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FLUORESCENCE EMISSION STUDY OF CdSe/ZnS QUANTUM DOT AND Au NANOPARTICLES COMPOSITE FOR APPLICATION IN QUANTUM DOT SOLAR CONCENTRATORS

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ABSTRACT: Fluorescence of core shell (CdSe/ZnS) quantum dots (QDs) and Au nanoparticles (NPs) composite has been studied for application in quantum dot solar concentrators (QDSC). We conclude two points from the particular QD/Au NP composite studied. One; for the particular Au NPs concentration, the relative fluorescence emission enhancement increases with decreasing QD concentration. Second; the enhancement is more pronounced for the Au nanoparticles whose surface plasmon resonance wavelength overlaps with the absorption peak of QDs. The fundamental concept that could describe the change in fluorescence emission of QDs in the presence of Au NPs is the locally enhanced electromagnetic field induced by the surface plasmon resonance in the Au NPs. This leads to change in absorption, excitation and emission rate for the QDs. The optimal concentration depends on the coupling and spacing between neighbouring QDs and Au NPs.

Keywords ; Concentrator, Au Nanoparticle, Surface Plasmon Resonace.

1. Introduction

The luminescent solar concentrator (LSCs) was suggested in late 1970s to concentrate and convert solar power into monochromatic light to increase the output of solar cells and decrease the cost of solar power generated electricity [1-2]. LSCs consist of luminescent species (organic dyes, /quantum dots, /rare earth materials) doped in a transparent polymer sheet. They absorb the incident solar radiation and, subsequently, re-emit luminescent light over all solid angles. The re-emitted light is guided via total internal reflection (TIR) to the sheet edges where solar cells are attached. The LSC therefore, uses active optics [3] to concentrate photons from a large aperture area to a reduced solar cell area, potentially resulting in lower cost photovoltaic devices. An additional benefit of photon concentration is an increase in photo-generated carriers and enhanced efficiency of the attached solar cell.

The originally the LSC was proposed with organic dyes and later on dyes has replaced by quantum dot and assign the name quantum dot solar concentrator (QDSC) [4]. QDs have some potential advantages over organic dyes; i.e. the ability to tune the absorption threshold simply by choice of dot diameter, and being crystalline semiconductors, QDs are more stable and less degradable than organic dyes [5]. However, conversion efficiency of QDSCs developed to–date [6-8**]** has been limited, firstly by, the low fluorescence quantum yield of the *commercially available* visible-emitting QDs [9] and NIR-emitting QDs [10**]**. Secondly, the devices suffer from re-absorption losses at higher concentrations of QDs [11-12] due to significant, or even in some cases total, overlap of the absorption and primary emission spectra. Some of these problems could be addressed through by exploiting plasmonic interaction between QDs and metal nanoparticles (MNPs). The plasmonic interaction could be used to increase the excitation and emission rate of QDs and consequently the efficiency of the QDSC. Furthermore the reduced optimal concentration would reduce both re-absorption and module cost.

1.2 Surface Plasmon Resonance (SPR): Plasmonic Interaction

When metal nanostructures have dimension smaller than the wavelength of the excitation light, energy can be confined in the small spatial regions through the excitation of localized surface plasmon resonance (LSPR). LSPR is a collective oscillation of conduction band electrons, induced by excitation light. MNPs behave like a nanoscopic antenna giving rise to strong enhancements of the local electromagnetic field (E_{loc}) intensity close to the NPs [13]. The enhanced electric field vector decays exponentially with distance away from the metal surface, with decay length of the order of one half of the excitation wavelength.

The emission of an optical emitter in the presence of MNPs can be formulated in classical terms, where the probability of emitting a photon is related to the local electric field intensity (photonic mode density (PMD)) [14]. The fluorescence process can be written as a product of two processes: (1) Excitation by the incident field, influenced by local environments; and, (2) emission, influenced by balance of radiative and non-radiative decay. These points, above, give us an insight on how to modify the fluorescence of the optical emitter (i.e. QDs) by altering the local PMD, which can be changed using MNPs exhibiting a localized surface plasmon resonance.

