Electronic Supplementary Information for:

Optically Coupled Gold Nanoallotropes: Plasmon Enhanced Luminescence from Gold Nanorod-Nanocluster Hybrids

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1. Synthesis and characterization of the nanoparticles

Table S1: Apparent ζ-potentials of Au@SiO2 NRs and the corresponding AuNRs@AuNCs prepared by adsorption of excess of AuNCs. Values in the table are mean ± standard deviation of three measurements.

Sample	Apparent ζ- potential [mV]
Au@SiO ₂ NRs (5 nm SiO ₂ shell)	-23.7 ± 2.3
Au@SiO ₂ NRs (12 nm SiO ₂ shell)	-25.2 ± 3.0
AuNRs@AuNCs (5 nm SiO ₂ shell, saturated by AuNCs)	-0.05 ± 0.08
AuNRs@AuNCs (12 nm SiO ₂ shell, saturated by AuNCs)	3.3 ± 0.30



Figure S1: Histograms of the measured dimensions of the AuNRs and the thicknesses of the silica shells in the two samples of Au@SiO2 NRs discussed (referred to as 5 and 12 nm shell). (a-c) The dimensions of AuNRs were obtained from SEM images by analyzing > 200 particles. (d-g) Silica shell thicknesses were measured from TEM images by analyzing > 100 particles. The results are presented as mean ± standard deviation. (h) Schematic illustration of the two main shell thicknesses – i.e., "shell width" and "shell length".

Coating AuNRs with SiO₂ can sometimes lead to different shell thicknesses along and in perpendicular direction to the main nanorod axis. Therefore, it is better to measure the shell thickness in these two directions separately. This is illustrated in Figure S1h, where the two investigated thicknesses are referred to as *shell width* and *shell length*. However, as evidenced in the histograms in Figure S1, for relatively thin shells (< 15 nm) the difference between their width and length is small. Therefore, in the main text we describe the corresponding Au@SiO₂ NRs just by a single number for the shell thickness (5 nm / 12 nm). Still, in cases where stoichiometry of the particles was important, both width and length of the shells were used for more accurate calculations of the surface of Au@SiO₂ NRs.



Figure S2: (a,b) Difference between regular TEM and HAADF-STEM imaging of AuNRs@AuNCs (12 nm shell), with the latter offering much better contrast between AuNCs and the silica shells. (c,d) HAADF-STEM images of AuNRs@AuNCs prepared from Au@SiO₂ NRs with 5 nm shell.



Although both surface and volume scaling fit the experimental data comparably well, there is an important difference between the models in the limit case of SiO_2 shell thickness approaching 0. While the surface scaling predicts no AuNCs attached to AuNRs as the available surface disappears, the volume scaling assumes a non-negligible amount of AuNCs (~1000) bound to AuNRs even without the SiO_2 shell.



Figure S4: HAADF-STEM images of Au@SiO₂ NRs (5 nm shell) with controlled loading of AuNCs. Based on the predicted attachment capacity (a) 25%, (b) 100% of the theoretical maximum number of AuNCs was used. Scalebars represent 50 nm in both images.

An analogous image analysis as for Figure 4a - d was also made for the two micrographs in Figure S4. Since it makes no sense to plot a linear correlation of two datapoints, only the coefficients of relative surface coverage are listed in Table S2 confirming that the AuNC loading can be controlled also for $Au@SiO_2$ NRs with 5 nm shell (see section 4 of Supporting Information for details of the calculation of the coefficient):

Table S2: Coefficients of relative surface coverage by AuNCs calculated by analysis of HAADF-STEM images of AuNRs@AuNCs with 5 nm shell and targeted AuNC loading of 25% and 100%.

Desired loading of AuNCs	Coefficient of relative surface coverage from image analysis
25%	0.038
100%	0.108



Figure S5: Optical characteristics of initial AuNCs: The absorption coefficient (violet line and the left axis), PL excitation spectrum (PLE) detected at 750 nm (black line), and three PL emission spectra taken under excitation at 405 nm (blue line), 510 nm (green line) and 633 nm (red line). All PL and PLE spectra were normalized to 1.



Figure S6: Measured (normalized) extinction of AuNRs and AuNCs. Both plasmonic bands of AuNRs can be used for excitation of AuNCs due to non-zero absorption of AuNCs even at 633 nm.



Figure S7: Maps of local electric field enhancement around AuNR excitation at (a) 633 nm and (b) 510 nm. Boundary element method was used for the calculation. Note that the scale of the intensity maps is 20x lower in (b) than in (a).

