Large emission enhancement and emergence of strong-coupling with plasmons in nano assemblies: Role of quantum interactions and finite emitter size.

Riya Dutta¹, Kritika Jain², Murugesan Venkatapathi^{2*} and J. K. Basu^{1†}

¹Department of Physics, Indian Institute of Science, Bangalore, 560012, India.

²Computational & Statistical Physics Laboratory, Indian Institute of Science, Bangalore 560012, India.

1 Experimental Methods:

a) Materials: Cadmium oxide (CdO) powder, Zinc oxide (ZnO), Trioctylphosphine (TOP), Selenium powder, Sulphur, Oleic acid (OA), ODE , Chloroform and Toluene, were obtained from Sigma-Aldrich (Germany) for the synthesis of QDs. Dodecanethiol (DDT), $HAuCl_4$, $NaBH_4$ granules, $NaOH$, Hexene also procured from Sigma-Aldrich and Acetone, hexane, HCL from HDFCL for AuNP synthesis. Deionized water (18.2 Megaohms-cm, Milipore) was used for all Langmuir-Blodgett (LB) film transfer.

b) Synthesis and characterization of Quantum Dot: The CdSe-ZnS core-shell quantum dots are prepared traditional hot-injection synthesis of CdSe cores followed by slow growth of a ZnS shell from solution. CdO and ZnO are mixed and dissolved in OA and ODE and the mixture is heated up to 310 deg C to get clear solution and then inject required amount of TOP-S and TOP-Se stock solution in the three neck flux containing hot Cadmium based growth solution. After injection, we maintain a constant temperature of 300 deg C for desired amount of time to get proper size of QD. This quantum dot has Cadmium selenide (CdSe) spherical core and it is covered by Zinc-Selenide (ZnS) shell. By keeping the temperature constant at 300 degree for 10 min, the formed QD has diameter around 6.7 nm and Photoluminescence emission at wavelength 570 nm.

c) Synthesis and characterization of Gold Nano Particle: Gold nanoparticles (AuNP) are made in water by borohydride reduction and phase-transferred to hexane. This dodecanethiolate-protected gold nanoparticles synthesis is a fast process and does not require a cleaning step. The stock solution of 50 mM gold chloride was made by dissolving $HAuCl_4 - 3H_2O$ with the same molar concentration of HCl in a glass vial and the aqueous stock solution of 50 mM borohydride was made by dissolving $NaBH_4$ granules with the same molar amount of $NaOH$. Now 100 μL of the $AuCl_4$ solution added with water and later injected 300 μL of the borohydride solution to that while stirring the mixture on a mechanical shaker for uniform

*muruges@iisc.ac.in

†basu@iisc.ac.in

steady mixing. The solution changes the colour from light yellow to orange. The concentration of gold ions (0.5mM) and the amount of borohydride solution was controlled to obtain smaller size Gold nanoparticle. The phase transfer is done with the help of acetone by vigorous shaking for 30 sec, during which gold nanoparticles are coated with hydrophobic organic ligands.

d) TEM IMAGES: The CdSe/ZnS core shell QD and DDT capped AuNP have been synthesized ¹⁻⁴ and drop casted on Carbon coated copper grid for Transmission Electron Microscopy (TEM) imaging. From the TEM images we can estimate the size and shape of the respective nanoparticles. The mean diameter calculated from different images of Core shell QD is about 6.7 ± 1 nm. The mean diameter of AuNP is 3.8 ± 0.8 nm.

Figure 1: (a) TEM images of CdSe-ZnS core shell quantum dot. (b) The histogram for average diameter is calculated from several images.

Figure 2: TEM images of Gold nano particle (AuNP). (a) shows the images of DDT capped AuNP and (c) shows the images of ODT capped AuNP. Mean diameter is (b) 3.7 nm and (d) 3.8 nm respectively.

e) UV ABSORPTION AND PL EMISSION: The UV absorption of the AuNP and QDs are measured with Perkin-Elmer UV-vis absorption spectrometer. The QDs and AuNPs are dissolved in Chloroform and measured PL and Absorption spectra. The absorption maxima for colloidal AuNPs appear at 520 nm which is off-resonant with the PL emission of the QDs. The corresponding spectras have been shown in the fig 3.

