Gold nanoparticles as nano-thermometers

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Experimental setup

Gold Nanorod temperature calculations

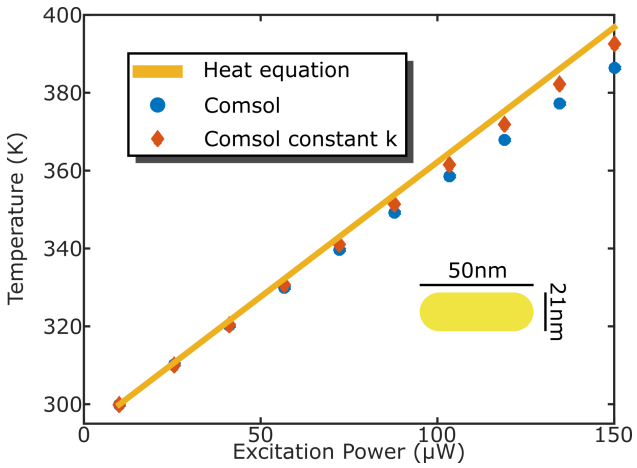

Figure S1: Calculated temperature for a 21 nm × 50 nm nanorod under different excitation intensities. The full line is the result of the simple model while the dots are the calculated values using Comsol. The circles are with the default heat conductivity and the diamonds are with a constant value.

Throughout the main text the temperature measured with the anti-Stokes emission is compared to the calculated temperature using a simple heat diffusion equation. For spheres, assuming a thermal conductivity much higher than the surrounding medium, the temperature increase is given by

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

where P is the dissipated power, k_{water} is the heat conductivity of water and R is the radius of the particle. 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 radius such that the total area is preserved.

Figure S1 shows the difference between the results from the equation (full line) and a finite element method calculation using Comsol (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 $0.61\,\mathrm{W(\,m\cdot K)^{-1}}$. The difference is accentuated at higher temperatures.

Luminescence power dependence

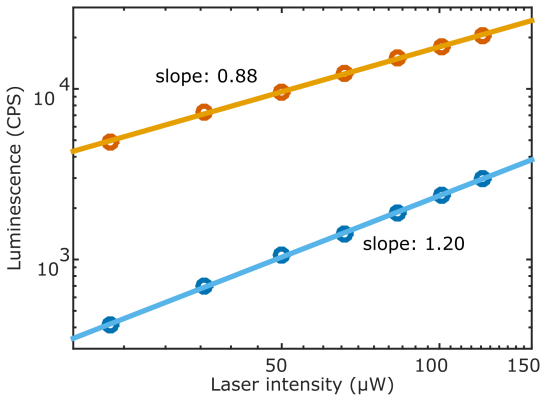

Figure S2: Stokes and anti-Stokes emission as a function of excitation power. The linear fit in logarithmic scale has a slope of 0.88 and 1.20 respectively, ensuring the 1-photon nature of both kinds of emission.

Figure S2 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 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 a more spherical shape at higher laser powers.

Anti-stokes luminescence form nanospheres

Particles that can withstand higher excitation powers and that have a well-defined plasmon resonance are of great interest, because they would allow to employ a single wavelength and also to reduce the exposure times to record the spectra. A well defined plasmon resonance also lowers the uncertainties associated with the initial lorentzian fit needed for the term I_{SPR} in equation 2. In principle gold nanospheres fulfill these requirements. They are known to withstand much higher excitation powers without reshaping nor melting.[1] Moreover the plasmon resonance of spheres shifts only slightly with radius, therefore it is possible to predict it using Mie theory and to eliminate the need of a second laser beam. Sphere samples however always show a shape distribution that cannot be neglected[2] and that induces deviations of the observed resonance from Mie's model.

Figure S3 shows the normalized luminescence spectra of three nanospheres of diameters 60 nm, 40 nm and 30 nm under 532 nm excitation. As for the nanorods, two very distinctive parts of the spectrum are distinguishable, the Stokes spectrum at longer wavelengths and the anti-Stokes spectrum at shorter ones. From Mie theory we would have expected a blue shift of the resonance with decreasing radius of the particles; however the 30 nm sphere seems to be the most red-shifted. This is most likely due to small anisotropies of the particles, giving rise to slightly different plasmon resonances. The inset in Fig.S3 shows a detail of the anti-Stokes emission for the three spheres without any further normalization. It has to be pointed out, however, that the excitation intensities were 1.2 mW, 2.0 mW and 3.6 mW to compensate for the lower cross sections of the smaller particles.