AuNRs with no SiO_2 shells were considered for the calculation. Electric field intensity was averaged over incident directions to get the symmetric field profile. The input parameters of the simulation are listed in Table S3.

AuNR length	49 nm
AuNR diameter	26 nm
Environment dielectric function ($\epsilon = n^2$)	1.33 ²
Excitation wavelength(s)	510 / 633 nm

2. Nonlinear PL intensity increase for 633 nm excitation

2.1 Energy transfer

The mean distance between adjacent AuNCs is considerably smaller when attached to Au@SiO₂ NRs compared to a solution of pure AuNCs. More specifically, at standard AuNC concentrations used in the experiments and assuming a homogeneous distribution in the colloidal solution, the mean distance of AuNCs is more than 150 nm. When attached to Au@SiO₂ NRs, on the other hand, the mean distance drops to less than 5 nm even at low AuNC loadings and goes as low as 2.6 nm at maximum surface coverage (the calculation is based on the experimentally determined maximum number of AuNCs that can be attached to a unit surface area of Au@SiO₂ NRs and on the average diameter of AuNCs of 1.2 nm as found from HRTEM images). A short interparticle distance is one of the essential prerequisites for ET.

Let us consider the non-saturated regime (Au@SiO₂ NRs still have capacity for the attachment of more AuNCs) and let us assume that the surface coverage of Au@SiO₂ NRs with AuNCs is perfectly homogeneous. The mean distance between neighboring AuNCs, r, will then depend only on their total number, n, and on the total available surface of Au@SiO₂ NRs, and will scale with the square root of n as:

$$r \sim 1/\sqrt{n} \tag{S1}$$

The specific distance dependence of the energy transfer k_{ET} for different ET models scales with interparticle distance as:

$$k_{\rm ET} \sim 1/r^{\rm y} \tag{S2}$$

Where y = 6, 4, and 3 for FRET, NSET and NVET, respectively. From (S1) and (S2) we can directly see the relationship between k_{ET} and n:

$$k_{\rm ET} \sim n^{y/2} \tag{S3}$$

Assuming that FRET is the cause for the decreasing dynamic PL intensity enhancement ξ , we would therefore expect the following proportionality:

$$\xi \sim 1/k_{\rm ET} \sim n^{-y/2} \tag{S4}$$

Now it is important to realize that while (4) is relevant for PL intensity enhancement, the data to be fitted represent dependence of PL intensity on AuNC concentration (Figures 5a and S9a). As shown in the main text of this paper, the enhancement (per nanocluster) is calculated from a derivation of this dependence (Figure 5b). Therefore, the fitting function f_1 should be found as an integral of $n^{-y/2}$:

$$f_1 \sim \int n^{-y/2} dn \sim -n^{-\frac{y}{2}+1} = -n^{-x}$$
 (S5)

From (S5) we can directly obtain the exponent *x* for different ET models:

$$x = \begin{cases} 2 \dots \text{FRET} \\ 1 \dots \text{NSET} \\ 1/2 \dots \text{NVET} \end{cases}$$

2.2 Colloidal stability of AuNRs@AuNCs

The excitation enhancement originates in the excitation light that is scattered by the nanorods and transformed into a locally enhanced field, in which the nanoclusters are placed. In addition to this scattering, the plasmonic resonance of AuNRs also causes absorption of the incoming light and the sum effect can then be measured as an extinction by means of conventional absorption spectroscopy. The ratio between absorption and scattering is fixed for a specific particle type and therefore measuring the extinction allows us to monitor any changes of scattering, too.

The excitation enhancement is directly proportional to the ratio between excitation light intensity in a sample with AuNRs I_{exc} and excitation light intensity in a sample of pure AuNCs $I_{exc,0}$ (= const.). At the same time, as stated above, I_{exc} depends on the intensity of the scattered light I_{sca} . We can therefore write:

$$\xi \sim \frac{I_{\text{exc}}}{I_{\text{exc},0}} \sim \frac{I_{\text{sca}}}{I_{\text{exc},0}} \sim I_{\text{sca}}$$
(S6)

