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ORIGINAL ARTICLE

Effect of Field Distribution on Linear and Nonlinear Optical Response of CdTe Quantum Dot in Presence of a Silver Nanosphere

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ABSTRACT

Linear and nonlinear optical response of CdTe Quantum Dots has drawn much attention of researcher and scientists. In this article we have simulated the photoluminescence (PL) properties of CdTe in presence of silver nanosphere. We found that the excitation near a Surface Plasmon Resonance (SPR) of Ag nano spheres will increase intensity of PL. However if the excitation is far from the SPR then the enhancement in intensity of PL depends on the polarization of incident excitation.

Keywords: *CdTe Quantum Dots, photoluminescence, upconversion photoluminescence, Discrete Dipole Approximation (DDA), DDSCAT*

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INTRODUCTION

Semiconductor Quantum Dots (SQD) have high nonlinear absorption coefficient, narrow PL width and higher photo-stability semiconductor quantum dots hence they are being used in different applications (Lucas T. A. da Rosa, *et al.,* 2021, Musa Çadırcı 2020 and Akeel M. Kadim *et al.* 2020). In such high resolution imaging upconversion photoluminescence (UCPL) is used. UCPL is a process in which carriers are excited by nonlinear absorption process followed by decay, resulting in Photo Luminescence (PL). In most of such imaging applications two-photon absorption generates the required electron-hole pairs in the semiconductor quantum dots (Ekaterina Kolesova *et al.* 2019, Anuushka Pal *et al.* 2018, and Poulami Dutta *et al.* 2016). Further, the absorption and emission properties of semiconductor quantum dots can be tuned over a wide spectral range by changing its size. In case of small metal nanoparticles (MNP) the collective oscillation of electrons, which are bound to oscillate within the boundary of particle, results in particle plasmon resonance (PPR) (also known as localized surface plasmon resonance). The particle plasmon resonances are very sensitive to the shape of the metallic nanoparticle. When excited with a wavelength near PPR the field inside and the field just outside the metal particles can be much higher than the applied field. By placing a semiconductor quantum dot near the metal NPs, i.e. by making a hybrid nanoparticle, it is possible to enhance the field inside SQDs (Junwei Yang *et al.* 2016 and Kathy C Nguyen *et al.* 2013). The increased intensity can increase the electron-hole generation and hence enhance the PL emission from the SQDs. Further, since the two-photon absorption depends on the square of the intensity the UCPL from SQDs can also get modified. The field enhancement properties of MNP will also get modified by the presence of SQD. It has been reported earlier that in proximity of metal NPs PL from SQDs is enhanced sometimes and quenched in some cases (Donald Selmarten *et al.* 2005, Haridas M *et al.* 2011 and Khurgin J.B. *et al*. 2009).

Our earlier experimental results showed enhancement in PL and quenching of UCPL of Ag-CdTe hybrid nanoparticles (Sabina Gurung *et al.* 2016). The interaction between the SQD and MNP can arise from various processes like electromagnetic interaction between the fields around the particles, charge transfer etc. The electromagnetic interaction can act even when the particles do not touch each other. In-order to understand the role of electromagnetic interaction in the coupled SQD-MNP system it is essential to study field distribution as a function of interpaticle distance. In this article, we report our results of field distribution calculation inside a single CdTe SQD when placed near single silver MNP. The results can be directly used for understanding the linear and nonlinear response of SQD in presence of MNP since for the calculations we have used realistic experimental data like the size of the particles and dielectric constants etc.

SIMULATION RESULTS AND DISCUSSION

We consider a hybrid consisting of a spherical silver nanoparticle (radius 5 nm) placed near a CdTe quantum dot (radius 1.3 nm) and both being suspended in water. We have used DDSCAT, an open-source FORTON based software pack (Bruce T. Draine *et al.* 1994, Draine B. T. *et al.* 1993, Bruce T. Draine *et al.* 2008 and Maxim A. Yurkin *et al.* 2015). In the Discrete Dipole Approximation (DDA) each particle is modelled as an assembly of point dipoles in a cubic lattice. Each of these elements is considered sufficiently small that only dipole interactions with the incident electric-field and the induced-fields in neighbouring elements need to be considered. This reduces the solution of the Maxwell equations to an algebraic problem of many coupled dipoles and is given by a system of 3N complex linear equations,

