

# PLASMONIC COUPLING CONTROLLED ABSORPTION AND EMISSION IN LIQUID LUMINESCENT SOLAR CONCENTRATOR

S. Chandra<sup>1\*</sup>, J. Doran<sup>2</sup>, S. J. McCormack<sup>1</sup>

<sup>1</sup> School of Engineering, Trinity College Dublin, The University of Dublin, Ireland

<sup>2</sup> School of Physics, Dublin Institute of Technology,  
Kevin Street, Dublin 08, Ireland

\*Corresponding author email: [schandra@tcd.ie](mailto:schandra@tcd.ie), Phone: + 353 1 896 3321

## ABSTRACT

Quantum dot (QDs) absorption and emission were studied in the presence of gold nanorods (Au NRs) for liquid quantum dot luminescent solar concentrator (QLSC) of 40×25×2 mm. The plasmonic coupling between QDs and Au NRs in the LSCs was manipulated by spacing between QDs and Au NRs through concentration distribution and orientation & aligning the Au NRs through applying an external electric field. The electric field controlled plasmonic interaction increased absorption of QDs by 10-13 % and corresponding emission enhancement is 6-14 %. The response of change in QDs absorption and emission has been categorized in three regions. Unresponsive; for a field strength of 0 -  $2.5 \times 10^4 \text{ Vm}^{-1}$ , active; in the range of  $2.5 \times 10^4 \text{ Vm}^{-1}$  -  $7.5 \times 10^4 \text{ Vm}^{-1}$ , and above  $7.5 \times 10^4 \text{ Vm}^{-1}$  fall in saturation region. The results have shown significant enhancement in absorption, fluorescence emission for liquid QLSC.

*Keywords: Quantum Dot, Plasmonic Coupling, LSC.*

## INTRODUCTION

Luminescent solar concentrator (LSCs) technology was proposed in the late 1970s [1, 3] as a means to concentrate solar radiation on a smaller area of solar cell to enhance their output. The main objective of this technology is to replace the large area of solar cells in a standard flat-plate PV panel by an inexpensive polymeric collector, thereby reducing the cost of the module and consequently solar power. A LSC system has advantages over other alternative concentrating systems: concentrates both direct and diffuse radiation, not subjected to a concentration ratio limitation [4, 5], and is static. An LSC plate consists of a transparent polymer sheet doped with a luminescent species (*organic dyes, quantum dots*), as illustrated in Figure 1a with a cross-sectional view in Figure 1b.

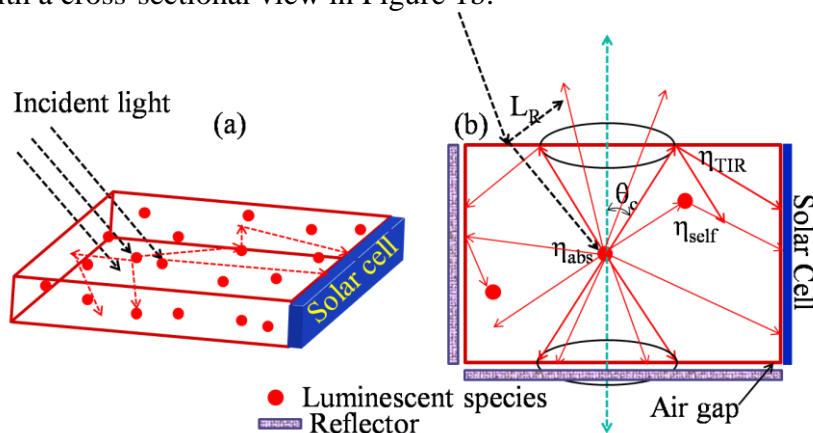


Figure 1: a) Schematic of LSC device without attached external reflectors, b) external reflectors attached LSCs cross-sectional view [6].