Figure 3: The UV absorption spectra of the AuNP and PL emission spectra of QDs.

Sample No	Sample index $Q_{\alpha}C$ ($\alpha=1-5$)	R_{c-c} (nm)	R (nm)
1.	Q_1C	8.3	1.56
2.	Q_2C	8.92	2.18
3.	Q_3D	10.17	3.43
4.	Q_4C	11.32	4.58
5.	Q_5D	12.57	5.83

Table 1: The table contains the sample indexes of reference QD films which are differed by different surface separations (R).

Figure 4: The compression isotherms of transferred films at constant area of surface pressure of 41 mN/m and 37mN/m for the Ref QD (Q_4C) and AuNP doped QD film (A_5C) respectively.

f) LANGMUIR BLODGETT TECHNIQUE FOR MONOLAYER PREPARATION: The idea of the method⁵⁻⁷ is to form a mono-molecular layer of an amphiphilic substance on the water surface having intrinsic control over the internal layer structure up to the molecular level. In the aqueous phase, the amphiphilic substance molecules are arranged on the air-water interface. QDs and AuNPs were mixed in various ratios in volatile solvent chloroform and spread over deionized water-filled Langmuir trough (Kibron MicroTrough G series, Finland). Sufficient waiting time was given (10 min) to evaporate the chloroform. All the experiments were done using a temperature regulated water circulator (Julabo, Germany), which keeps the water sub-phase at constant temperature of 25 deg C. By compressing the barriers from both sides of the Teflon trough at the constant speed of 10 mm/min, we can allow the QDs to arrange themselves together in a compact nature and surface pressure (Π) was monitored using a dyne probe sensor. The by vertical method the layer of QDs can be transferred to RCA cleaned glass cover slip at a very slow rate of 0.5 mm/min for further studies. We have transferred various films at $\Pi= 40\text{mN/m}$ and 37mN/m for respective Ref QD (Q_4C) and AuNP doped QD films (A_5C). The AuNP doped films are transferred at same area corresponding to that of ref. QD film to keep QD number density constant as discussed earlier⁸⁻¹⁰. Typical surface pressure (Π)-surface area(A) isotherms⁹ for bare QD films and a nanoparticle-doped QD monolayer is shown in Fig 4.

Figure 5: AFM topographic map of the surface features of the films. We have chosen the region containing breakage so that the height of layer can be approximated with respect to the substrate. (a) Ref QD film- (Q_4C) and (b) MNP doped QD film- (A_5C) height profile shows the height of the layer (a) 10.75 nm. (b) 10.6 nm that confirms about monolayer.

g) AFM IMAGES: This figure shows the AFM topography images of the samples. Here surface topography^{9,11} of the samples was imaged using AFM (Park-Korea) in non-contact mode. The images are analysed by XE Image Processing Programme. AFM images shows the compact monolayer of CQDs over very large area and we find the region with breakage in the compact layer to calculate the height of the monolayer in compared to the background substrate surface. The height difference shows the formation of monolayer.

Figure 6: TEM images shows monolayer of CdSe-ZnS core shell quantum dots with different capping groups (a) OA and (b) TBAI, (c) It shows the schematic model of the monolayer films. (d) The RDF for the different system is calculated from these images.

h) RADIAL DISTRIBUTION FUNCTION: The radial distribution function (RDF) or pair correlation function ¹⁰ in a system of particles (atoms, molecules, colloids, etc.), describes how density varies as a function of distance from a reference particle. This simplified definition holds for a homogeneous and isotropic system. With the ImageJ software we have calculated the RDF for each AuNP surrounded by several QDs. Normalization factor = $\rho \times \pi \times [(r + \delta r)^2 - r^2]$ where, ρ = number density, r = points of the peaks in the histogram, δr = standard deviation of the corresponding peak. The average surface separation between QDs remain comparable in both ref.QD and AuNP doped QD film.

Figure 7: TEM images of (a)Ref. QD film- Q_4C (b) MNP doped QD film- A_5C film. Dark features represent MNPs. QD monolayer with (c) longer (Q_4C) (d) smaller (Q_1C) surface separation.