$$\sum_{j=1}^{N} \mathbf{A}_{\mathrm{ij}} \mathbf{P}_{\mathrm{j}} = \mathbf{E}_{inc,\mathrm{i}} , \qquad (1)$$

where P_{j} are unknown polarization of j_{th} dipole, $E_{\mathrm{inc,i}}$ is incident electric field at r_i, and A_{ij} is interaction matrix given by

$$\mathbf{A}_{\mathrm{ij}} = \frac{\exp\left(ikr_{ij}\right)}{r_{ij}} \left[k^2 \left(\hat{r}_{ij}\hat{r}_{ij} - 1_3\right) + \frac{ikr_{ij} - 1}{r_{ij}^2} \left(3\hat{r}_{ij}\hat{r}_{ij} - 1_3\right) \right]. \qquad (2)$$

The set of equations given by Eq. (1) are solved for unknown polarization P_{j}. Using these results we can calculate the scattered electric field anywhere around the hybrid system using:

$$\mathrm{E}_{sca} = \frac{k^2 \exp\left(ikr\right)}{r} \left[\sum_{i=1}^{N} \exp\left(-ik\hat{r}.\vec{r}_j\right) \left(\hat{r}\hat{r} - 1_3\right) \overline{\mathbf{P}_{\mathrm{j}}} \right]. \qquad (3)$$

To ensure accuracy of the results, we have kept the inter-dipole spacing such that the product $|mkd| < 0.1$, here m is the ratio between the refractive index of silver to that of the surrounding medium, k is propagation vector and d is the inter-dipole separation. The complex refractive index of the silver taken from an earlier experimental report (Johnson P. B. *et al.* 1972, E. D. Palik 1998) and the refractive index of the water is taken to be 1.33. To take care of quantum confinement effects, the refractive index of CdTe SQD was estimated from experimental absorption spectrum (Fig.1) of CdTe SQD colloid using field calculations and bulk dielectric constant of bulk CdTe and following the procedure reported in ref. Marcelo Alves Santos *et al.* 2010.

The experimental extinction spectrum of Ag nanospheres (radius 5 nm) in water along with the calculated spectrum is shown in Fig. 1. The deviation in PPR peak wavelength between experiment and calculation can be due to the presence of capping agents in the experimental NPs. The extinction spectrum of the CdTe-Ag hybrid formed by 1 nm separation between CdTe SQD and Ag MNP is also shown in Fig. 1. The extinction spectrum of hybrid is dominated by response of Ag NP and has a peak at 385 nm. Thus in case of one-to-one interactions the optical response of metal will dominate in deciding the optical response of SQD-MNP hybrid.