LSCs absorb incident solar radiation, and subsequently, re-emit light over all solid angles. The re-emitted light which falls within the critical angle is guided via total internal reflection (TIR) to the sheet edges where solar cells are attached. In a quantum dot solar concentrator (QDSC) [7] the organic dyes are replaced by QDs. QDs have some potential advantages over organic dyes such as wavelength tunability [8, 9]. The conversion efficiency of QDSCs developed to-date [10] has been limited by; re-absorption and scattering losses [11], overlap of the absorption and emission spectra, and escape cone losses. Some of these problems could be addressed by exploiting plasmonic interaction between QDs and metal nanoparticles (MNPs). The plasmonic interaction has potential to increase the excitation and emission rate of QDs, direct the emission, and consequently improve the efficiency of QDSCs.

## PLASMONIC INTERACTION

MNPs (particularly gold and silver) possess unique optical properties of a localized surface plasmon resonance (LSPR) which is a collective oscillation of conduction band electrons, induced by excitation light. MNPs behave like a nanoscopic antenna [12] giving rise to strong enhancements of the local electromagnetic field intensity close to the NPs [13, 14]. When a fluorescent emitter (e.g. QDs, organic dye) is placed in the range of enhanced local electric field intensity, plasmonic interaction takes place which can enhance light absorption, the excitation rate, and radiative and non-radiative decay rates of the optical emitter. The emission can be controlled through the modification of the local electromagnetic boundary condition (or PMD) near the optical emitter. Plasmonic coupling depends on several parameters: spacing between optical emitter and MNPs; orientation of MNPs with respect to optical emitter; and overlap of surface plasmon resonance (SPR) frequency of MNPs and absorption and emission of optical emitter.

This work has examines: the control of the plasmonic interaction through orienting Au NRs with respect to QDs in ethanol media. The spacing was controlled by the concentration distribution of QDs and Au NRs in the composite. The plasmonic interaction was studied through measured absorption and fluorescence emission of QDs in QD/Au NR composites.

## METHOD

*Spheroid Au NRs synthesis:* A two-step continuous process was used to synthesize an aqueous colloidal suspension of spheroid Au NRs of aspect ratio ~1.85. Firstly, the gold precursor (*gold (III) chloride trihydrate* ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was reduced to seed-like particles in the presence of polyvinylpyrrolidone (PVP) by ascorbic acid (AA). In a continuous second step the following were added; silver nitrate ( $\text{AgNO}_3$ ), AA, and sodium hydroxide (NaOH) which led to the growth of spheroid Au NRs and spherical NPs. The gold precursor concentration was fixed throughout synthesis process, and 1.35 weight ratio of AA to  $\text{AgNO}_3$  formed the spheroid shape of Au NRs. PVP protected Au NRs were extracted from the parent solution by centrifuging 8000 rpm for 30 minutes at 10 °C, and re-dispersed in ethanol. Their extinction spectra is presented in Figure 2.

A red-shift of ~5 nm was observed in the longitudinal SPR band, which is due to the difference in refractive index of water and ethanol. Au NRs and their plasmonic coupling with QDs were studied in the ethanol media in liquid LSCs. The core-shell CdSe/ZnS QDs (QD 610) was supplied by Evident Technology, USA, and their absorption and emission peak wavelength 575 and 610 nm, respectively.

