Fluorescence Enhancement of CdSe Quantum Dots with Au Nanocrystals

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Abstract

Linear and nonlinear fluorescence were studied in cadmium selenium quantum dots (CdSe QDs) with gold nanocrystals (Au NCs). Linear photoluminescence measurements in CdSe QDs and Au NCs mixed solutions (1:1 and 5:1 mixing ratio by weight) showed significant fluorescence-intensity quenching effect, compared to a QDs-only sample. Another set of thin film samples gave over 3 times of enhancement in the nonlinear florescence measurement.

Introduction

Semiconductor QDs are nanoparticles with unique optical properties. Those properties, like large two-photon absorption coefficient, narrow emission and broad absorption spectra, and size-tunable fluorescence, have made them good substitutes for dyes that are typically used as fluorescent tags in biological applications. To understand and improve the QDs' efficiency in such applications, surface plasmon enhanced fluorescence was studied. The optical properties of small metal particles have been an attractive field of study for years, since they interact with incident light strongly and change the optical properties significantly. Such extraordinary properties can be explained by the excitation of coherent free electron oscillations, or surface plasmon polaritons. As a result of the high polarizability induced by such modes, a strong electrical field develops about the nanocrystals surface. This locally-enhanced electromagnetic field can be helpful to achieve enhanced fluorescence.

Materials and Experimental Design

We investigated the changes in fluorescence intensity for two sets of thin film samples. The first set is composed of a monolayer of 5-nm-diameter CdSe QDs, a monolayer of 4.5 nm Au NCs and a separating section consisting of 4, 5, 14, 16 and 18 layers of polymethyl methacrylate (PMMA) to control the distance between the monolayers of QDs and NCs. The second set consists of a monolayer of 4.3 nm in diameter CdSe quantum rods (QRs) and the same monolayer of Au NCs. This set was assembled in a similar way as the first set, but using varying layers of amorphous silicon dioxide (SiO_2) to separate the QRs and gold monolayers. The setup of the linear fluorescence measurement is shown schematically in Figure 1. An argon laser was used to excite the sample, and the fluorescence was collected by two lenses and sent to a monochromator.

A photon-multiplier tube (PMT) and a lock-in amplifier were used to increase the sensitivity and signal-to-noise ratio of the setup. The nonlinear fluorescence measurement was done in a similar way except that: a mode-locked Ti-sapphire laser (wavelength ~ 800 nm, pulse width ~ 200 fs, repetition rate ~ 76 MHz and peak power > 10 kW) was used instead of the argon laser. Also to eliminate the loss introduced by the monochromator, we collected the fluorescence directly with a PMT.

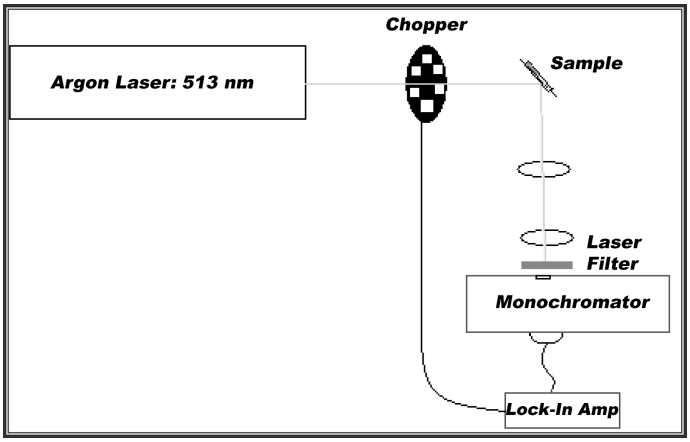

Figure 1: Schematic of linear experimental setup.

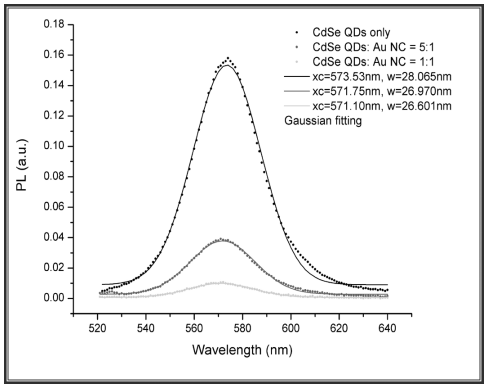

Figure 2: Photoluminescence intensities for samples in solution: Linear Experiment.