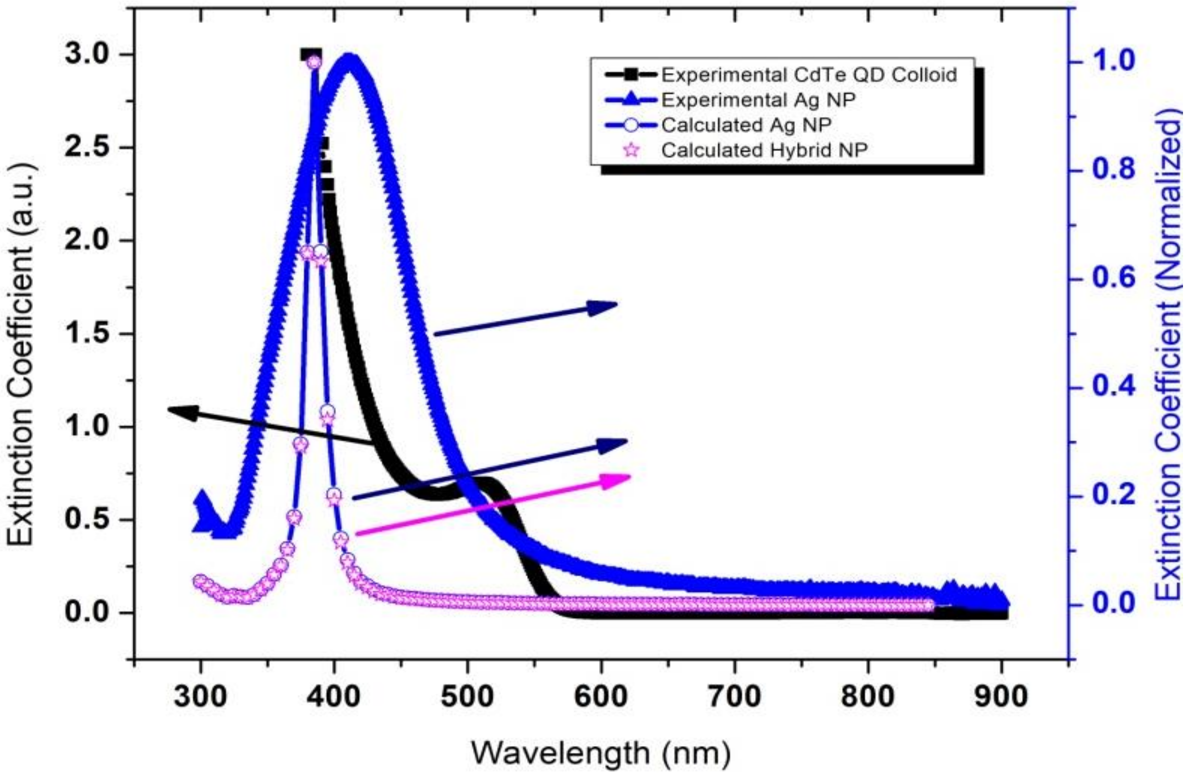


Fig. 1: The experimental and calculated extinction efficiencies

