Exciton-Plasmon Interactions in Quantum Dot – Gold Nanoparticle Structures – Supporting Information

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All reagents were used as received from Sigma-Aldrich. All DNA oligo-nucleotides were obtained from Integrated DNA Technologies (IDT). We used CdSe/ZnS streptavidin quantum dots from Invitrogen (Qdots Invitrogen). Gel electrophoresis sample extraction kit was obtained from Gebaflex technologies. DI water (18.3 MΩcm^{-1}) was used in all experiments.

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1 Gold NP synthesis

1.1 17 nm gold NP Synthesis

A 20 ml solution of 0.2% w/v Na3-Citrate + 25 µl of 1% w/v Tannic Acid heated to 600 C is added under vigorous stirring to a solution which consists of 1 ml of 1% w/v NaAuCl4 diluted to 80 ml DI water. The solution is heated to boil and is then boiled for another 10 minutes and cooled to room temperature.

1.2 80nm gold NP synthesis

1 ml of 17 nm gold NP solution is put in a 50 ml plastic falcon tube.

1. 1 ml of 0.01% NaAuCl4 is added under stirring on vortex.
2. Sequentially 40 µl of 40 mM hydroxyl amine is added under vigorous stirring.
3. Steps 1-2 are repeated until a volume of 10 ml is reached.
4. The NP solution is transferred to an erlenmeyer, heated to boil, boiled for 10 min and cooled to room temperature.
5. Steps 1-2 are repeated until a volume of 100 ml is reached, on a magnetic stirrer.
6. BSPP (bis-P-sulfonatophenylphosphine) is added to the solution with a final concentration of 93 mM and left overnight at room temperature.

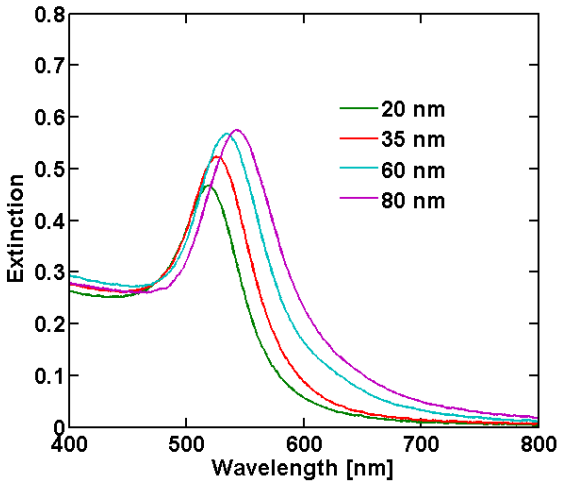


Figure 1: The Extinction spectra of NP different sizes for the above reaction.

2 QD-NP conjugates Synthesis

2.1 DNA Hybridization:

DNA sequences:

- **Sequence 1**- 5'-biotin-GCAGTAACGC TATGTGACCG-3'-thiol
- **Sequence 2**- 5'-CGGTCACATA GCGTTACTGC-3'

dsDNA - Sequence 1, and **Sequence 2** at a concentration of 0.5 mM are mixed in a 1:1 ratio, reacted with with TCEP (tris-carboxyethylphosphine) with a final concentration of 5 mM TCEP and stirred on vortex. The solution is left for at least 20 min for hybridization at room temperature and then diluted to 1 µM in DI water.

2.2 QD-DNA hybrids:

Streptavidin coated QD (Qdots Invitrogen) emitting at 565 nm,585 nm ,605 nm, 655 nm and 705 nm, at a concentration of 1 µM are reacted with **dsDNA** at 1:1 ratio (for NP-QD conjugates) ratio and at 1:2 ratio (for NP-QD-NP conjugates).

2.3 QD-NP conjugates:

1. For creating structures having multiple QDs and a single gold NP, QD-DNA hybrids (1:1 QD:DNA) are added to 80 nm gold NP solution at 100:1 ratio at equal volumes. After overnight at room temperature the excess unreacted QD-DNAs are separated with 6 cycles of centrifugation and resuspension after removing the supernatant (600g at a benchtop centrifuge for 5 minutes.)