Results and Discussion

In the beginning, linear fluorescence measurements were done with QD/Au solutions mixed at different ratios: samples with QDs only, and QD/Au mixed at 1:1 and 5:1 ratios were compared. The results are shown in Figure 2. The QDs-only sample showed the strongest fluorescence, and the more Au NCs in the other two samples, the less fluorescence they gave. From the curve-fitting, we were not able to distinguish any significant center wave-length or full-width-at-half-maximum changes for all three samples tested. Although it seems to be quenching with more gold in the solution, the results are inconclusive since there are too many uncertainties, like re-absorption of fluorescence by Au NCs and uncontrollable spacing between QDs and NCs.

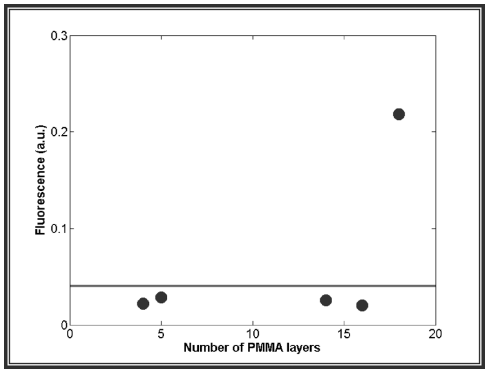

Figure 3: Average photoluminescence intensities for thin-film samples with PMMA: Linear Experiment.

Having this in mind, we obtained the QD/Au thin film samples which had the nanoparticles separated at "specific" distances using PMMA layering in between them. This batch of samples consisted of thin films with QDs only, and QDs and gold NCs separated with 4, 5, 14, 16 and 18 PMMA layers. We noted, though, that the samples had visible surface unevenness, which is why, during the linear and nonlinear experiments, we decided to scan through the sample with the laser and obtain an average of the intensities. For the QD/Au thin film samples with PMMA layering, Figure 3 shows the average of the fluorescence intensities for varying PMMA layers in the linear experiment. The red line represents the average intensity for the QDs-only sample. From the intensity plots generated with the fluorescence data obtained, there is no significant fluorescence quenching or enhancement in these samples.

The 18-layer PMMA sample seems to be totally different from others, and we believe that there might have been some mistakes during fabrication (possibly the PMMA layers folding upon themselves). Figure 4 shows the data obtained for the nonlinear fluorescence experiments on the same samples with PMMA layering. Without considering the 18-layered sample, over 3-fold of fluorescence enhancement has been observed in the 4-layered sample compared with the CdSe QDs only sample (red line). Furthermore, the optimum spacing seems to be smaller than 4-layered thickness. To further investigate the optimum spacing between the CdSe QDs and Au NCs, thinner and more precisely controlled layers are needed.

The final set of samples consisted of QR/Au thin films fabricated more precisely with SiO_2 layering to separate the nanoparticles from each other. The surface of the samples was much more even than the previous set of samples; unfortunately, we could not perform the planned experiments because of laser malfunction.

Conclusions and Future Work

We have shown that over 3-fold of nonlinear fluorescence enhancement in CdSe QDs monolayer with Au NCs can be obtained. Future work will be done with the last set of samples when the laser is available, but similar results are expected for the nonlinear experiments. Once this is done, we will be able to calculate the optimal distance between the nanoparticles and fabricate the QD/NC particles so that they can be used in biological applications.

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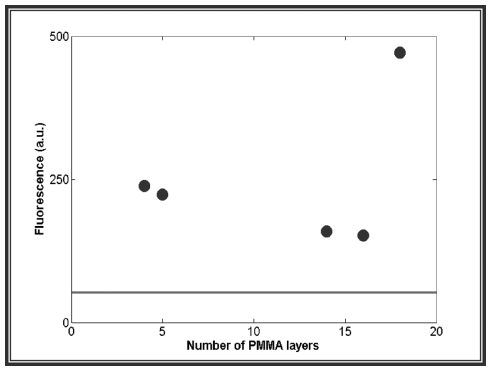

Figure 4: Average photoluminescence intensities for thin-film samples with PMMA: Non-linear Experiment.