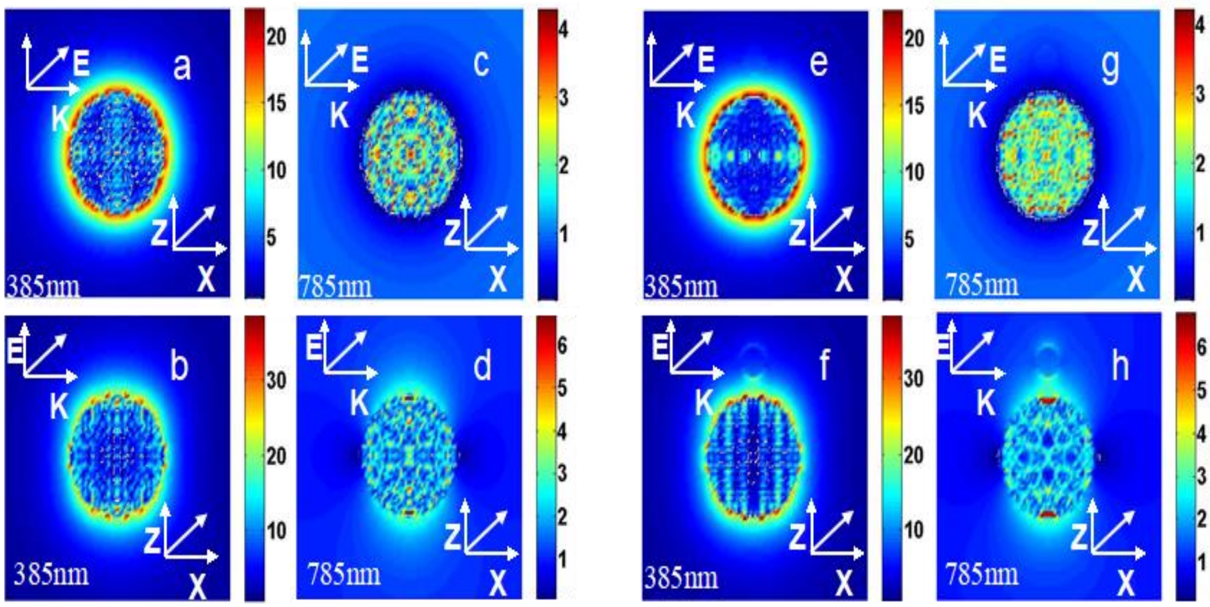
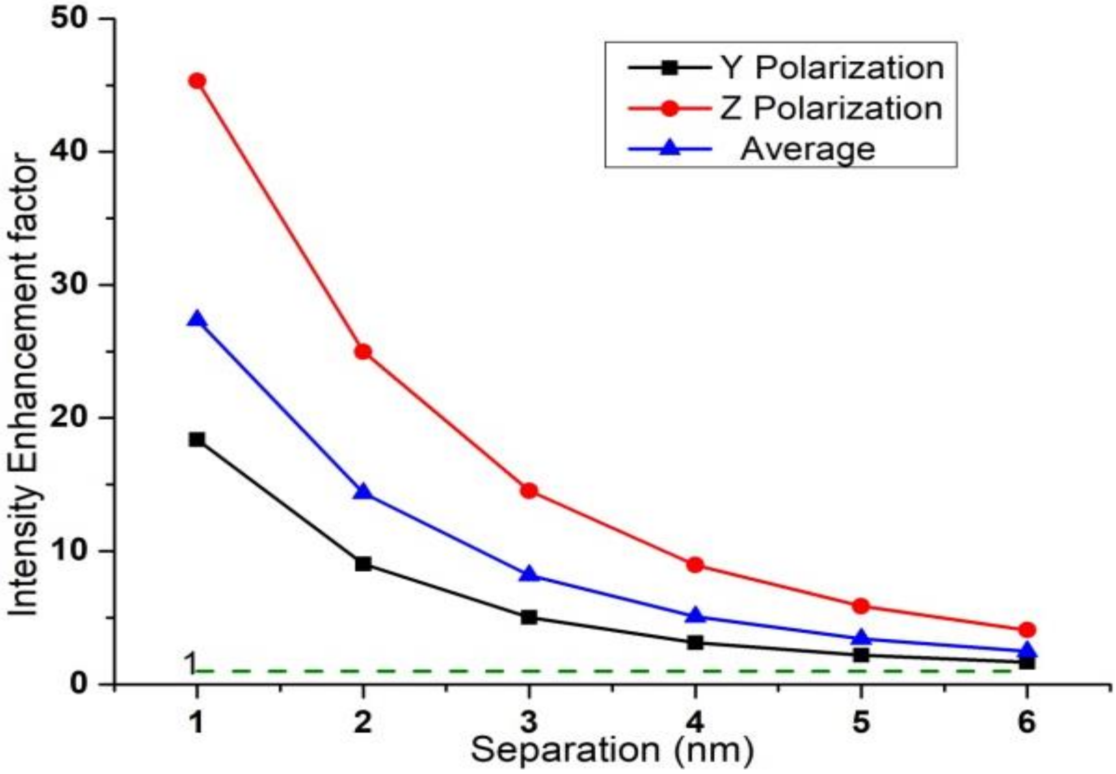
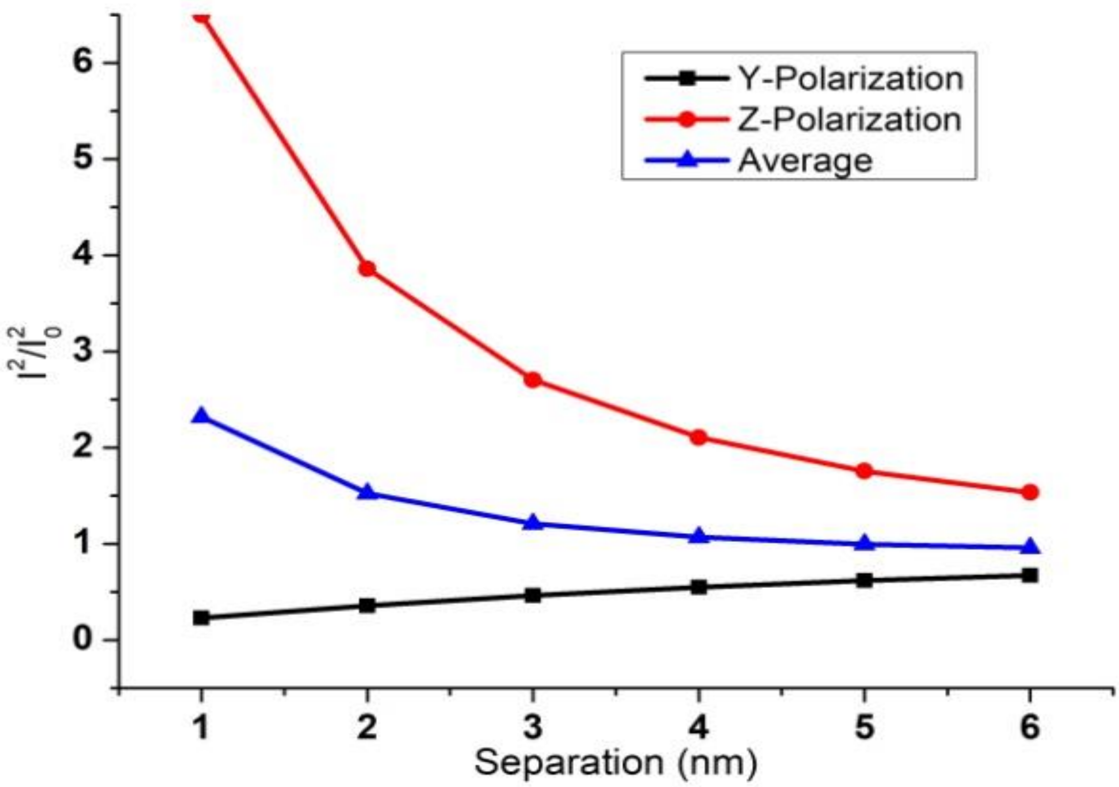


