Supplemental Document

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Fluorescence decay enhancement and FRET inhibition in self-assembled hybrid gold CdSe/CdS/CdZnS colloidal nanocrystal supraparticles: supplement

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Supplementary Materials

1. Electromagnetic modeling of multilayer layer spherical structures

The calculation of the Purcell factor for a GSP with a defined geometry is based on the modeling of the radiated energy. We adopt notations of ref. [1]. We note the spherical wave functions with center O as Ξ_m (m is an integer) for the diffractive field (singular in O) and ξ_m for the incident one (regular in O). We limit the development up to $m = [1 : M]$. The maximum value M is estimated through a convergence test. In the following, T, A, B, G are $M \times M$ matrices, a^{inc}, A^{diff}, a^{stack}, A^{stack}, A, B, M are vectors of size M. $\times$ refers to the matrix product and I is the identity matrix of size $M \times M$. The calculation consists in 4 steps:

- First step: the GSP in vacuum is illuminated by an internal dielectric dipole $\overrightarrow{S}$ (blue arrow, see figure 1) located at point M. The diffracted field outside the GSP is $B = \sum_m B_m \Xi_m$ (green arrows). The vector B can be computed by Mie theory (following [1]).

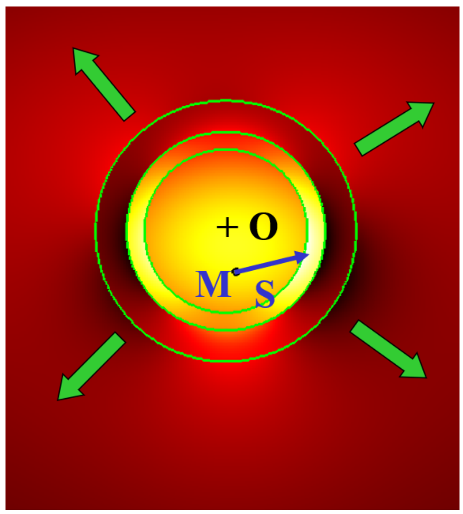

Fig. S. 1. Emission of a dipole inside a GSP.

- Second step: the GSP in vacuum (without any internal dipole) is illuminated by an incident field $a^{\text{inc}} = \sum_m a_m^{\text{inc}} \xi_m$ (yellow arrows, figure 2). The diffracted field outside the GSP is $A^{\text{diff}} = \sum_m A_m^{\text{diff}} \Xi_m$ (green arrows). We have $A^{\text{diff}} = T \times a^{\text{inc}}$ where the matrix T is also computed by Mie theory.

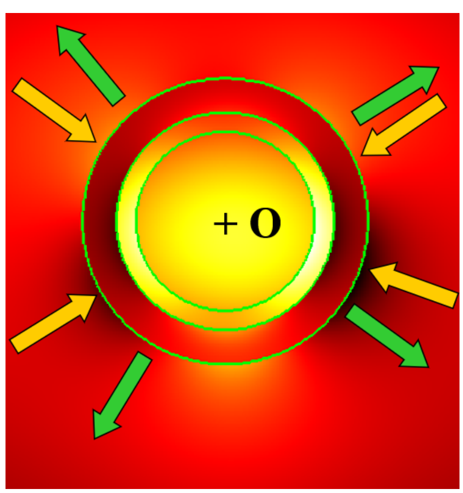

Fig. S. 2. Field diffracted by a GSP.

- Third step: a stack without the GSP is illuminated by an incident field coming from O: $A^{\text{stack}} = \sum_m A_m^{\text{stack}} \Xi_m$ (green arrows, see figure 3). The diffracted field is $a^{\text{stack}} = \sum_m a_m^{\text{stack}} \xi_m$ (yellow arrows). We have $a^{\text{stack}} = G \times A^{\text{stack}}$. The matrix G is computed using [2].

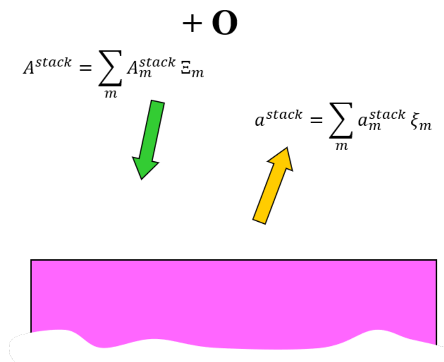

Fig. S. 3. Field diffracted by the stack.

