Gold nanoparticles as nano-thermometers

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Anti-Stokes emission form gold nanorods

We model the photoluminescence generation in gold nanorods with successive steps taking place between absorption of light and re-emission of luminescence. Figure S1 shows the energy-momentum representation of the photoluminescence processes in gold nanorods. After excitation with monocrhomatic light of energy $\hbar\omega_L$, a collective oscillation of electrons is generated, i.e. a surface plasmon (SPR). Once the coherence is lost (dephsasing time ~fs), the state can be described as an electron-hole pair. Then, three scenarios are possible: electron and hole may recombine radiatively after one or more interactions with the thermal baths of lattice phonons and charge carrier thermal excitations: i) if the energy difference between electron and hole states is lower than the initial one after excitation we obtain Stokes emission upon a radiative recombination; ii) if electron and hole transiently increase their energy difference at the bath's expense before recombining radiatively, we observe anti-Stokes emission; iii) if electron and hole recombine non radiatively, their energy difference is transferred to the baths and no photon is emitted. The latter process is the most probable one.

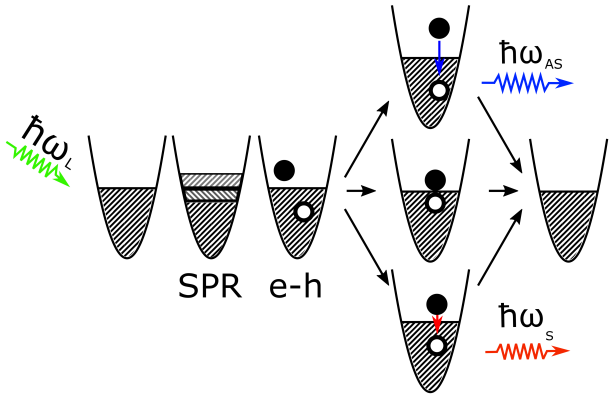

Figure S1: Anti-Stokes luminescence process from a single gold nanorod.

Experimental setup

The experimental setup consisted on a home-made confocal microscope, schematically shown in figure S2, similar to the one presented before.[1] The microscope allows the detection of individual nanorods in the sample and the measurement of their photoluminescence spectra. We use continuous wave lasers at 532nm or 633nm to excite the transverse and longitudinal plasmon resonances, respectively. Both lasers are reflected at a 50/50 beam splitter that allows the simultaneous detection of the anti-Stokes and Stokes emission of the particles. We employ an objective lens to focus the excitation beam into a diffraction limited spot and we collect the emitted photoluminescence using the same objective in an epi-configuration. A confocal pinhole of 50 μm is placed between a pair of lenses with 10 cm focal length to reduce the unwanted background from the solvent above the nanorods. Then we could select between an APD or the spectrometer to perform a raster-scan image or an emission spectrum, respectively. We reject the laser light with appropriate notch filters.

Additionally, the temperature of the sample can be controlled with a special holder that allows water flow, a heater and a thermocouple to measure the temperature of the sample.

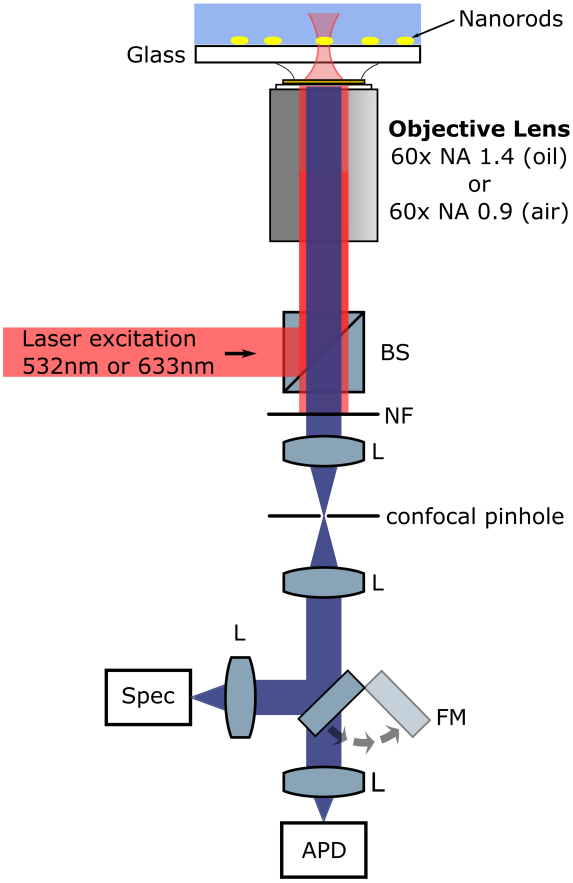

Figure S2: Scheme of the experimental setup. The sample consists of individual gold nanorods immobilized on glass. BS: beam splitter. NF: notch filter to remove excitation light and detect Stokes and anti-Stokes photoluminescence. L: lens. FM: flip mirror. SPEC: spectrometer. APD: avalanche photodiode.

