

Incorporation of colloidal quantum dots into the gap of plasmonic bowtie antennas

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We demonstrate the deterministic incorporation of colloidal CdSe/CdS core-shell quantum dots emitting at $\lambda = 620$ nm into the gap of plasmonic Ag bowtie antennas. The antennas were fabricated using a lift-off process employing electron beam lithography and electron gun evaporation of silver on a copper seed layer. Nano-patterning of the wet-chemically synthesized quantum dots was done using a previously devised lift-off process and a state-of-the-art electron beam lithography system for the alignment. Placing colloidal quantum dots in the gap of plasmonic antennas can significantly reduce their intrinsic radiative lifetime and hence increase the emission rate for the application as a room-temperature single-photon source.

Introduction

Colloidal quantum dots (QDs) usually consist of a 2-20 nm diameter semiconductor core embedded in a higher bandgap shell material for electronic passivation. Organic ligands covering the shell prevent agglomeration of the QDs when they are suspended in an appropriate solvent. Due to the quantum confinement effect colloidal QDs exhibit size tuneable emission, combined with high photoluminescence quantum yield. The discovery of these favourable intrinsic properties almost thirty years ago [1, 2] has sparked extensive research into amongst other areas the application of colloidal QDs for optical and optoelectronic devices [3]. Examples range from of light emitting devices (LEDs) [4] to fluorescent labelling [5] and room-temperature single photon emitters [6].

In their application as on-demand single photon sources, wet-chemically synthesized colloidal QDs compete with matured single photon sources based on epitaxially grown quantum dots operating at cryogenic temperatures [7, 8]. The stronger electronic confinement in colloidal QDs allows for room temperature operation, the brightness of such a single-photon source is however limited by the intrinsic radiative lifetime, which is typically in the range of ~ 10 ns for colloidal QDs compared to typically ~ 100 fs for epitaxial QDs at a temperature of ~ 5 K [9]. A way to overcome this limitation is to incorporate the emitter in a cavity, where in the weak coupling regime the intrinsic radiative lifetime is decreased by the Purcell Effect [10]. Plasmonic gap antennas can offer high radiative enhancement due to their small mode volume, which comes at the cost of additional loss, limiting the quantum efficiency of the source. Up to 540-fold decrease in the emission lifetime has been shown, while retaining single-photon emission for colloidal QDs incorporated into plasmonic nanocavities using a purely probabilistic method [11]. Though, for practical applications and simplified characterisation a more deterministic fabrication approach would be desirable. In this work we demonstrate the incorporation of patches of colloidal quantum dots into the gap of plasmonic bowtie antennas by overlay alignment using electron beam lithography as a pathway towards a deterministically defined, bright room-temperature single photon source with colloidal QDs.

Antenna design and simulation

To show the capabilities of our process we chose the frequently used plasmonic bowtie antenna geometry for which up to 1240-fold single molecule fluorescence enhancement has been reported [12]. Figure 1a illustrates the simulated geometry with a single colloidal QD incorporated in the gap of a plasmonic silver bowtie antenna. The dipole moment \vec{d} of the QD is aligned with the dipole mode of the plasmonic antenna. For efficient collection of the vertically emitted light by a microscope objective, the antenna is placed on a 50 nm thick SiO_2 spacer above a silver mirror.

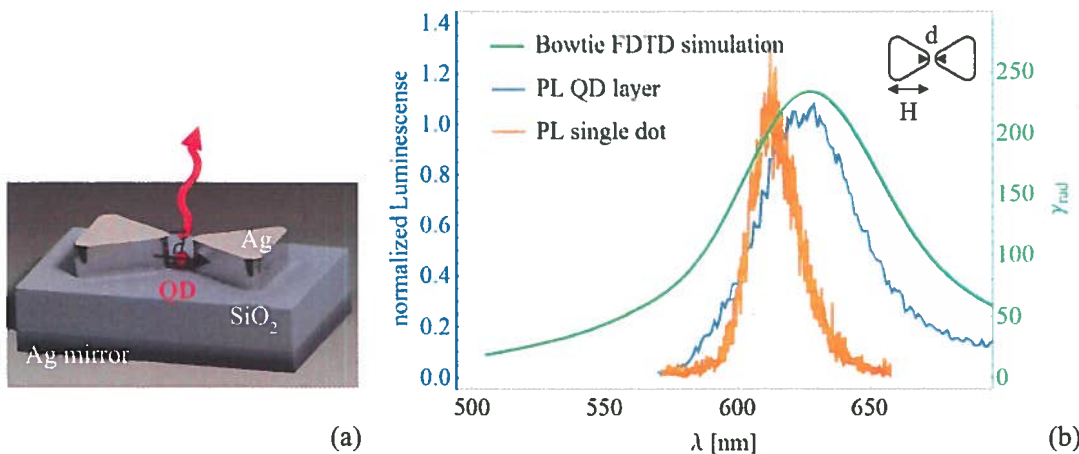


Figure 1: Illustration of the simulated Ag bowtie antenna with a colloidal QD incorporated into the gap (a). Comparison of the simulated radiative enhancement γ_{rad} with the emission spectrum of an individual and an ensemble of colloidal CdSe/CdS core-shell QDs (b).

For the application as a single photon source the radiative enhancement γ_{rad} of a dipole emitter in a plasmonic cavity is a relevant figure of merit, since it ultimately limits the achievable brightness of the source and the excitation power usually has to be limited to retain anti-bunched emission.