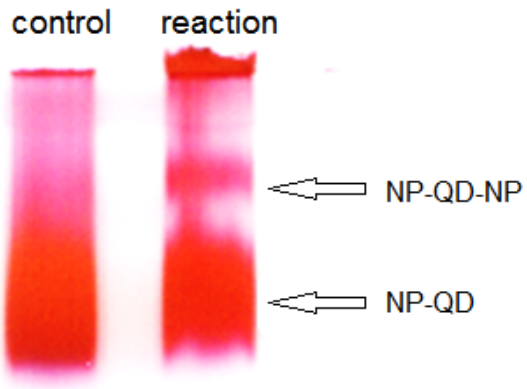
2. For creating structures having a single QD attached to a single gold NP, QD-DNA hybrids (1:1 QD:DNA) are reacted with NPs at 1:1 ratio.

3. For creating structures having a single QD attached between two gold NP, QD-DNA hybrids (1:2 QD:DNA) are reacted with NPs at 1:2 ratio.

4. The reaction products of 2. and 3. are purified by gel electrophoresis using 1% agarose with a 1/2xTBE in a current of 40 mamps. The desired are cut from the gel and are extracted using dialysis micro tubes (Geba-Flex microtubes dialysis kit). A small fraction of the products is examined by TEM.

The selection of the reaction products was done in the following manner:

Complexes consisting of NPs with many QDs were prepared in a process where the solution is saturated with QDs. The challenge here is to separate them from the non-reacting QDs, and this is done by six cycles of centrifuging, and not by electrophoresis (2.3.1). Gel electrophoresis was used to separate between NP-QD and NP-QD-NP objects. This is relatively straightforward as evidenced by the image below, which clearly shows the two bands. The lower band contains also a small fraction of single NP with more than one QDs. These objects can't be separated using this method; however, they are rare and easily identified in the optical measurements: their polarization dependence shows a-periodicity.