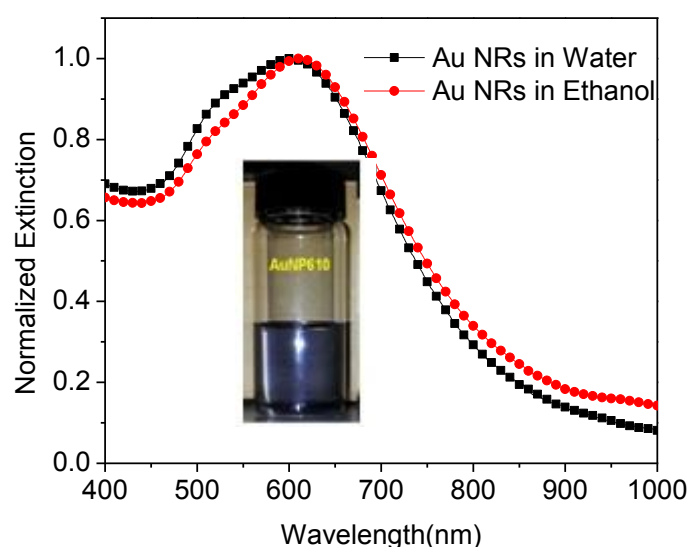


Figure 2: a) Normalized extinction spectra of Au NRs 610 in parent solution (water) and dispersed in ethanol and photograph of their solution in inset (the extinction spectra was measured by UV/Vis/NIR spectrometer)

### LIQUID LSC and Au NRs ORIENTING SETUP

The electric field controlled orientation of Au NRs in the QDs/Au NRs was carried out in a custom made transparent conducting electrode mould cell of  $40 \times 25 \times 2$  mm, as shown in Figure 3a, which is similar to liquid LSCs. The electric field controlled Au NRs orientation setup is presented in Figure 3b was constructed to allow the measurement of the absorption and fluorescence emission simultaneously as a function of applied electric field. The composite of Au NR 610 and QD 610 were prepared suspending 0.04 wt% QD 610 and 1 and 3 ppm of Au NR 610 in ethanol. The fluorescence emission was measured at the edge of cell hence the arrangement is similar to the liquid solar concentrator.

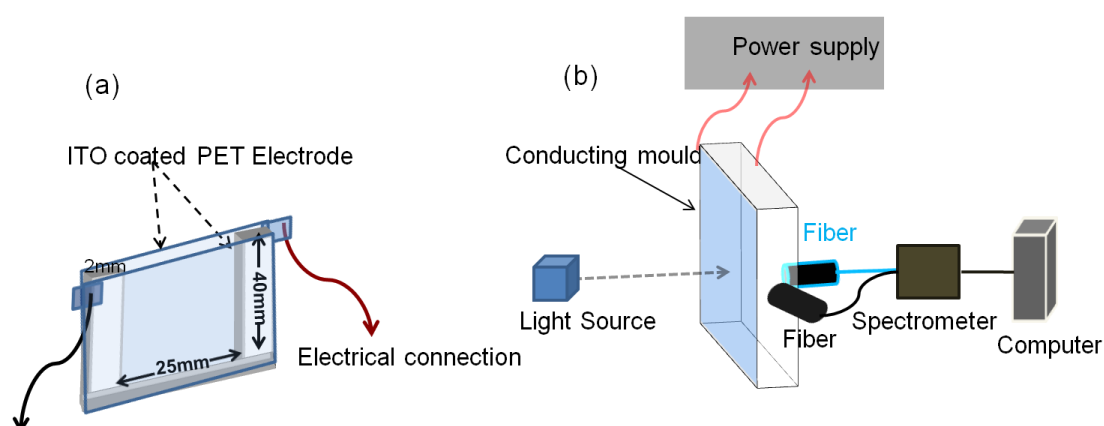


Figure 3: a) Custom made transparent conducting electrode mould cell of  $40 \times 25 \times 2$  mm cell, and b) block diagram of Au NRs orientation setup and AC electric field of 50 Hz was applied.

## RESULTS

The absorption and edge emission of QDs was measured with an applied electric field. The absorption and emission of QDs alone showed less than  $\pm 0.5\%$  variation in applied electric field, which can be considered constant. Therefore, change in absorption and emission upon adding Au NRs is solely attributed to plasmonic coupling. Absorption and fluorescence emission were measured simultaneously as a function of applied electric field strength. The absorption of the QDs in composites started responding to the electric field at  $\sim 2.5 \times 10^4 \text{ Vm}^{-1}$  and nearly saturated at  $\sim 7.5 \times 10^4 \text{ Vm}^{-1}$ , as shown in Figure 4a