Figure S8a shows that the decreased colloidal stability of AuNRs@AuNCs mainly affects the longitudinal plasmonic peak of AuNRs and translates into a gradually decreasing extinction (scattering) of the particles with increasing AuNC loading. Figure S8b shows this decrement over the whole range of relative AuNC concentrations examined. Note that the drop of extinction (scattering) is almost linear for AuNC loading of 20-80% and then essentially stops when attachment saturation is reached. Let us denote the fraction of scattered light intensity by nanorods as S (I_0 is the intensity of the incoming radiation):

$$S = \frac{I_{\rm sca}}{I_0} \tag{S7}$$

Now, the measured quantity (extinction or scattering) is in fact by definition a logarithmic function of *S*. Therefore, with the linear decrease of scattering we can write:

$$-ln(S) \sim k * n \tag{S8}$$

where *k* is the slope of the linear decrease and *n* is the number of nanoclusters attached. From (S6), (S7), and (S8) we can finally derive:

$$\xi \sim S \sim \frac{1}{e^{kn}} \tag{S9}$$

And for the same reason as in the previous case, the fitting function f_2 is found as an integral of the result in (S9):

$$f_2 \sim \int \frac{1}{e^{kn}} dn \sim -e^{-kn} \tag{S10}$$

3. PL enhancement – complementary data



Figure S8: Mild aggregation of AuNRs@AuNCs evidenced by decreasing intensity and increasing full width at half maximum (FWHM) of the longitudinal plasmonic peak of AuNRs. (a) Extinction spectra of AuNRs@AuNCs with increasing AuNC loading. Spectra are normalized to a fixed value at 390 nm to highlight the fact that the longitudinal peak is undergoing much larger changes than the transversal peak. (b) Normalized peak extinction of the longitudinal plasmon of AuNRs measured for the full range of relative AuNC concentrations.



Figure S9: Comparison of two fitting functions used for the calculation of the dynamic enhancement in the non-saturated region of AuNRs@AuNCs with a 12 nm shell and 633 nm excitation. The gray area represents the region of absolute fit error.



Figure S10: Results of PL intensity enhancement in AuNRs@AuNCs for (a) 633 nm excitation, (b) 510 nm excitation, for a sample with a 5 nm shell. PL intensity as a function of the relative amount of AuNCs added, compared with PL intensity of pure AuNCs and AuNCs mixed with but not attached to AuNRs (AuNRs+AuNCs). Solid lines are fits of the data as described in the main text. The horizontal axes were normalized to the maximum loading capacity of the Au@SiO2 NRs used. The dashed vertical lines indicate the range, where attachment saturation is expected (100% ± standard deviation). The dashed lines in (b,d) indicate the important thresholds for reliability of the calculated PL enhancement (>20% of AuNCs), attachment saturation (>100% of AuNCs), and the threshold for positive PL enhancement (>1).

4. Image analysis for partial AuNC loading quantification

To quantify the relative AuNC loading on Au@SiO₂ NRs for samples discussed in Figure 4, we performed an image analysis using ImageJ software. We developed a general strategy, where image contrast, brightness and color threshold were used to discriminate specific features of the particles. A set of four processed images was generated for each input original HAADF-STEM image as shown in Figure S11. Due to the very similar brightness and contrast of AuNCs with edges of AuNRs, we could not isolate AuNCs from the rest of the features in HAADF-STEM images and residuals of the AuNR edges were always present (Figure S11b). To avoid a measurement error, we chose a setting that isolated these edges only (Figure S11c), and subsequently we subtracted the edges from the image with AuNCs (Figure S11f). To account for the variable dimensions of AuNRs and their silica shells, we also determined the size of Au@SiO₂ NRs (Figure S11d) and of the AuNR core alone (Figure S11e). By subtracting these two, we defined the area from which the detected AuNCs were counted (Figure S11g). Thanks to using grayscale thresholding (only black or white pixels left in the image) we could calculate the relative AuNC loading as a ratio between the number of white pixels in an image with AuNCs only and the number of white pixels corresponding to silica shells on AuNRs. Using notation from Figure S11, this is the ratio between the number of white pixels in Figure S11f and in Figure S11g. This number is what we call "coefficient of relative surface coverage" in Table S2. Although such number has no direct relation to the real surface coverage, it can be used to compare AuNC loading in different samples.

The same procedure was applied to all samples. At least 5 HAADF-STEM images were analyzed for each sample and only images obtained under the same conditions (magnification) were used for comparison. To account for the varying number of particles in different images, the mean value of AuNC loading for a given sample was weighted by the total surface of Au@SiO₂ NRs in individual images.



Figure S11: Quantification of the relative AuNC loading on Au@SiO₂ NRs by analyzing HAADF-STEM images of AuNRs@AuNCs. Four processed images were generated from the original HAADF-STEM image. (a) original HAADF-STEM image, (b) isolated AuNCs with residuals of edges of AuNRs, (c) isolated edges of AuNRs, (d) Au@SiO₂ NRs, (e) core AuNRs. (f) Isolated AuNCs generated as a result of subtracting (b)–(c). (g) Isolated SiO₂ shells generated as a result of subtracting (d)–(e).