Fluorescence Emission Study of Cdse/ZnS Quantum Dot and Au Nanoparticles Composite for Application in Quantum Dot Solar Concentrators

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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 Resonance.
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 (HAuCl₃·3H₂O) of high purity ≥ 99.9%, poly vinylpyrrolidone (PVP) of Mₙ 10,000, HPLC grade toluene, sodium hydroxide (NaOH) of Mₙ 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 (HAuCl₃·3H₂O) precursor. Gold (III) chloride trihydrate (HAuCl₃·3H₂O) was reduced in ethanol at a refluxing temperature of 80°C in the presence of PVP (Mₙ=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. 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.

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°C for 24 hours (Fig.3).

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 excited 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, \( \Gamma_{exc} r_0 \propto [p,E_{exc} r_0,\omega] \) proportional to electric field intensity \( E_{exc} r_0,\omega \) at the molecule [20];

\[
\Gamma_{exc} r_0 \propto [p,E_{exc} r_0,\omega]^2 \quad \text{Eq. (1)}
\]

where, \( E_{exc} r_0,\omega \) is the incident plus surface plasmon enhanced electromagnetic field, \( p \) the transition dipole moment, \( \omega \) 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];

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

where, \( \gamma \) is the total decay rate, \( \gamma = \gamma_{nr} + \gamma_r \), and \( \gamma_r \) and \( \gamma_{nr} \) 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 excited at 525 nm and emission was measured in range 550-625nm.

The percent change in fluorescence emission for QDs/Au NPs composite of varying QDs and Au NPs are given in Table.1.

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.
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 non-radiative 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.

Acknowledgements
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5. Reference

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

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<th>Sample</th>
<th>Normalized Total Integrated Emission</th>
<th>% Change in Relative Fluorescence Emission</th>
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0.01 % QDs Concentration

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<th>% Change in Relative Fluorescence Emission</th>
</tr>
</thead>
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