The response can be divided in three regions of electric field strength (i) unresponsive region from 0 to  $2.5 \times 10^4 \text{ Vm}^{-1}$  where the field strength is not enough to overcome Brownian motion of Au NRs in solution; (ii) active region from  $2.5$  to  $7.5 \times 10^4 \text{ Vm}^{-1}$  is the range where the electric field strength exerts enough rotation moment on Au NR to exceed thermal energy ( $k_B T$ ) and resistive force of medium. It showed the response to the field which led them to be oriented and aligned [15]; (iii) saturation region from  $7.5 \times 10^4 \text{ Vm}^{-1}$ , illustrating that the orientation and alignment process is completed. The QDs enhanced fluorescence emission follows the absorption in Figure 4b. The enhanced emission contributed by increased absorption of QDs due to plasmonic coupling with Au NRs. The applied electric field controlled the orientation and alignment of Au NR in composites therefore manipulated plasmonic coupling and consequently the absorption and fluorescence emission of QDs in the composites.

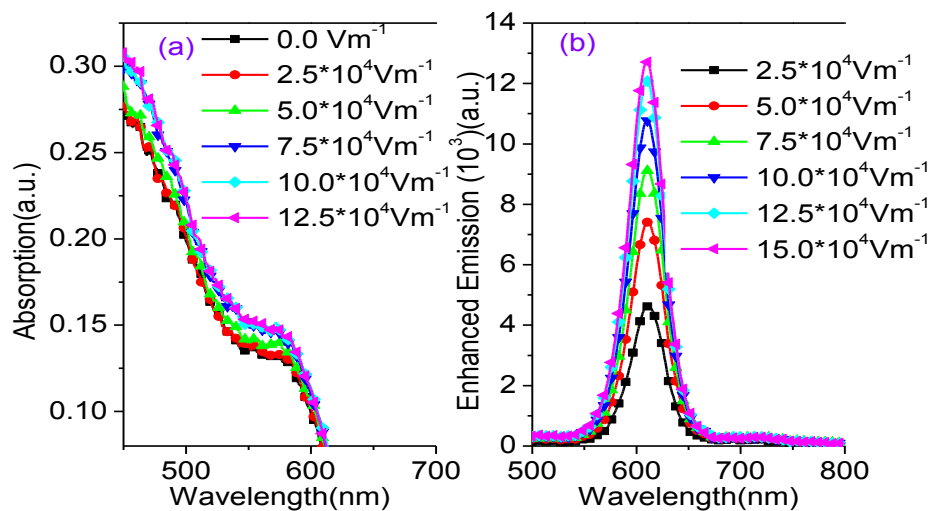


Figure 4: The composite 0.04 wt% QD 610 and 1 ppm of Au NR 610 in applied AC electric field, a) absorption of QDs in composite, b) QDs enhanced emission at edge of conducting cell for composite.

Au NRs concentration was increased from 1 ppm to 3 ppm to study plasmonic coupling dependency on both the spacing and orientation while the QDs were fixed. The increase in absorption is higher compared to 1 ppm of Au NRs in Figure 5a, however, the enhancement in emission is less which is possibly by non-radiative relaxation of excited QDs to Au NRs, due to decreased spacing between QD-Au NRs at higher concentration of Au NRs [16], which compensated the enhanced emission. The higher concentration of Au NRs leads to a background tail at longer wavelengths in the fluorescence emission as in Figure 5b.