Figure 8: The RDF for MNP based QD films. These graphs represent different center to center (R_{c-c}) separation from MNP to surrounding QDs. From that We calculate surface to surface separation (R).

Figure 9: It shows splitting in PL emission spectra of QDs from different samples. The distorted peaks are fitted with Lorentzian function.

i) PHOTOLUMINESCENCE MEASUREMENT: PL measurements on our samples were performed using a WITec alpha SNOM setup in confocal mode as described earlier ^{8,10}. The layer of respective samples is transferred on glass substrate for spectral study. 488 nm Argon (Ar) Laser is used for Photoluminescence excitation in Confocal mode and the transmitted light was detected either using a photomultiplier tube or a charge coupled device detector. The emission light is collected using a high collection efficiency objective magnification 100x ((Nikon NA-1.51, oil immersion) and the light is guided to a spectrograph (grating 300 g/mm, spectral resolution in energy scale-6.2 meV). The PL emission intensity (emitted photon counts) from the AuNP based QD films are higher than the bare QD film. Here we have calculated the enhancement in AuNP doped film in comparison with the reference QD film. The Enhancement factor from PL measurement ¹⁰⁻¹² is defined as $EF_{PL} = \frac{I_{doped}}{I_{ref}}$ where I_{doped} and I_{ref} are PL emission counts from the MNP doped QD film and reference QD films.

j) ENERGY SPILTING IN PL EMISSION SPECTRA: For the spectral study, we have accessed the higher resolution with grating of 600g/mm (spectral resolution in energy scale-3 meV). All excitations were performed with the blue line (488 nm) of an Ar ion laser using 50x objective for higher area illumination, Signal is collected in transmission mode with objective having magnification 100x (Nikon NA-1.51).

k) TIME RESOLVED PHOTOLUMINESCENCE MEASUREMENT: TRPL measurement has done with MicroTime 200 fluorescence lifetime microscope system that study the fluorescence dynamics and lifetime imaging. With MicroTime 200, sub-micrometre spatial and pico-second time resolution can be achieved and it is combined with a high precision PiFoc element for 2D/3D imaging. The excitation is based on fiber coupled pulsed laser Diode. In this confocal microscope, scanning is facilitated through a piezo table optionally combined with a high precision PiFoc element for 2D/3D imaging. We have used Time-resolved Confocal Fluorescence Microscope with Unique Single Molecule Sensitivity mode for investigation of fast dynamics Fluorescence Lifetime Imaging (FLIM). The excitation is based on Fiber coupled Pulsed Laser Diode. We have used the laser source of 507 nm. The repetition rate has selected at 2 MHz to ensure maximum lifetime range. 100x air objective is used to excite and collect signals from the samples. Average decay rate for different ratio of AuNP in QD films is calculated as a function of R. We do the measurement using the software (SymPhoTime 64). The temporal behaviour of the measured PL intensity is given by

$$I(t) = Ae^{-\gamma t}. \quad (1)$$

Triple exponential decay fit is used to determine the lifetime from decay profiles ¹³.

$$Y = A_1 e^{-\frac{x}{\tau_1}} + A_2 e^{-\frac{x}{\tau_2}} + A_3 e^{-\frac{x}{\tau_3}} \quad (2)$$

The Decay rate (Γ^{exp}) has calculated from average lifetime ¹⁴ of QDs in each film. Decay rate enhancement factor is calculated as the ratio of decay rate of AuNP doped QD film to the decay rate of reference QD film.

$$\tau_{avg} = \frac{\sum A_i * (\tau_i)^2}{\sum (A_i * \tau_i)} \quad (3)$$

$$\Gamma^{exp} = \frac{1}{\tau_{avg}} \quad (4)$$

$$EF_{exp} = \frac{\Gamma_{doped}^{exp}}{\Gamma_{ref}^{exp}} \quad (5)$$

Figure 10: The temporal behaviour of the measured PL intensity of ref QD film Q_4C and MNP doped film A_5C . The decay curves are modelled by triple exponential decay.