When luminescent species (optical emitter) is placed in the range of enhanced $\boldsymbol{E_{loc}}$ field of MNPs, it can modify absorption, excitation rate, radiative and non radiative decay rate and consequently total fluorescence and quantum yield. There are two possible ways to enhance the fluorescence emission of a QD in the vicinity of MNPs: an increase in the excitation rate of the QDs and an increase in the fluorescence quantum yield of the QDs. One; when SPR wavelengths overlap to absorption spectra of luminescent species, both, the absorption and excitation is increased [15]. These interactions have been subject to theoretical as well as experimental [16] investigation. The second effect involves an increase in the fluorescence quantum yield of the optical emitter and

is maximized when the MNPs resonance wavelength coincides with the QD emission band. This mechanism provides a possibility for extending the range of luminescent species. In this paper a composite material model for QDSC is presented. We studied the first effect in this paper.

2. Experimental Detail

2.1 Materials

The materials used for synthesis of the Au NPs and QD/Au NP composites were; Gold precursor gold (III) chloride trihydrate ($HAuCl_4.3H_2O$) of high purity ≥ 99.9%, poly vinylpyrrolidone (PVP) of M_w 10,000, HPLC grade toluene, sodium hydroxide (NaOH) of M_w 40.00 g/mol (*Sigma Aldrich, Ireland)*, and analytical grade ethanol (*Lennox, Ireland*). Core-shell CdSe/ZnS quantum dots (*Plasma Chem, Germany*) were used as the fluorescent material and clear casting epoxy resin (*ABL Resin & Glass, UK*) was used as the dispersion medium. Samples were prepared in a polymethylmethacrylate (PMMA) cuvette of 1 cm path length. All glassware were cleaned with detergent, acetone, and ethanol and finally rinsed with deionised water from a Millipore system.

2.2 Preparation of QDs and Au NPs Composite

The PVP-stabilized spherical (10±1nm) Au NPs were synthesized in ethanol by chemical reduction of gold (III) chloride trihydrate ($HAuCl_4.3H_2O$) precursor. Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$) was reduced in ethanol at a refluxing temperature of 80°C in the presence of PVP (M_w=10000) and NaOH [17]. These Au NPs_A and Au NPs_B were dispersed in epoxy resin using a magnetic stirrer and their extinction spectra shown in Fig.1. The epoxy resin contains two parts; resin and hardener, mixed in the ratio 100:42 by weight.

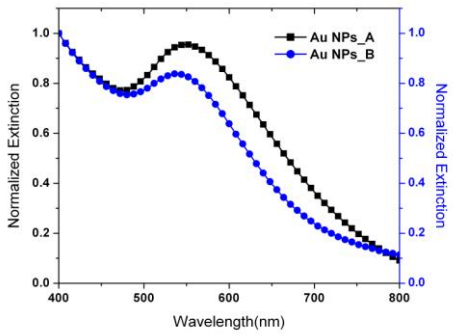

Fig.1: The extinction spectra of Au NPs_A and Au NPs_B in epoxy resin (A Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer was used to measure UV- Vis absorption spectra).

The SPR wavelength of Au NPs is red shifted by 13nm in epoxy resin compared to that in ethanol solution. This is as a result of the difference in refractive indices of ethanol and epoxy (ethanol n≈1.36 and epoxy n≈1.5). A change in refractive index is indicative of a change in the local dielectric environment of the Au NPs, which ultimately alters the distribution of surface electrons on the nanoparticles and consequently the SPR wavelength [18].

Core-shell type CdSe/ZnS quantum dots were used as the fluorescent material for the QDSC. Their typical absorption and emission spectra (in toluene, 0.125mg/ml) are shown in Fig. 2.

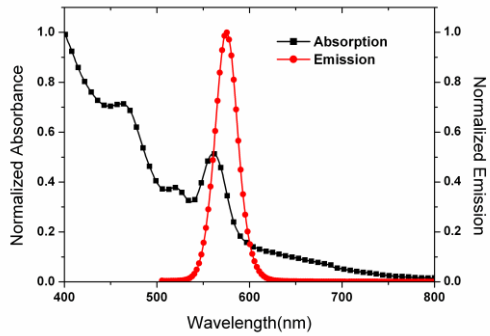

Fig.2 : Normalized absorption and emission spectra of the QD 570 CdSe/ZnS quantum dots in toluene (0.125mg/ml).