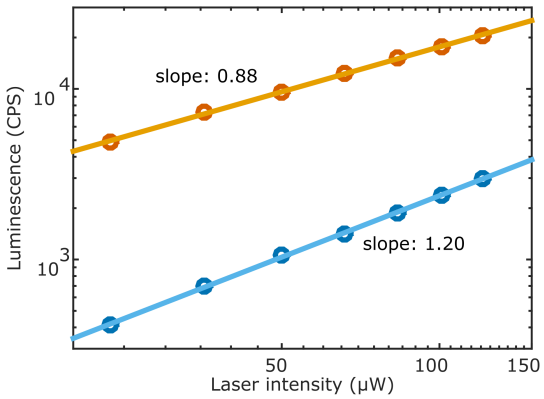

Figure S3: Stokes and anti-Stokes integrated emission as a function of excitation power. The linear fit in logarithmic scale has a slope of 0.88 and 1.20 respectively, confirming the 1-photon nature of both kinds of emission.

Luminescence power dependence

Figure S3 shows the intensity of the Stokes (red) and anti-Stokes (blue) emission for several excitation powers. In both cases the linear fit in logarithmic scale has a slope close to 1, being 0.88 for the Stokes and 1.20 for the anti-Stokes, confirming that both types of emission are single-photon processes. The anti-Stokes has a higher slope due to dependence on T in the equation 2 in the main text. The behavior is independent of the plasmon resonance position. It is important to note that the excitation intensity cannot be increased much beyond what is shown because nanorods would start reshaping towards more spherical shapes at higher laser powers.

Gold Nanorod temperature calculations

Throughout the main text the temperature measured with the anti-Stokes emission is compared to the calculated temperature using the heat diffusion equation. For spheres in an homogeneous water environment and assuming an infinite thermal conductivity for the metal, the temperature increase is given by

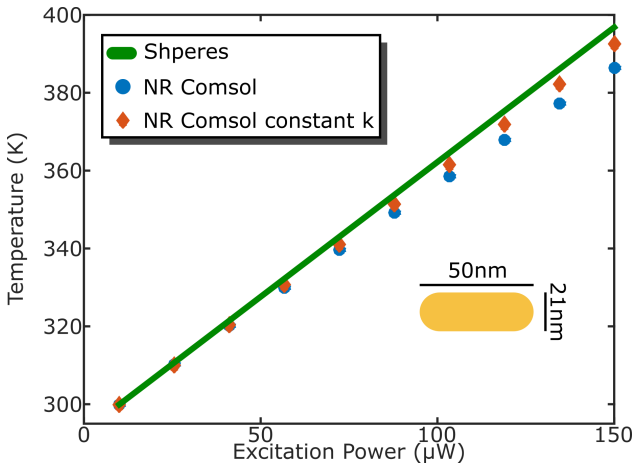

Figure S4: Calculated temperature for a nanosphere (full line) and for a 21 nm × 50 nm nanorod (dots) under different excitation intensities. The dots are numerically calculated values using COMSOL Multiphysics commercial software. The circles where obtained with the temperature-dependent heat conductivity of water and the diamonds with a constant value of $0.61\,\mathrm{W}(\mathrm{m}\cdot\mathrm{K})^{-1}$.

$$\Delta \mathrm{T}(P) = \frac{P}{4\pi k_{\mathrm{water}} R} \tag{1}$$

where P is the dissipated power, k_{water} is the heat conductivity of water and R is the radius of the particle.[2] The dissipated power can be easily derived from the cross section of the particle at a given wavelength and the intensity of the focused laser beam. For nanorods we assumed an equivalent sphere with radius such that the total rod area is preserved.

Figure S4 shows the difference between the results from the sphere (full line) and a finite element method calculation (dots) for a nanorod of length 50 nm and diameter 21 nm. The cross section and dissipated power were kept the same. The blue circles are the results given by using the built-in material properties of water, i.e. a thermal conductivity that depends on temperature. The diamonds are the results when the thermal conductivity is fixed to $0.61\,\mathrm{W}(\mathrm{m}\cdot\mathrm{K})^{-1}$. The difference is accentuated at higher temperatures.

References

(1) Carattino, A.; Keizer, V. I.; Schaaf, M. J.; Orrit, M. Background suppression in imaging gold nanorods through detection of anti-stokes emission. *Biophysical journal* **2016**, *111*, 2492–2499.

(2) Baffou, G.; Quidant, R. Thermo-plasmonics: using metallic nanostructures as nano-sources of heat. *Laser Photon. Rev.* **2013**, *7*, 171–187.