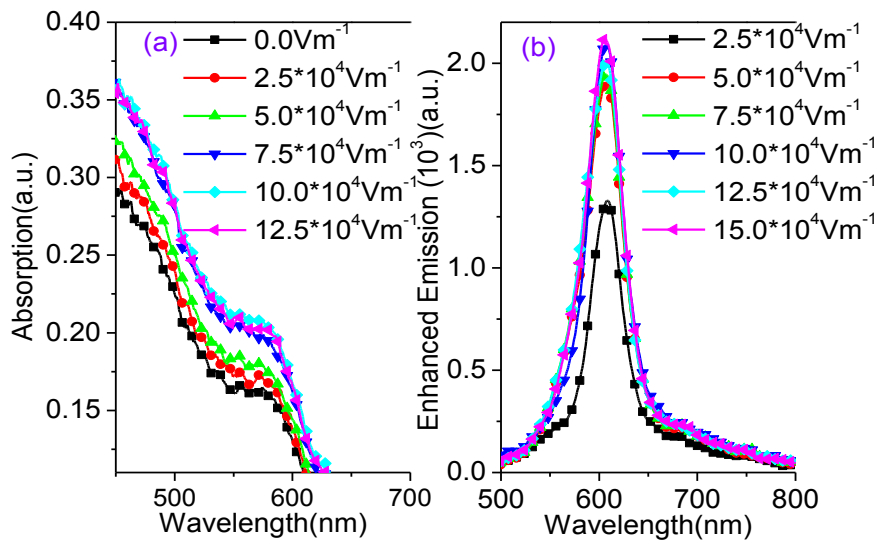


Figure 5: Composite of 0.04 wt% QD 610 and 3 ppm of Au NR 610 in an applied electric field, a) QDs absorption in composite, b) QDs enhanced fluorescence emission at the edge of conducting cell for composite.

The enhancement in absorption and fluorescence for the 1 ppm composite is  $\approx 10\%$  and  $\approx 15\%$ , respectively, presented in the Figure 6a. The 3 ppm composite, absorption and emission enhancement differed compared to 1 ppm composite in the Figure 6b, which may be explained by competition between enhanced emission and non-radiative relaxation of QDs. The enhancement in fluorescence emission can be attributed by two factors; (1) the increased absorption rate of QDs; (2) the possibility that the orientation of the Au NRs controlled the plasmonic interaction between Au NRs and QDs and re-directed the emission of QDs.

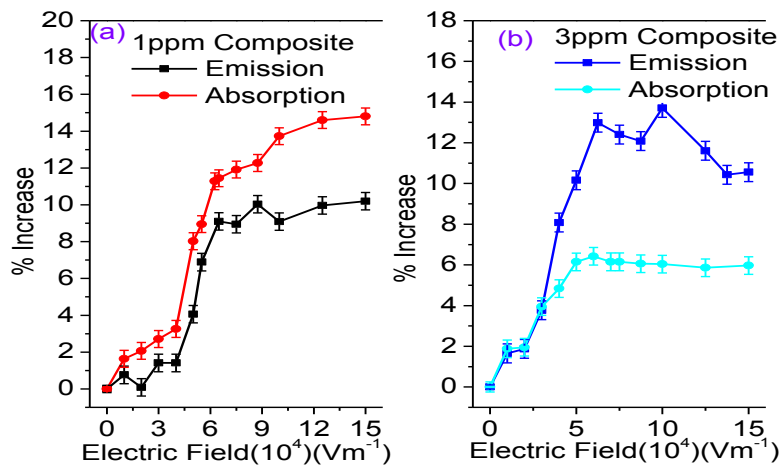


Figure 6: % changes in integrated absorption and emission of QDs in composite 0.04 wt% QD 610 and 1 and 3 ppm of Au NR 610 for the applied electric field.

## CONCLUSIONS

The fabricated transparent conducting electrode mould cell was demonstrated as a liquid LSC of  $40 \times 25 \times 2$  mm. The absorption and emission of QDs alone remained unchanged in applied electric field hence a change in absorption and emission of QDs in the composite of QDs/ Au NRs is solely contributed by the plasmonic coupling between QDs and Au NRs. QDs

absorption and emission in the composite of Au NRs /QDs increased as function of applied electric field strength. The electric field response to orient and align the Au NRs in the composite of QDs/Au NRs is divided in the three region of unresponsive, active, and saturation. The increase in QD absorption in the applied electric field is 13 % for the composite of 3 ppm Au NRs, and 10 % for the 1 ppm composite. However, the corresponding QDs emission enhancement is 14 % greater for the 1 ppm Au NRs composite compared to 6 % for the 3 ppm composite .

