon-modulated emissions of quantum dots coupled to aluminum dimers with sub-20-nm gaps

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1. Photoluminescence mapping setup

Our PL-mapping setup (Figure S1a) was custom built on the existing transmission measurement setup, where Hg-lamp and an optical bandpass filter were used as the excitation source. Among the available bandpass filters (BPF) in our experiments (370 nm, 434 nm, 546 nm, and 579 nm), the 434 nm BPF filter was chosen for PL measurements due to its far detuning from the quantum dot emission at 618 nm. The example of measured PL signals is shown in Fig. S1b, where the measurement was done under dark field geometry. The spikes near 434 nm represent the excitation signals from Hg-lamp after bandpass filter, which repeat itself due to second order grating effect around 800-900 nm range. The PL-signals of the CdSe/CdS quantum dots are clearly observed within 500-700 nm wavelength band. The full-width at half-maximum (FWHM) of the PL signals is 60 nm, which is ~2x wider than the quantum dots in suspension. This is due to the quenching associated with the silica substrate. Similar effects are also observed in the case of dye molecules inside the polymer matrix.

Figure S1. (a) The PL-mapping setup based on the 434-nm band pass filtered mercury lamp excitation. (b) The example of PL signals from quantum dot substrate under dark field geometry for X and Y output polarizations. The signals after 800 nm are an artifact from the 2nd-order effect of the grating used in the spectrometer.

2. Resonance characteristics of plasmonic dimer

Fig. S2. Extinction cross sections of a plasmonic dimer ($s = 80$ nm, $g = 10$ nm) and their corresponding $|E|^2$ -field distributions shown in Insets.

Fig. S3. Measured transmission spectra of gold dimer on ITO glass. The dimer size (s) and thickness are 80 nm and 30 nm, respectively. The dimer gaps decreased from $g = 30$ nm to $g = 10$ nm.

3. Time-resolved micro-PL results based on free-space excitation

Another time-resolved micro-PL setup to validate our results is based on free space excitation technique with the excitation path and the emission collection from the side using a visible microscope objective (20x, NA = 0.40). The samples were excited with a 10 MHz pico-second laser pulses at 371 ± 5 nm with a beam-spot size of 800 nm. The imaging part includes a CCD camera sensitive from visible to near infrared. The PL spectra was measured by subsequently directing the emission to a grating spectrometer with a Peltier-cooled photo-detector (Edinburgh Instruments) and an acquisition card. For time-resolved micro-PL measurements, the emission was filtered with the same grating while the slit set for a 5-nm bandwidth resolution. The PL intensities and PL dynamics of quantum dots coupled to dimer with 20 nm gap are presented in Figure S2. The measured PL intensity enhancements based on this setup are $PLEX \sim 3.2$ and $PLEY \sim 1.8$, in good agreements with the results based on the PL mapping setup based on Hg-lamp ($PLEX \sim 3.43$ and $PLEY \sim 2.19$). For the interpretation of the time-resolved PL signals, which were obtained at $\lambda = 620$ nm, we used biexponential model $I(t) = A \exp(-t/\tau_a) + B \exp(-t/\tau_b)$ to fit the fast (τ_a) and slow (τ_b) decay processes of the quantum dot emissions with and without Al dimers. The fitting parameters for the quantum dot film (without dimer) are $\tau_a = 4.78$ ns, $\tau_b = 12.91$ ns, $A = 0.43$, $B = 0.5$. The fast process does not correspond to Auger non-radiative recombination as the τ_a is in the order of ~ns instead of ~ps. The fitting parameters for the quantum dots coupled with 20-nm gap dimer (along the X polarization) are $\tau_a = 3.4$ ns, $\tau_b = 11.52$ ns, $A = 0.54$, $B = 0.39$. The Purcell factor is therefore deduced by the ratio of these fast processes, $F_{p,X} = 4.79/3.41 \sim 1.4$. The fitting parameters for the quantum dots coupled to Al dimers (along the Y polarization) are $\tau_a = 3.7$ ns, $\tau_b = 11.61$ ns, $A = 0.49$, $B = 0.45$; and the corresponding Purcell factor is

$F_{P,Y} = 4.79/3.7 \sim 1.29$. These Purcell factors reproduce the results obtained from FLIM ($F_{P,X} = 1.5$ and $F_{P,Y} = 1.29$).

Figure S4. PL intensities and PL dynamics of the quantum dots with (red curves) and without (blue curves) 20-nm gap Al dimer for emissions along (a-b) X-polarization, and (c-d) Y-polarization.

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