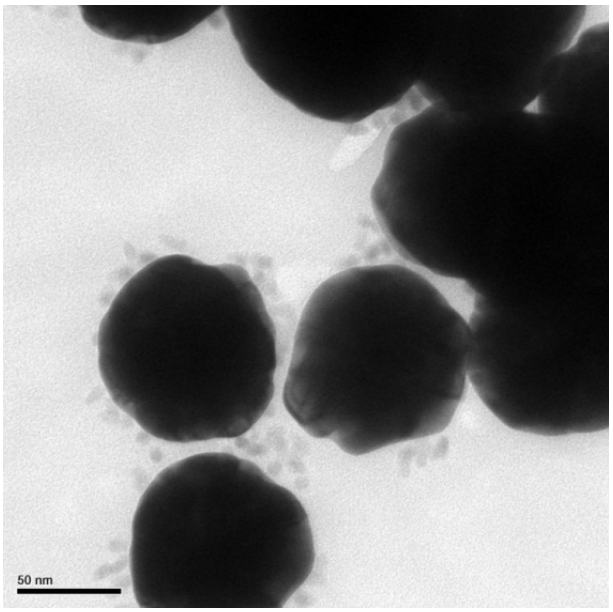


3 Characterization and Measurement.

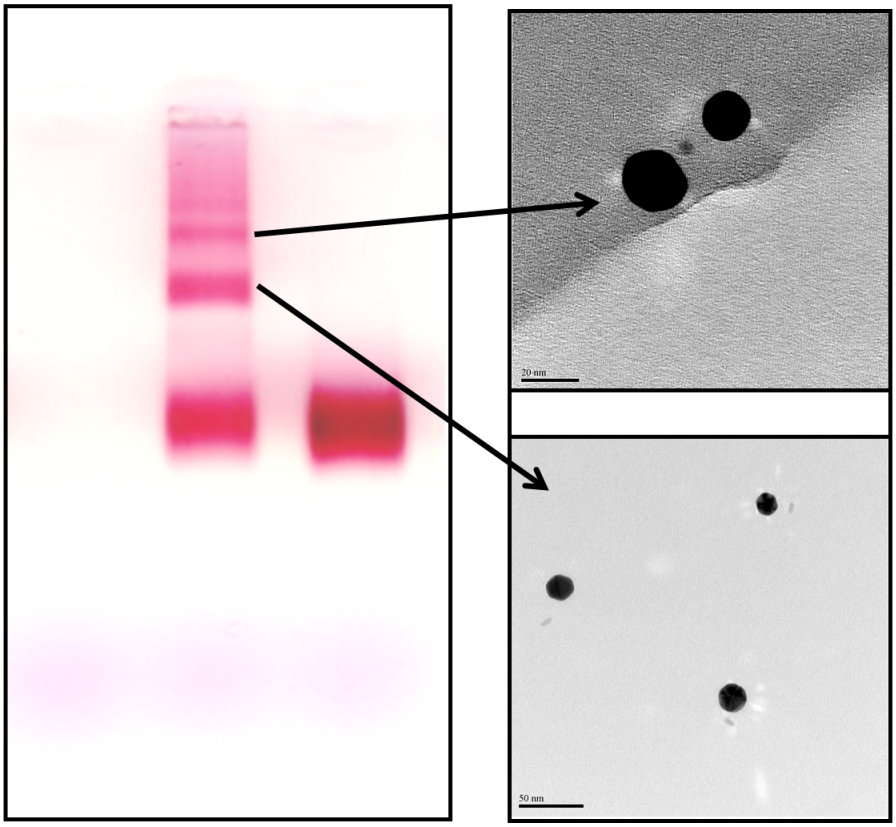
3.1 TEM

TEM images were acquired using a Philips CM-120 TEM in bright mode. Grids 400 mesh were purchased from TED Pella inc.

Obtaining an ensemble image of the complexes is not simple. The first difficulty comes from the fact that a 5 nm diameter CdSe/ZnS QD attached to a single 80 nm NP could be seen in TEM only if the NP-QD axis is parallel to the grid. At a different orientation the high absorbing gold NP hides the CdSe/ZnS. Thus, a zoom out view typically shows the NP, and only a careful search reveals the QD. The second problem is more technical: to obtain many particles in the field of view one needs to have a high concentration of objects in the applied solution. However, this typically gives rise to particle aggregation upon drying on the surface of the TEM grid. The image below shows such an aggregate that is formed under high concentration, and after drying. Hence, for the TEM imaging we worked with low concentration solutions.



In order to determine the yield of the process we ran a similar reaction with 20 nm diameter NPs. In this case the ratio between the NP diameter, the DNA length and the QD diameter is more favorable, and it is much easier to resolve the QD in the TEM images. Our measurements show a relatively high yield: 90% (out of 40 objects) for NP-QD (second band), and around 50% for NP-QD-NP (third band).



3.2 Single Objects Optical Measurements

Optical measurements on single objects were performed on an inverted Nikon microscope in an epifluorescence configuration. We use an oil immersion X60 1.4NA objective and a 532 nm laser excitation (Cobbolt Samba-532 diode laser). The polarization of the laser is varied with a Newport PR-950 polarization rotator. Collected light is dispersed by an imaging spectrometer (Andor SR-303i) and collected by an EMCCD (Andor ixonEM+897). The beam profile is characterized by illuminating a calibration sample of green ink and measuring the spatial profile of its emission. We obtain a nice Gaussian shaped focused spot, with a width of 2 μm. This width is wide enough to ensure that the illumination intensity experienced by the objects is fixed when brought to the spot center, and narrower than the average distance between the objects, such that there is a single object only in the spot. We have verified that the intensity profile does not change under the rotation of the polarization.