2 Theoretical Methods

In the previous section, we described experimental methods for the results presented in the figures 2, 4a and 4b of the paper. In this section, theoretical methods are described for results presented in the figures 3 and 4c. There is a direct correspondence between experimental and theoretical results. From the TEM images shown in Figure 1 and Figure 2, the size of QDs and AuNPs were estimated. The mean diameter of QDs is 6.7 ± 1 nm and that of AuNPs is 3.8 ± 0.8 nm. We calculated enhancement factors theoretically by modeling a quantum emitter of the same size (6.7 nm) and AuNP (3.8 nm) as given in section 3. Also, we consider emission wavelength of 570 nm for theoretical calculations modeling the quantum emitter, which matches with the peak of photoluminescence emission wavelength of QDs. We plotted enhancement factors (Fig. 3) and energy shifts (4c) for similar separations between MNP and QE for direct comparison with experimental results presented in figures 2, 4a and 4b.

In this section, first we briefly recall a known method for calculating self-energy matrix of a multipole emitter with N modes interacting with other polarizable matter (and N is taken to be 3 in simulations here). Then, we apply the strong-coupling theory of partition of density of optical states to this problem of multipole emitter near a metal nanoparticle. This gives us the additional decay rates arising due to metal nanostructures, in the case of emitters with charge distributions of a finite size, at very small separations. This extension to multipoles is motivated by the experimental observations which even though are well predicted by the strong-coupling model of a point dipole as far as the enhancements and emission rates are concerned (figure 3), the observed energy shifts are larger (figure 4). We show that the larger energy shifts are well captured by this extended model which simply takes into account the finite size of the quantum dots, and this effect becomes significant at small separations.

a) Evaluation of collective eigenstates of N -coupled dipoles proximal to metal nanoparticle The total self-energy of N coupled Lorentz dipole oscillators proximal to metal nanostructure is given by:

$$\Sigma_{jk}^{total}(\omega) = \frac{-2\pi q^2 \omega}{mc^2} \mathbf{e}_j \cdot \mathbf{G}(\mathbf{r}_j, \mathbf{r}_k; \omega) \cdot \mathbf{e}_k - \delta_{jk} \frac{i\Gamma_o}{2} \quad (6)$$

$$\Sigma_{jk}^{total} = \Delta_{jk} - \frac{i\Gamma_{jk}}{2} \quad (7)$$

Here q is the oscillating charge, m is its mass, and c is speed of light. Δ_{jk} and Γ_{jk} are $N \times N$ matrices. Each component of matrix $\Delta_{jk} = Re(\Sigma_{jk}^{total})$ represents virtual photon exchange between two dipoles at position r_j and r_k in presence of metal nanostructure and matrix $\Gamma_{jk} = -2Im(\Sigma_{jk})$ represents total decay rates of the coupled system. Green dyadic $\mathbf{G}(\mathbf{r}_j, \mathbf{r}_k; \omega)$, represents interaction between two dipoles at position r_j and r_k in presence of metal nanostructure. This model was first treated analytically under long-wavelength approximations for a spherical metal particle¹⁵ and was later extended to arbitrary geometries without long-wavelength approximations using a computational volume integral approach which was shown in¹⁶. The total decay rate Γ in the metal is decomposed into its radiative (Γ^r) and non-radiative (Γ^{nr}) contribution to the dyad $\mathbf{G}$ by a factorization using real and imaginary parts of polarizability of dipole granules, which represent the metal nanoparticle in this volume integral approach, and this was shown elsewhere¹⁶.

Note that here all self-energy components are normalized by Γ_o^r for evaluations, where $\Gamma_o^r = \frac{2\sqrt{\epsilon_o}\mu^2 k^3}{3\hbar}$ and μ is the electric dipole moment; k , ϵ_o and $\hbar$ are the wave number, free-space permittivity and reduced Planck's constant.

b) Multipole emitter strongly coupled to matter In this section, we will focus on additional contribution of the nanostructure to self-energy of a multipole emitter represented by N modes, that are in turn generated by randomized and separated N dipoles. This gives us the additional decay rates arising due to metal nanostructures, in the case of emitters with charge distributions of a finite size.