The CdSe/ZnS QDs were dispersed in epoxy resin, which is reported as a suitable matrix material for a QDSC device, retaining the fluorescence quantum yield of QDs [19]. The CdSe/ZnS QDs/Au NPs composites were prepared as follows: first the QDs were dispersed in the hardener (0.02 % and 0.01% weight percentage) by magnetic stirring, this was followed by the addition of Au NPs_A and Au NPs B (1.0 to 2.0ppm). Finally the composite was cast and cured in a 1cm polymethylmethacrylate (PMMA) cuvette at 25 ^{0}C for 24 hours (Fig.3).

Fig.3: QD 570 dispersed in epoxy resin and casted in 1cm polymethylmethacrylate (PMMA) cuvette.

3. Results and Discussion

3.1 Fluorescence emission of composite (0.02 % QD) with varying Au NP type and concentration

Fig.4 shows the fluorescence emission of composite (0.02 % QDs) with varying the concentration of Au NPs_A and Au NPs_B. The fluorescence measurements were recorded using a Perkin Elmer LS55B luminescence spectrometer, where luminescence was collected at a 90° angle to the excitation beam. The fluorescence intensity changes with Au NPs concentration (1.0 and 1.5ppm) for both types of Au NPs. We see that the fluorescence

emission intensity depends sensitively on the concentration of Au NPs as well as type of Au NPs. The emission intensity is initially enhanced with Au NPs concentration (1.0ppm) and, eventually, further increases of Au NP concentration (1.5ppm) leads to reduction of the emission intensity.

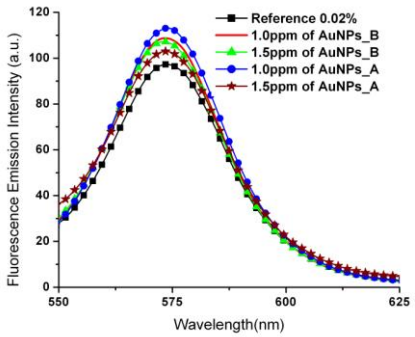

Fig.4: Fluorescence emission of composite (0.02 % QDs) with varying the Au NPs_A and Au NPs_B concentration. Samples were excitated at 525 nm and emission was measured in range 550-625nm.

The relative fluorescence enhancement is higher for AuNPs_A compare to Au NPs_B for the constant Au NPs concentration. This could be explained; as the influence of the enhanced electromagnetic field on the excitation rate of the fluorescent species $\Gamma_{exc}\ r_0$, is straightforward, $\Gamma_{exc}\ r_0$ proportional to electric field intensity $E_{exc}\ r_0, \omega$ at the molecule [20];

$$\Gamma_{exc}\ r_0 \propto \left| p.E_{exc}\ r_0, \omega \right|^2 \text{.....Eq. (1)}$$

where, $E_{exc}\ r_0, \omega$ is the incident plus surface plasmon enhanced electromagnetic field, p the transition dipole moment, ω the transition frequency. The $E_{exc}\ r_0, \omega$ is more pronounced at SPR wavelength [21]. The maximum enhancement occurs when the NP plasmon resonance wavelength coincides with the QD absorption band. The total fluorescence emission rate is given by [20].

$$\Gamma_{em} = \Gamma_{exc} \left[\frac{\gamma_r}{\gamma} \right] \text{.....Eq. (2)}$$

where, γ is the total decay rate, $\gamma = \gamma_{nr} + \gamma_r$, and γ_r and γ_{nr} are the radiative and non radiative rates, respectively.

The Au NPs _A and Au NPs_B have SPR wavelength at 555 and 540 nm (Fig.1), respectively. The QD absorption peak is 560 nm. The Au NPs_A have a greater extent of spectral overlap with QD absorption, compare to Au NPs_B. This leads to higher fluorescence enhancement for Au NPs_A, compare to Au NPs_B for constant Au NPs concentration (1.0ppm).

3.2 Fluorescence emission of composite (0.01 % QD) with varying Au NP type and concentration: Further increase in relative fluorescence enhancement.

The QD concentration was decreased to 0.01% and Au NPs concentration varied up 2.0 ppm for both types of Au NPs and their fluorescence emission are shown in Fig.5 and Fig.6.