- Fourth step: the GSP with the dipole $\overrightarrow{S}$ is now above the stack (see figure 4). The field diffracted outside the GSP is $A = \sum_m A_m^{\text{stack}} \Xi_m$ (green arrows). A is unknown but we have: $A = B + T \times G \times A$ so that $A = (I - T \times G)^{-1} \times B$. The spatial distribution of the electric field $\overrightarrow{E}$ can be then computed everywhere. At last, the power emitted by the dipole $\overrightarrow{S}$ writes: $-\frac{1}{2}\Re(\overrightarrow{S^*}.\overrightarrow{E}(M))$ ($\Re$ means that the real part is considered).

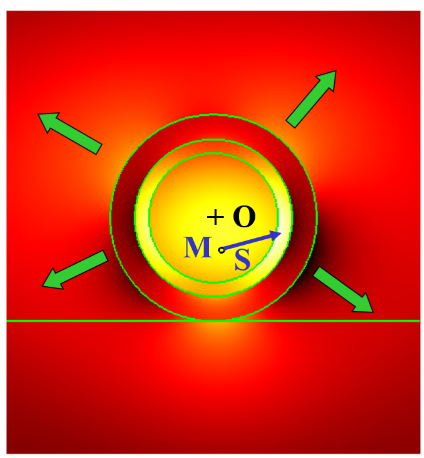

Fig. S. 4. Emission of a dipole inside a GSP located above the stack.

2. Refractive index of the rough gold layer

We rely on reference [35] to model the optical properties of the gold nanoshell. First, we fit the permittivity of reference [36] with a Drude model in the range 700-1000 nm, out of the band of interband absorption in gold. From this fit, we get the plasma frequency, ω_p, and the absorption term of the Drude model, γ. By subtracting the two permittivities, we obtain the permittivity responsible for the interband absorption of gold, ϵ_{intra}. The model of the gold permittivity that we use can be summarized as:

$$\epsilon_{\text{Au}} = \epsilon_{\text{inter}} + (1 - \frac{\omega_p^2}{\omega^2 - i.C_T.\gamma}) \quad (1)$$

where, C_T is a free parameter that allows to take into account the increase of the optical loss obtained for very thin and polycrystalline gold layers [3].

To model the roughness of the gold layer, we sub-divide the gold nanoshell into two layers: the inner one is continuous with a permittivity equal to ϵ_{Au}, and the outer is considered as a porous layer with a permittivity being the average between the permittivities of vacuum and gold:

$$\epsilon_{\mathrm{porous}} = (1 + \epsilon_{\mathrm{Au}})/2. \tag{2}$$

3. Calculation of the normalized decay rates of supraparticles

The calculations of the normalized decay rates shown in fig. 5 are done following the steps below:

- The decay rate of each NC can depend on its position inside the aggregate. We take into account this dependency by calculating the dissipated energies of the dipole for 50 different positions, from the center to the interface NCs/silica, and for the two possible orientations of the dipole. Calculations are done at $\lambda = 625$ nm.
- The aggregation of the NCs can lead to the opening of some non-radiative channels by creation of defects, this is why we add to the previously calculated dissipated energies a term taking into account this loss. A value of this term, E_{defects} , corresponding to 35 % of the dissipated energy of a dipole in vacuum allows to get a good agreement with the decay rates measured on both SPs and GSPs.
- We average the dissipated energies over the dipole positions weighted by the number of NCs for each position and orientation of the dipoles, which gives us an average dissipated energy for the supraparticles.
- It is common to calculate the ratio between the decay rates measured on supraparticles with the one measured on single NC lying on glass substrate, a ratio above one revealing an acceleration of the emission. In order to compare theory and experiments, we conclude our calculation by diving the calculated dissipated energy of the supraparticles with the dissipated energy of a dipole separated of a silica substrate by the radius of a NC ($\sim$ 4 nm).

4. Influence of the substrate on the calculation of the decay rates

In the calculations shown in fig. 5, we neglect the glass substrate on which the supraparticles are deposited. Supraparticles are considered to be located in an homogeneous environment, i.e. in vacuum. We verified for different positions of NCs inside the supraparticles that the normalized decay rates are not very sensitive to the presence of the glass substrate, as shown on fig. 5. We point out that it is not the case for NCs which have their center much closer to the glass surface compared to the supraparticles.