## REFERENCE

1. Weber WH, Lambe J. Luminescent greenhouse collector for solar radiation. *Applied Optics*, Vol. 15: pp 2299-2300, 1976.
2. Goetzberger A, Greubel W. Solar energy conversion with fluorescent collectors. *Applied Physics*, Vol.14, pp123-139, 1977.
3. Rapp CF, Boling NL. Luminescent Solar Concentrator. *Proceedings of the 13<sup>th</sup> IEEE Photovoltaic Specialists Conference*, pp 690-693, 1978.
4. Smestad GP, Ries R, Winston R, Yablonovitch E. The thermodynamic limits of light concentrators. *Solar Energy Materials*, Vol.21,pp99-111,1990.
5. Richards BS, Shavlav A, Crokish P. A low escape cone loss luminescent solar concentrator. *Proceedings of 19<sup>th</sup> European Photovoltaic Solar Energy Conference*, Paris, 2004, pp 113-116, 2004 .
6. Chandra, S., McCormack, S.J., Kennedy, M., Doran, J.: Quantum dot solar concentrator: Optical transportation and doping concentration optimization. *Solar Energy* , 2015, Vol. 115, pp552-561, 2015.
7. Barnham, K. , Marques, J. L. , Hassard, J. ,O' Brien, P. : Quantum dot concentrator and thermodynamic model for the global red-shift, *Applied Physics Letter*, Vol. 76 ,pp 1197–1199, 2000.
8. Alivisatos, A. P. : Perspective on the physical chemistry of semiconductor nanocrystals, *Physical Chemistry*, Vol. 100 pp 13226–13239 , 1996.
9. Chen, H. Du, C. , Krishnan, R. , Krauss, T. D. , Harbold, J. M. , Wise, F. W. , Thomas, M. G. , Silcox , J. : Optical properties of colloidal PbSe nanocrystal, *Nano Letter* , Vol. 2, pp1321–1324, 2002.
10. Rowan, B. C. , Wilson, L. R. , Richards, B. S.: Advanced material concepts for luminescent solar concentrator, *IEEE*, Vol. 14, 1312–1322. 2008 .
11. Chatten, A. J. , Barnham, K. W. J. , Buxton, B. F. , Ekins-Daukes, N. J. , Malik, M. A.: New approach to modelling quantum dot concentrators, *Solar Energy Mater and Solar Cells*, Vol. 75, pp 363–371, 2003.
12. Schuck, P. J. , Fromm, D. P. , Sundaramurthy, A. , Kino, G. S. , Moerner, W. E.: Improving the mismatch between light and nanoscale objects with gold nanoantennas, *Physical Review Letter* Vol.94, pp 017402–017405, 2005.
13. Calander, N., Willander, M.: Theory of surface-plasmon resonance optical field enhancement at prolate spheroids, *Applied Physics* Vol. 92, pp 4878–4884, 2002.
14. Muhlschlegel, P. , Eisler, H. J. , Martin, O. J. F. , Hecht, B. , Pohl, D. W. : Resonant optical antennas, *Science* , Vol. 308 , pp 1607–1609, 2005 .
15. Zijlstra, P., van Stee, M., Verhart, N., Gu, Z., Orrit, M.: . Rotational diffusion and alignment of short gold nanorods in an external electric field. *Physical Chemistry*, Vol. 14,, 4584-4588, 2012.
16. Chandra, S., McCormack, S.J., Kennedy, M., Doran, J., Chatten, A. J.: (2012). Enhanced Quantum Dot Emission for Luminescent Solar Concentrators using Plasmonic Interaction. *Journal of Solar Energy Materials & Solar Cells*, Vol. 98, pp 385-390, 2012 .