Enhanced quantum dot emission for luminescent solar concentrators using plasmonic interaction

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ABSTRACT

Plasmonic excitation enhanced fluorescence of CdSe/ZnS core-shell quantum dots (QDs) in the presence of Au nanoparticles (NPs) has been studied for application in quantum dot solar concentrator (QDSC) devices. We observe that there is an optimal concentration of Au NPs that gives a maximum 53% fluorescence emission enhancement for the particular QD/Au NP composite studied. The optimal concentration depends on the coupling and spacing between neighboring QDs and Au NPs. We show the continuous transition from fluorescence enhancement to quenching, depending on Au NP concentration. The locally enhanced electromagnetic field induced by the surface plasmon resonance in the Au NPs leads to an increased excitation rate for the QDs. This is evidenced by excitation wavelength dependent fluorescence enhancement, where the locally enhanced field around the Au NPs is more pronounced close to the surface plasmon resonance (SPR) wavelength. However, at higher concentrations of Au NPs non-radiative energy transfer from the QDs to the Au NPs particles leads to a decrease of the emission, which is confirmed by detection of both a double exponential lifetime decay in, and a decrease in the lifetime of the QDs. The overall fluorescence emission enhancement depends on these competing effects; increased excitation rate and non-radiative energy transfer.

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1. Introduction

Solar energy harvesting technologies are currently experiencing substantial investment and growth, driven by the aim of generating low cost (per kilowatt-hours) solar electricity. One approach is to reduce the amount of semiconductor material utilized, which is facilitated by concentrating the solar power from a large aperture area to a smaller area using inexpensive concentration techniques [1], thereby reducing the cost of the module and consequently the cost of solar electricity. The fluorescent or luminescent solar concentrator (LSC) was first suggested in late 1970s [1–7]. 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 [6] 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 [7].

1.1. Quantum dot solar concentrators (QDSC)

In a quantum dot solar concentrator (QDSC) [8] the luminescent species are QDs. QDs have some potential advantages over organic dyes; i.e. the ability to tune the absorption threshold simply by the choice of dot diameter, and being crystalline semiconductors, QDs are more stable and less degradable than organic dyes [9]. QDs of various absorption thresholds and high fluorescence quantum yields (FQY) have been synthesized. For example, visible emitting core-shell (CdSe/ZnS) QDs have demonstrated fluorescence quantum yield up to 84% [10] and NIR-emitting PbS quantum dots in the range of 12%–81% [11]. However, conversion efficiency of QDSCs developed to date [12–15] has been limited, firstly by, the low fluorescence quantum yield of the *commercially available* visible-emitting QDs [16] and NIR-emitting QDs [17,18]. Secondly, the devices suffer from re-absorption losses at higher concentrations of QDs [19–21] due to significant, or even in some cases total, overlap of the absorption and primary emission spectra. Some of these problems could be addressed by exploiting plasmonic interaction between QDs and metal nanoparticles (MNPs). The plasmonic interaction could

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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 costs as QDs are currently relatively expensive at around ~ 5960/g [22].

1.2. Surface plasmon resonance (SPR)

Metal nanostructures possess the unique optical properties of a localized surface plasmon resonance (LSPR), which is a collective oscillation of conduction band electrons, induced by excitation light as shown in Fig. 1. MNPs behave like a nanoscopic antenna [23] giving rise to strong enhancements of the local electromagnetic field intensity close to the NPs [24–26]. 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 [27].When a fluorescent emitter (e.g. QDs, 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 fluorescent species.

1.3. Plasmonic interaction

Total fluorescence of an optical emitter is determined by radiative recombination of the excited electron–hole pair, by coupling of the excited state to the vacuum oscillations of the local environment, which competes with non-radiative processes [28–30]. This complete fluorescence process 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)) [31]. 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 decays. 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.

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. 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 [32]:

$$\Gamma_{exc}(r_0) \propto |pE_{exc}(r_0,\omega)|^2 \tag{1}$$

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 maximum enhancement occurs when the NP plasmon resonance wavelength coincides with the QD

absorption band [33–35]. 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 [36–38]. The total fluorescence emission rate is given by [32]

$$\Gamma_{em} = \Gamma_{exc}\left[\frac{\gamma_r}{\gamma}\right] \tag{2}$$

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.

It is clear that emission can be controlled through the modification of the local electromagnetic boundary condition (or PMD) near the optical emitter. This phenomenon depends on many parameters, such as metal type, MNP size and shape, MNP-QD separation, and fluorescence quantum yield of the QD. The overall effect of plasmonic interaction in a given system is determined by competition between excitation enhancement (increased light absorption), emission enhancement (increased radiative decay), and quenching (increased non-radiative decay). Our work has exploited the first phenomenon.

2. Materials and 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 ($HAuCl_4 \cdot 3H_2O$) of high purity $\geq 99.9\%$, 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. Characterization techniques

A Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer was used to measure UV-vis absorption spectra. Luminescence measurements were recorded using a Perkin Elmer LS55B luminescence spectrometer, where luminescence was collected at a 90° angle to the excitation beam. The fluorescence lifetime of the QD/Au NP composites in epoxy was recorded using a time-correlated single photon counting (TCSPC) technique.

2.3. Sample preparation

2.3.1. Au NPs dispersion in epoxy resin

The PVP-stabilized spherical (10 ± 1 nm) Au NPs were synthesized in ethanol by the chemical reduction of gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) precursor. Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) was reduced in ethanol at a refluxing temperature of 80 °C in the presence of PVP ($M_w = 10,000$) and NaOH [39]. These Au NPs were dispersed in epoxy resin using a magnetic stirrer as shown in Fig. 2. The epoxy resin contains two parts; resin and hardener, mixed in the ratio 100:42 by weight.

The SPR wavelength for MNPs is critically determined by four factors; the density and effective mass of the electrons, the shape of the MNPs, and the size of the charge distribution. The charge distribution depends on the local dielectric environment of the MNPs and changing this environment can affect the plasmon oscillation frequency, due to the varying ability of the surface to
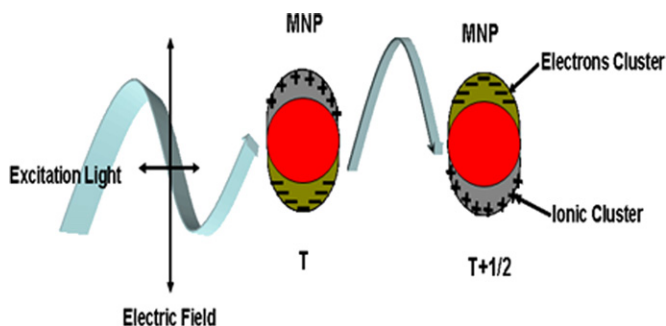

Fig. 1. Schematic representation of the surface plasmon excitation in metal nanoparticles.