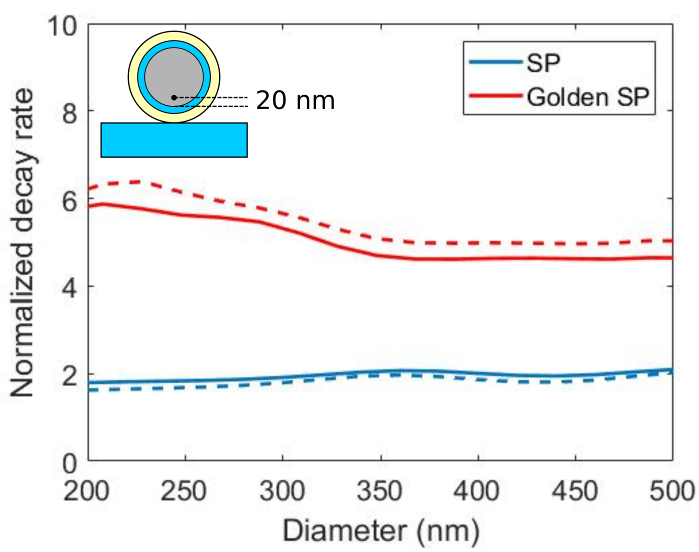

Fig. S. 5. Normalized decay rates as a function of the supraparticle diameter. The calculations have been done with (solid) and without (dashed) the glass substrate, and with (red line) and without (blue line) the gold nanoshell, for a NC 20 nm away from the NCs/inner silica interface.

5. Radiative efficiency

Due to the presence of the gold nanoshell, a fraction of the luminescence of the NCs is absorbed before being radiated out of the GSPs. The figure 6 shows that the radiative efficiency of GSPs is about 30%. In order to focus on the optical loss due to the gold absorption, we have neglected the losses $E_{defects}$ due to the aggregation process for this calculation.

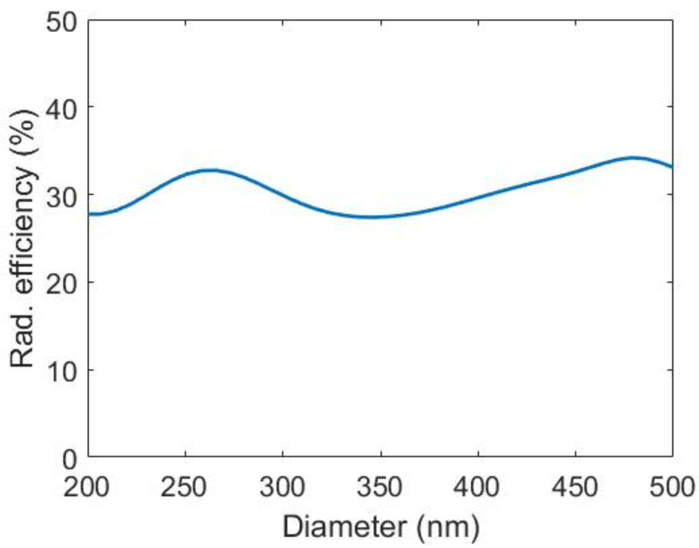

Fig. S. 6. Radiative efficiency as a function of the GSP diameters.

6. Wavelength dependence of the decay rates

As shown by figure 7, the calculated normalized decay rate shows no strong dependence on the wavelength in the range of emission of the NCs.

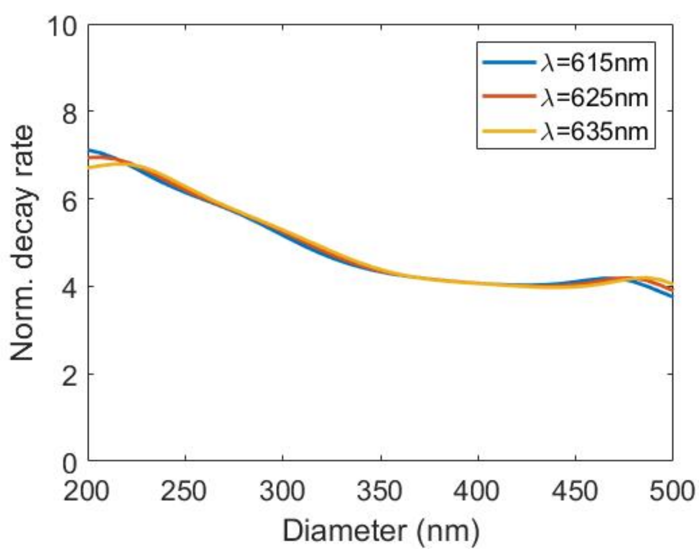

Fig. S. 7. Normalized decay rates as a function of the GSP diameters for three different wavelengths.

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