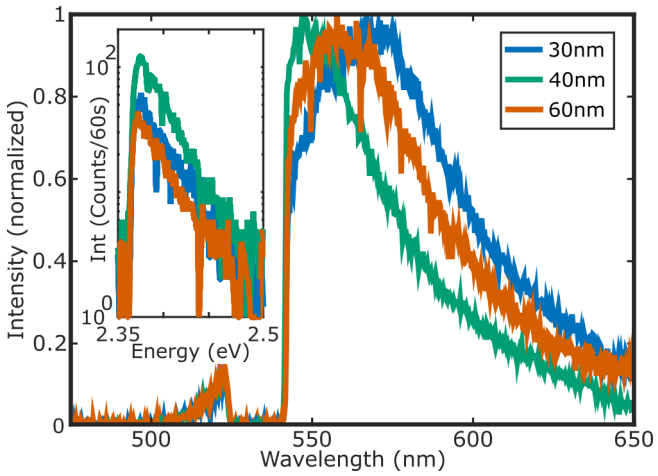

Figure S3: Normalized luminescence spectra of spheres with diameters of 60 nm, 40 nm and 30 nm under 532 nm excitation. The inset shows the detail of the anti-Stokes emission without normalization. The excitation powers for the three particles were 1.2 mW, 2.0 mW and 3.6 mW respectively.

Spheres not only have a smaller cross section than nanorods of the same volume, but their quantum yield is also one order of magnitude lower than that of rods.[3] The weaker emission from these particles can be compensated by increasing the excitation power. The maximum power that can be employed is given by either reaching the melting temperature of gold or by inducing a phase transition of the surrounding liquid. The first would induce an irreversible change in shape of the particles[4] the latter would induce a change in the refractive index of the medium and therefore would induce a shift in the plasmon resonance.[1]

Figure S4 shows the extracted temperature of the three particles while increasing the medium temperature. It is possible to see that the small 30 nm diameter sphere is 150 K hotter than both the 40 nm and 60 nm. The three curves show an increasing trend, but in this case the variation of medium temperature amounts to less than 5% the temperature of the particles. The extracted temperature is several tens of degrees above what would be expected from the heat equation, considering the absorption cross section given by Mie theory. The reason for the discrepancies between the measured values and the expected values can be accounted for by the computation of the plasmon resonance term I_{SPR} in eqn. 2.

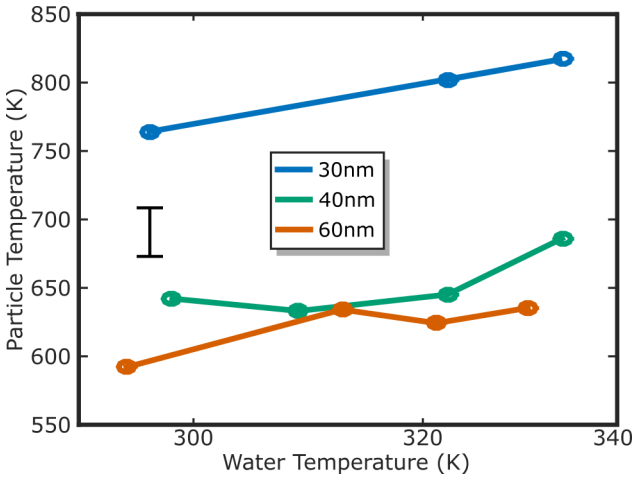

Figure S4: Extracted temperature from the same particles as in fig. S3 at different medium temperatures.

As explained earlier for nanorods, the fitting of the anti-Stokes emission is highly sensitive to the plasmon position relative to the laser employed. In the case of nanospheres, the resonance is slightly shifted to the red from the 532 nm laser. Small errors in the determination of the plasmon resonance will generate larger errors in the temperature extracted. The differences between the plasmon observed in fig. S3 and the results of Mie scattering calculations most likely are due to particles that are not spherical. If this was the case, the calculated cross section and plasmon resonance will not coincide with the particles under study, leading to larger errors.

The use of spheres would be beneficial for some applications that require higher excitation powers or smaller particles. The intrinsic heterogeneity of the samples, however, prevents the use of a single wavelength for the measurements. Ideally, white light scattering of single gold nanospheres would provide the information on the plasmon resonance needed for the correct fitting of the anti-Stokes emission.

References

(1) Hou, L.; Yorulmaz, M.; Verhart, N. R.; Orrit, M. Explosive formation and dynamics of vapor nanobubbles around a continuously heated gold nanosphere. *New J. Phys.* **2015**,

17, 13050.

(2) Lee, Y.-J.; Schade, N. B.; Sun, L.; Fan, J. a.; Bae, D. R.; Mariscal, M. M.; Lee, G.; Capasso, F.; Sacanna, S.; Manoharan, V. N.; Yi, G.-R. Ultrasmooth, highly spherical monocrystalline gold particles for precision plasmonics. *ACS Nano* **2013**, *7*, 11064–70.

(3) Yorulmaz, M.; Khatua, S.; Zijlstra, P.; Gaiduk, A.; Orrit, M. Luminescence quantum yield of single gold nanorods. *Nano Lett.* **2012**, *12*, 4385–91.

(4) Zijlstra, P.; Chon, J. W. M.; Gu, M. White light scattering spectroscopy and electron microscopy of laser induced melting in single gold nanorods. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5915–5921.