Fig. 2: (a)-(d) |E|-Field plots for single Ag NP at two different wavelengths and at two different polarizations. (e)-(h) similar |E|-Field plots for Ag NP with CdTe QD just above with 1 nm separation



(a)



(b)

Fig. 3: (a) Intensity factor (I/I_0), the ratio between the average intensity inside the CdTe SQD with and without MNP with illumination at 385 nm and (b) (I^2/I^2_0) when illumination wavelength is 785 nm.

In a typical experimental situation the PL of CdTe is excited by ~ 400 nm (which is at the PPR of Ag NP) while the UCPL is excited by 800 nm. To keep the situation same, we calculate the electric field distributions at 385 nm which is the PPR peak wavelength in the simulation result and also at 785 nm. Due to the symmetry in the system there are two polarization directions in which the responses are different: (1) along the line joining the centres of the two particles and (2) perpendicular to it. The simulated |E|-field distributions for all these four situations for the single Ag MNP and SQD-MNP hybrid system are shown in Fig. 2 (a)-(d) and Fig.2 (e)-(h) respectively. These plots shows that in the hybrid system |E| field at PPR (385 nm) are enhanced for both polarizations. However for the case of 785 nm |E| is quenched when the field is along Y direction and enhanced while it is along Z direction.

The PL of a SQD will strongly depend on the intensity of incident field inside it. Therefore we calculate the average intensity inside the CdTe SQD with (I) and without (I_0) Ag MNP nearby. We have calculated the intensity ratio, I/I_0, the enhancement or quenching factor for PL. Figure 3 a) shows the dependence of this intensity factor on the separation between the SQD and MNP. In a colloidal sample it is expected that there will be randomly oriented SQD-MNP hybrids interacting with the applied field. An approximate average factor for such samples can be calculated by averaging the intensity factor along the three main axes (X, Y and Z). This average intensity factor is also plotted in Fig. 3 (a). It is evident that at 385 nm (at PPR), the PL is always enhanced irrespective of polarization of excitation if the interaction between the MNP and SQD is only electromagnetic. This enhancement reduces with increase in the separation between the particles. Beyond a separation of 5 nm the field enhancement is not significant.

To understand the third-order nonlinear response of the hybrid system we have also calculated the ratio of the squared intensities in CdTe SQD for the two different polarizations as well as for a random oriented hybrid system and shown in Fig.3 (b). It is clear that if electromagnetic field enhancement is the only interaction between the particles, there will be enhancement and quenching of UCPL depending on whether the applied field is along the direction of the line connecting the two particles or perpendicular to it respectively. In a randomly oriented system the UCPL is expected to remain nearly same as that of the original sample for separation more than 4 nm.

CONCLUSION

We have studied the effect of presence of an Ag nanosphere on the normal PL and two-photon induced UCPL of a single CdTe QD. Irrespective of the polarization of excitation light and separation between two spheres there is always an enhancement of intensity inside the CdTe if excited at wavelength close to PPR. At the same time when excited at wavelength far from the PPR, the enhancement or quenching of square of intensity factor depends on the direction of polarization of excitation light. The magnitude of the enhancement and quenching depends also on the separation between them in both PL and UCPL cases. These results will be useful for understanding the linear and nonlinear optical response of hybrid nanostructures.

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