The self-energy matrix in equation (9) is decomposed into its metallic contribution (Σ) and the contribution due to direct interaction among the N coupled dipoles in the absence of metal nanostructures (Σ^o).

$$\Sigma_{jk}^{total}(\omega) = \Sigma_{jk}^o(\omega) + \Sigma_{jk}(\omega) \quad (8)$$

where

$$\Sigma_{jk}(\omega) = \frac{-2\pi q^2 \omega}{mc^2} \mathbf{e}_j \cdot \mathbf{G}_m(\mathbf{r}_j, \mathbf{r}_k; \omega) \cdot \mathbf{e}_k \quad (9)$$

$\mathbf{G}_m$, the metallic contribution of green dyadic is calculated by subtracting $\mathbf{G}_o$, representing interaction between the N coupled dipoles in the absence of metal nanostructures, from the total green dyadic $\mathbf{G}$.

$\mathbf{G}_o$ is calculated using the Green dyadic solutions of following :

$$\nabla \times \nabla \times \mathbf{G}_o(\mathbf{r}, \mathbf{r}_j; \omega) - k^2 \mathbf{G}_o(\mathbf{r}, \mathbf{r}_j; \omega) = \mathbf{I} \delta(\mathbf{r} - \mathbf{r}_j). \quad (10)$$

where $\mathbf{I}$ is a unit dyad, the wave number $k = \sqrt{\epsilon_c} \omega$, and $\delta(\mathbf{r} - \mathbf{r}_j)$ represents a point source.

This gives us the dyadics for interaction among the point-dipoles:

$$\mathbf{G}_o(\mathbf{r}_i, \mathbf{r}_j; \omega) = (\mathbf{I} + \frac{\nabla \nabla}{k^2}) g(|\mathbf{r}_i - \mathbf{r}_j|) \quad (11)$$

where $g(r) = \frac{e^{ikr}}{4\pi r}$. The details of calculation of $\mathbf{G}$ for an arbitrary structure using such dipole granules was shown elsewhere¹⁶.

The eigenstates of $\Sigma_{jk}(\omega)$, the metallic part of self-energy matrix (after an integration over ω for broad-band sources) are calculated using :

$$\Sigma|J\rangle = \Delta_J - i\frac{\Gamma_J}{2}|J\rangle \quad (12)$$

where $|J\rangle$ are eigenstates of self-energy matrix Σ . Specifically, vectors J represent one of three modes of emission here. The imaginary part of eigenvalues of Σ represents additional decay rate in emission due to nanostructure. While the real part of eigenvalues of Σ represents energy shift in emission due to nanostructure, it is also related to the frequency of Rabi oscillations and the Rabi-splitting energy ΔE_J .

$$2\hbar|\Delta_J| = \Delta E_J \quad (13)$$

Also note that the equivalent entry-wise decomposition for each interacting entity pair given by ‘ j ’ and ‘ k ’.

$$\Sigma_{jk} = \Delta_{jk} - i\frac{\Gamma_{jk}}{2} \quad (14)$$

An extension to the theory of density of optical states was shown to be required to include effects of strong coupling of an emitter with absorbing matter, and was presented elsewhere considering dipole emitters¹⁷. This extension removed the anomalous divergence of observed enhancements of photoluminescence and fluorescence in case of limiting small metal nanoparticles, and also surface-enhanced-Raman-spectroscopy where only emitters with very small separations with the metal are typically excited. Note that the quantum nature and interpretation of the interactions are salient here, and models of broadly observed effects with multiple types of sources seem to be relatively insensitive to the degree of quantum representation

of the emitter itself, as expected. In this regime, fluctuations leaking from limiting small metal nanostructures contribute to additional radiative rates and a corresponding inhibition of non-radiative rates. This is represented by entries of a matrix Γ_{jk}^{leak} and calculated as :

$$\Gamma_{jk}^{leak} = e^{-\frac{\hbar\Gamma_{jk}}{\Delta E_{jk}}} \cdot \Gamma_{jk}^{nr(1)} \quad (15)$$

Here the superscript (1) refers to the dipole mode contribution of the metal nanoparticles. Then mode-wise Γ^{leak} is calculated by the expectation (vector-matrix-vector product)

$$\Gamma^{leak} = \langle J | \Gamma_{jk}^{leak} | J \rangle \quad (16)$$

In the strong-coupling regime, it was shown that the a significant fraction of non-radiative component of the dipole mode of metal nanoparticle can manifest as a radiative component ¹⁷. There, the expressions represented a single point dipole emitter interacting with a metal nanostructure. Here we have extended this theory to the multipole emitter, by first deflating the additional self-interaction involved in a multipole emitter (Σ^o), and retrieving the components due to only the metal for any eigenstate J of the multipole emitter.

