

SPONTANEOUS EMISSION FROM CDSE IN VICINITY OF PLASMONS

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Introduction

Excitons in quantum dots (QDs) have a strong quantum electrodynamic coupling with the localized surface plasmon (LSP) in metal nanoparticles if it is placed within the SP field's penetration depth. In this regime an electron-hole pair in the confined nanostructure may recombine into a SP mode instead of into free space and emit a photon. The degree of spontaneous emission rate modification for a given wavelength depends on the SP's density of state at that wavelength [1]. The plasmon-mediated photoluminescence (PL) enhancement can be determined by the balance between the resonant energy transfer from the QDs to the gold (Au) surface and the electric field enhancement.

Experiment

Au nanoparticles (NPs) were prepared by the reduction of gold by sodium citrate [2]. After a mixture solution of 1 mM of HAuCl₄ was refluxed with vigorous stirring for ~30 minutes in 550 ml of water, 50 ml of 12-mM sodium citrate was rapidly inserted and stirred for additional 30 minutes to prepare Au nanoparticles with diameter ~32 nm. After the reaction solutions were reached room temperature, the residual solutions were filtered through 0.45- μ m polymer membrane filters. The resulting colloidal particles were characterized by an UV-Vis spectrometer (Agilent 8453), and transmission electron microscopes (FEI, Technai G2 F30 Super-Twin, 300 kV, and Hitachi, H-9000NAR, 300 kV). Nanocrystal CdSe/ZnS-COOH core/shell quantum dots (QDs) were provided by the Ocean NanoTech LLC.

The Au-CdSe/ZnS hybrid structure was assembled on quartz slides. The quartz was treated with oxygen plasma (30 Pa, oxygen 100 ml/min, and 100 watts) for 300 sec. After that

the hydroxylated quartz was silanized in ethanol containing 1 wt. % APTES in order to form the amino functional group on the surface of the hydroxylated quartz and washed with ethanol and dried with nitrogen gas. Finally, the dried quartz was baked at 120 °C for 15 minutes. The reactivated-quartz was spotted with the high concentration gold nanoparticles for 12 hours at room temperature, and washed with DI water and dried with nitrogen gas (see Fig.1). For preparing a spacer with ~1 nm – ~50 nm distance between QDs and NPs, 0.1-ml of poly(methyl methacrylate) (PMMA, C2 950k) was casted at 5000 rpm for 30 sec on the Au NPs-attached quartz plate, and baking them at 120 °C for 2 min, sequentially. The spacer distance between Au NPs and CdSe QDs was controlled by oxygen plasma treatment (30pa, oxygen 100ml/min, and 100 watts) for 7 min, 12 min, 17 min, 20 min, 25 min, 27 min, and 30 min, respectively. For the spacer with ~50 nm - ~100 nm between QDs and NPs, 0.1-ml of PMMA was casted on the Au-attached quartz plate at 3500 rpm for 30 sec, baked at 120 °C for 2 min, and treated with oxygen plasma for 7 min, 12min, 17 min, and 22 min, respectively. After treatment of oxygen plasma, 0.1-ml of 1% casein in solution (1xPBS) was spin-coated at 3500 rpm for 30 sec on the PMMA-quartz. Then, 0.1-ml CdSe/ZnS QD was finally casted on the plate at 3500 rpm for 30 sec. For comparison purpose a quartz plate without Au nanoparticles was prepared by spin coating a PMMA layer and then CdSe/ZnS QDs. The plasmon-mediated PL enhancement for the hybrid CdSe-Au structures was investigated. The excitation source was a CW HeCd laser (Melles Griot, 45-MRM-803-120) operated at 325 nm at 40 mW. The PL of the hybrid composite was collected using an optical fiber (Ocean Optics, P600-2-VIS-NIR), a long wavelength pass filter at 455 nm and a spectrometer (Ocean Optics USB4000, Resolution: 1 nm).

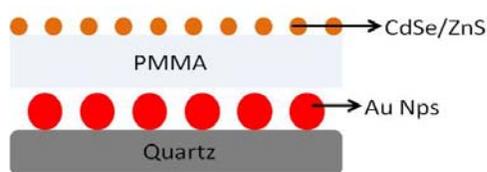


Fig. 1 Schematic Structure of the Au-CdSe/ZnS hybrid structure on a quartz slide.

Results and Discussion

Absorption and PL spectra of the CdSe/ZnS-COOH in aqueous solution are shown in figure 1. The maximum absorption occurs at 520 nm while the PL peak is located at ~545 nm.

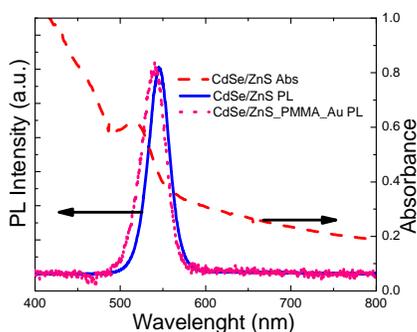


Fig. 2 Absorption and PL spectra of CdSe/ZnS-COOH in aqueous solution and in the presence of Au NPs.

The PL peak of hybrid Au-PMMA-QDs was located at ~540 nm with ~5-nm blue shift compared with that of QDs without Au NPs. The plasmon effect on the CdSe/ZnS PL was characterized by comparing the PL of the QDs in the presence and in the absence of Au NPs. The figure 3 shows the CdSe/ZnS_PMMA PL spectra with and without Au NPs with laser excitation at 325 nm. The origin of the PL band is assigned to the transition from the lowest exciton state in CdSe/ZnS QDs in the hybrid material. The PL intensity of the hybrid QD/NPs material is superior to that of QDs assembled on PMMA films. The difference between the results suggests the existence of the field localization and the electronic interaction between the CdSe/ZnS and Au NPs.

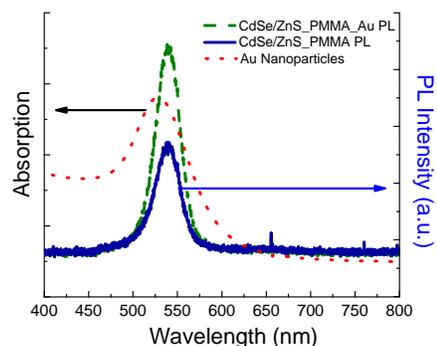


Fig. 3 Absorption of Au NPs (red) and PL spectra of CdSe/ZnS - in absence (blue) and presence (green) of Au NPs.

Conclusion

Hybrid nanostructures of CdSe/ZnS quantum dots in the proximity of Au NPs were prepared to study their luminescence properties through exciton-plasmon coupling. Depending on the distances between QDs and NPs, large luminescence enhancements and quenching from the exciton recombination in the QDs were observed. The PL enhancements and quenching rates were also sensitive to the coherent coupling conditions between the absorption and emission spectra of QDs and the plasmon resonance absorption of NPs. The PL enhancement and quenching can be explained by local field enhancement, energy transfer rate, and modes of couplings between exciton and plasmon.

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References

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