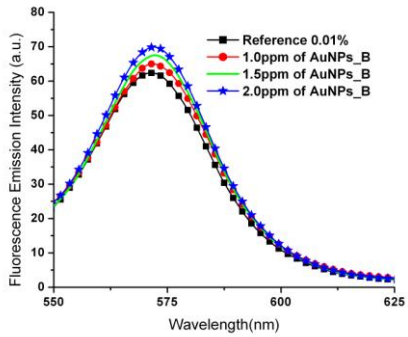

Fig.5: Fluorescence emission of composite (0.01 % QDs) with varied Au NPs_B concentration from 0.0 to 2.0ppm. Samples were excitated at 525 nm and emission was measured in range 550-625nm.

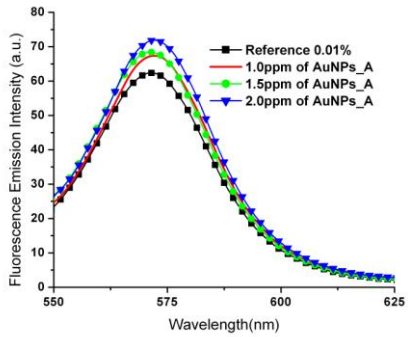

Fig.6: Fluorescence emission of composite (0.01 % QDs) with varied Au NPs_A concentration from 0.0 to 2.0ppm. Samples were excitated at 525 nm and emission was measured in range 550-625nm.

From Fig.5 and Fig.6 relative fluorescence enhancement is higher for composite 0.01% than the 0.02 %. It shows that increase in emission intensity for higher Au NPs concentration (up to 2ppm). The percentage change in fluorescence emission for QDs/Au NPs composite of varying QDs and Au NPs are given in Table.1

Table I: The change relative fluorescence emission with varying QDs and Au NPs concentration and types.

0.02% QDs Concentration		
Sample	Normalized Total Integrated Emission	% Change in Relative Fluorescence Emission
Reference	1.000	0.0
1.0ppm AuNPs_ B	1.084	8.5
1.5ppm AuNPs_ B	1.078	7.9
1.0ppm AuNPs_ A	1.124	12.5
1.5ppm AuNPs_ A	1.112	11.2
0.01% QDs Concentration		
Reference	1.000	0.0
1.0ppm AuNPs_ B	1.061	6.1
1.5ppm AuNPs_ B	1.069	6.9
2.0ppm AuNPs_ B	1.107	10.7
1.0ppm AuNPs_ A	1.084	8.4
1.5ppm AuNPs_ A	1.096	9.6
2.0ppm AuNPs_ A	1.168	16.8

The concentration-depend change in fluorescence emission of QD/Au NPs composite may be explained by spacing distribution between QDs and Au NPs. The spacing between the optical emitter and MNP is an important factor that controls the plasmonic interaction and consequently the fluorescence emission. The plasmonic interaction is highly dependent on the QD-Au NP spacing, as the enhanced field decays exponentially away from the MNPs. Only emitters (i.e. QDs) located in the range of the enhanced field experience plasmonic interaction. If the QDs are too close to the MNP (less than a few nm), then the possibility exists that the excited state QD electron and hole can tunnel to the Au NP through *nonradiative* relaxation [22]. In the case of the 0.02 % QD composite samples, this phenomena could occur which leads to decrease in fluorescence for higher than 1.0ppm Au NPs not for 0.01% composite.

4. Conclusions

It is clear that fluorescence emission of QDs can be controlled through the modification of the local electromagnetic boundary condition (or photon mode density) around it. This phenomenon depends on many parameters, such as metal type, MNP size and shape, and MNP-QD separation (controlled by concentration of QDs and Au NPs). The overall effect of plasmonic interaction in a composite is determined by competition between excitation enhancement and quenching (non-radiative decay at below the critical spacing between MNP-QD). The relative fluorescence enhancement increases as the concentration of QDs decreases from 0.02 % to 0.01 %. This is probably due to change in the distribution of spacing between MNP and QD as both QDs and Au NPs concentration varied.

This gives us insight on how to increase the fluorescence emission at lower concentration of QDs which can ultimately, decrease re-absorption losses in an optimally designed quantum dot solar concentrator (QDSC). These are initial results. Further experimental work is required (with lower QD concentration) to carry out , life time measurement to investigate QD state in localized enhanced electromagnetic field of MNPs and non-radiative quenching effects at higher MNPs concentration . Other QD types utilizing the full useful solar spectrum will be studied and QDSC device fabrication.

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