The effective decay rates of a mode thus become:

$$\Gamma_{eff}^r = \Gamma_o^r + \Gamma^r + \Gamma_{leak} \quad (17)$$

and

$$\Gamma_{eff}^{nr} = \Gamma_o^{nr} + \Gamma^{nr} - \Gamma_{leak} \quad (18)$$

The quantum efficiency of a mode is :

$$Q_J = \frac{\Gamma_{eff}^r}{\Gamma_{eff}^r + \Gamma_{eff}^{nr}} \quad (19)$$

The total quantum efficiency is then :

$$Q = \frac{1}{N} \sum_{J=1}^N Q_J \quad (20)$$

c) Enhancement factors for repeated excitation In case of repeated excitation of the emitter, the increase in ground state population due to the metal nanoparticle has to be taken into account to evaluate the enhancement in the photon counts. Factors of enhancements of fluorescence and photoluminescence can be expressed as the product of enhancement in quantum efficiency and increase in rates of excitation. Given a particular intensity of exciting radiation, note that a relative increase in rates of emission (signifying increase in the ground-state population) would result in an increase in the rate of excitation as well. The same holds for an increasing intensity of exciting radiation given any particular rate of emission and ground-state population. The enhancement rate for an emitter (or a mode) due to the metal is given by :

$$\Phi = \frac{Q}{Q_o} \left(P_1 + \frac{(\Gamma^r + \Gamma^{nr})}{\Gamma_o^r} P_2 \right) \quad (21)$$

The first term i.e. $\frac{Q}{Q_o}$ represents enhancement in quantum efficiency and the term in bracket represents an increase in excitation rate. P_1 is the probability of first excitation which is always 1 here for both the measurement and computation. P_2 depends on the maximum number of photons available after first excitation. Since absorption of photons from laser can be represented by a Poisson process, P_2 can be calculated as following :

$$P_2 = \sum_{x=0}^k e^{-\left(\frac{(\Gamma^r + \Gamma^{nr})}{\Gamma_o^r}\right)} \frac{\left(\frac{(\Gamma^r + \Gamma^{nr})}{\Gamma_o^r}\right)^x}{x!} \quad (22)$$

where k is the maximum number of photons available for additional excitations due to the presence of metal nanostructure. The value of k can go from zero to infinity and hence P_2 can go from 0 to 1 depending on the intensity of incident laser.

Limiting Cases :

(i) For $k = 0$, inserting $P_2=0$ in equation (22) to represent a single excitation, the minimum value of enhancement in the emission is given by:

$$\Phi_{min.} = \frac{Q}{Q_o} \quad (23)$$

(ii) For $k = \infty$, $P_2=1$. Hence, inserting $P_2=1$ in equation (22) in equation (21) and using $P_1=1=\frac{\Gamma_o^r}{\Gamma_o^r}$, maximum value of enhancement in number of emitted photons is given by:

$$\Phi_{max.} = \frac{Q}{Q_o} \left(\frac{\Gamma_o^r + \Gamma^r + \Gamma^{nr}}{\Gamma_o^r} \right) \quad (24)$$

Factors of enhancements for repeated excitation can be evaluated using $k = 1, 2, \dots$. These represent the increase in exciting radiation for the evaluated decay rates of the emitter. These enhancements are averaged over 3 modes and random polarization of the charge distribution of emitters. Factors of enhancement for such an increasing rate of repeated excitation was illustrated in figure 3 of the main manuscript.

d) Enhancement factors for single excitation The enhancement factor for the time-resolved Photoluminescence (TRPL) experiments is defined as $EF_{TRPL} = \frac{I_{doped}}{I_{ref}}$, where I_{doped} and I_{ref} are emitted photon counts from the AuNP based hybrid films and the corresponding reference QD film. This maximum photon counts have been considered at $t=0$, immediately after the excitation. As in the PL spectroscopy experiments where a continuous laser excites the sample, the enhancement factor from TRPL measurement also shows similar non-monotonicity with slightly lower maximum value (fig 11a). Similar predictions by the theoretical model with varying quantum efficiency of the reference QD samples are shown in Fig 11(b).