We used a commercial FDTD solver (Lumerical [13]) to simulate and optimize the antenna design in order to match it to the emission of colloidal CdSe/CdS core-shell quantum dots emitting at $\lambda = 620$ nm. Figure 1b compares the simulated radiative enhancement of a QD placed in the gap of a bow-tie antenna with the emission spectrum of colloidal CdSe/CdS QD synthesized with the *flash* method [14]. The antenna dimensions chosen for the simulation were a gap-width of $d = 15$ nm, an antenna height of $H = 60$ nm, a corner fillet radius 10 nm, a thickness of 2 nm for the copper seed layer and a 20 nm thick silver layer topped with a 2 nm thick gold layer for oxidation protection. The full width at half maximum (FWHM) of the simulated antenna resonance was 95 nm, compared to a FWHM of 51 nm for a QD ensemble and 23 nm for an individual CdSe/CdS QD. The simulation further predicts radiative enhancement factors $\gamma_{rad} > 200$ with quantum efficiencies $> 50\%$ for this particular geometry.

Fabrication process flow

The bowtie antenna structures and alignment markers were produced with a lift-off process using AR-P 6200.09 (All Resist) positive electron beam resist. Therefore the

resist was diluted with anisole at the ratio of 1:1, spin-coated at 3000 rpm on silicon samples with a prefabricated silver mirror and a 50 nm SiO₂ spacer layer and baked on a hot-plate set to 150°C for 1 min, resulting in a resist thickness of 80 nm. The design was exposed with a 50 kV electron beam lithography system (Raith Voyager) using an area dose of 180 μC/cm² and a 5 nm step size. The samples were developed in n-Amyl acetate for 1 min, rinsed with isopropanol and dried with a nitrogen gun before a 10 s O₂ plasma cleaning step (AV Vision 320 RIE) to improve the metal adhesion. A 2 nm copper seed layer was evaporated (Leybold 560) prior to 20 nm of silver and the 2 nm gold layer for oxidation protection, the metal lift-off was done with the dedicated remover AR 600-71 using ultrasonic agitation.

For the overlay-patterning of the colloidal QDs we adapted a lift-off procedure [15] using again 1:1 diluted AR-P 6200.09 positive resist spin-coated at 5000 rpm and baked on a hot-plate set to 150°C for 1 min. A 10 s O₂ plasma cleaning step was performed to thin the resist down to a thickness of 40 nm before overlay exposure of the openings. Dot doses were varied from 5 – 50 fC to change the diameter of the holes and the samples were developed in n-Amyl acetate for 1 min. Figure 2a shows a SEM micrograph of an Ag antenna covered with 40 nm of AR-P 6200 resist and an opening (15 fC dot dose) overlaid with the gap of the antenna. For better contrast the SEM pictures in Figure 2 are of structures fabricated on bare silicon samples. Colloidal CdSe/CdS core-shell QDs with a diameter of ~10 nm were deposited on the samples using a Langmuir Blodgett (LB) through system (Nima 312D) set to a target pressure of 25 mN/m. The QD lift-off was done using a 1:1 mixture of Toluene and the dedicated remover AR 600-71 and ultrasonic agitation, subsequently rinsing the sample with isopropanol. Figure 2b shows a resulting partial patch of colloidal QDs overlaid with the gap of the plasmonic Ag bowtie antenna (30 fC dot dose).

To further enhance the reliability of the overlay alignment, we plan to use automated marker recognition instead of manual alignment for future samples. In addition, the QD patterning efficiency can be improved by reducing both the thickness of the Ag antennas and of the AR-P 6200.09 resist for the overlay step. We foresee that these improvements will enable the incorporation of single colloidal QDs into the gap of plasmonic bowtie antennas.

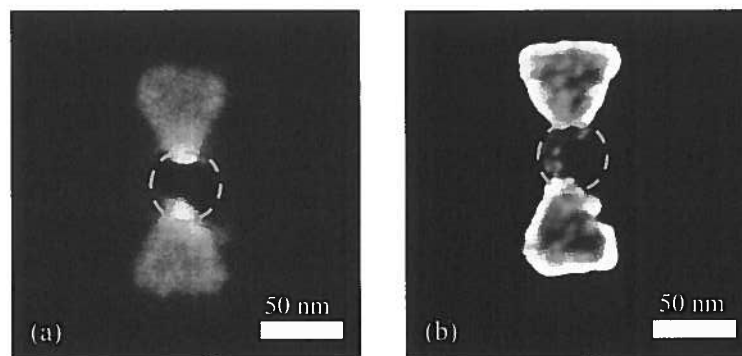


Figure 2: SEM micrographs of the fabricated structures, (a) shows the antenna covered with 40 nm of AR-P 6200 resist with an opening (highlighted by the dashed circle) overlaid with the antenna gap for the following colloidal QD deposition. A different structure after QD lift-off in (b) shows a partial QD patch (highlighted by the dashed circle) in the gap of the antenna. For better contrast the SEM pictures are of structures fabricated on bare silicon samples.

Conclusion

We demonstrate the deterministic incorporation of colloidal CdSe/CdS core-shell quantum dots emitting at $\lambda = 620$ nm into the gap of plasmonic Ag bowtie antennas. Scaled down to the level of single QD emitters this process promises to enable the fabrication of arrays of high brightness single photon sources using colloidal QDs. Photoluminescence lifetime and intensity measurements on the fabricated samples are currently underway to confirm the radiative enhancement predicted by simulations.

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