Figure 11: (a) The enhancement factor (EF_{TRPL}) is quantified from TRPL measurement at $t=0$ as a function of R. (b) Enhancement factors (EF_{theory}) predicted for single excitations for various quantum efficiencies of the reference sample.

1. Hao, J.-j., Zhou, J. & Zhang, C.-y. A tri-n-octylphosphine-assisted successive ionic layer adsorption and reaction method to synthesize multilayered core-shell cdse-zns quantum dots with extremely high quantum yield. *Chemical Communications* **49**, 6346–6348 (2013).
2. Yu, W. W., Qu, L., Guo, W. & Peng, X. Experimental determination of the extinction coefficient of cdte, cdse, and cds nanocrystals. *Chemistry of Materials* **15**, 2854–2860 (2003).
3. Martin, M. N., Basham, J. I., Chando, P. & Eah, S.-K. Charged gold nanoparticles in non-polar solvents: 10-min synthesis and 2d self-assembly. *Langmuir* **26**, 7410–7417 (2010).
4. Kühnle, A. *et al.* Adsorption of dodecanethiol on cu (110): Structural ordering upon thiolate formation. *Langmuir* **18**, 5558–5565 (2002).
5. Dabbousi, B., Murray, C., Rubner, M. & Bawendi, M. Langmuir-blodgett manipulation of size-selected cdse nanocrystallites. *Chemistry of Materials* **6**, 216–219 (1994).
6. Heath, J. R., Knobler, C. M. & Leff, D. V. Pressure/temperature phase diagrams and superlattices of organically functionalized metal nanocrystal monolayers: the influence of particle size, size distribution, and surface passivant. *The Journal of Physical Chemistry B* **101**, 189–197 (1997).
7. Collier, C., Saykally, R., Shiang, J., Henrichs, S. & Heath, J. Reversible tuning of silver quantum dot monolayers through the metal-insulator transition. *Science* **277**, 1978–1981 (1997).
8. Haridas, M., Basu, J., Gosztola, D. & Wiederrecht, G. Photoluminescence spectroscopy and lifetime measurements from self-assembled semiconductor-metal nanoparticle hybrid arrays. *Applied Physics Letters* **97**, 189 (2010).
9. Tripathi, L., Praveena, M. & Basu, J. Plasmonic tuning of photoluminescence from semiconducting quantum dot assemblies. *Plasmonics* **8**, 657–664 (2013).
10. Praveena, M., Mukherjee, A., Venkatapathi, M. & Basu, J. K. Plasmon-mediated emergence of collective emission and enhanced quantum efficiency in quantum dot films. *Physical Review B* **92**, 235403 (2015).
11. Haridas, M., Tripathi, L. & Basu, J. Photoluminescence enhancement and quenching in metal-semiconductor quantum dot hybrid arrays. *Applied Physics Letters* **98**, 27 (2011).
12. Govorov, A. O. *et al.* Exciton- plasmon interaction and hybrid excitons in semiconductor- metal nanoparticle assemblies. *Nano letters* **6**, 984–994 (2006).
13. Achermann, M., Petruska, M. A., Crooker, S. A. & Klimov, V. I. Picosecond energy transfer in quantum dot langmuir- blodgett nanoassemblies. *The Journal of Physical Chemistry B* **107**, 13782–13787 (2003).
14. Geddes, C. D. & Lakowicz, J. R. *Advanced concepts in fluorescence sensing: Part A: Small molecule sensing*, vol. 9 (Springer Science & Business Media, 2007).

15. Pustovit, V. N. & Shahbazyan, T. V. Plasmon-mediated superradiance near metal nanostructures. *Physical Review B* **82**, 075429 (2010).
16. Venkatapathi, M. Collective eigenstates of emission in an n-entity heterostructure and the evaluation of its green tensors and self-energy components. *J. Optical Society of America B* **31**, 3153–3163 (2014).
17. Jain, K. & Venkatapathi, M. Strong-coupling of emitter with absorbing matter: A regime for enhancement of light emission. *Physical Review Applied* **11**, 054002 (2019).