Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Thermal diffusivity measured with a single plasmonic nanoparticle

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1 Sensitivity of the phase delay to parameter changes

Calculations have also been performed for Gaussian beams, which significantly decreases computation times and still captures the main dependencies. It is found that the optically detected phase delay depends on the particle size (see Fig. S1 A and B), refractive index, the detection aperture and the characteristic of the incident detection laser beam. The size dependence results from the fact that the heated gold nanoparticle with the refractive index profile acts as a modulated scatterer and a thermal lens at the same time. The contribution of either mechanism changes with particle size. For small particles the thermal lensing is dominant whereas for large particles the scattering contribution is considerably enhanced.[1] A size dispersion of 12% and an average radius of $R = 5\,\mathrm{nm}$ result in an error of the measurement of the thermal diffusivity of less than 1%.

The temperature dependence of the thermorefractive coefficient of the surrounding material and the dn/dT of the nanoparticle alter the results of the calculation only weakly. This has the effect that the frequency dependencies of photothermal signal's amplitude and phase delay do not depend on the heating power. We find that the displacement between both laser foci along the optical axis does not change the phase delay in the distance dependence between the nanoparticle and the detection laser focus (see Fig. S1 B). The displacement between detection and heating laser alters amplitude and position of the maximal photothermal signal.[2] Therefore, the phase delay at the position with maximal signal amplitude is changed. In the main text only numerical calculations using exact beam descriptions are compared to the experimental data to obtain the thermal diffusivity of the material surrounding the gold nanoparticle.

2 Correction of the phase delay

The acoustooptic modulator and the photodiode have phase delays that depend on the modulation frequency. To correct for that the phase delay of the modulated heating laser ϕ_{heat} is measured. This phase delay is very stable and only change by less than 0.001 rad over days. The phase delay which is induced by the thermal transport ϕ is calculated by subtracting ϕ_{heat} from the phase delay measured by the lock-in amplifier.

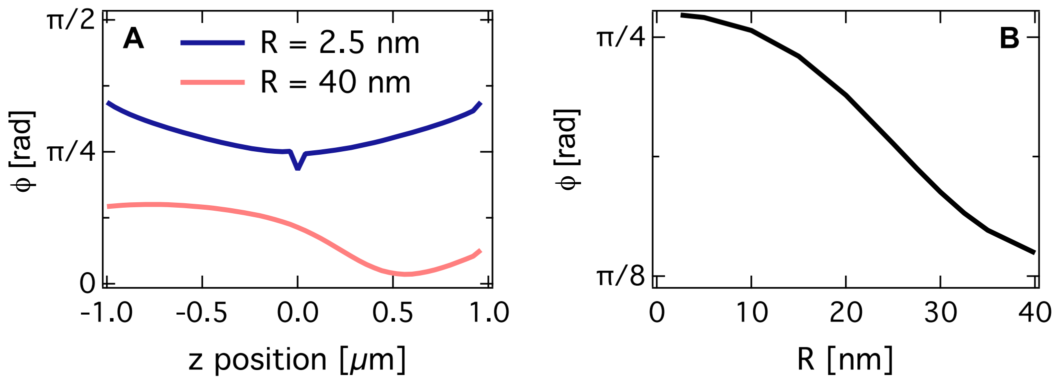

Figure S1: **A** Calculated phase delay for two differently sized gold nanoparticles at $R_{\text{th}} = 150\,\text{nm}$ assuming a Gaussian intensity profile in der Laser focus in PDMS. **B** Phase delay for nanoparticles with different diameters at $z = -320\,\text{nm}$.

3 Extraction of thermal diffusivities

The phase delay ϕ is measured at a particular modulation frequency f. The phase delay from the measurement is than compared to the scattering calculation and the corresponding thermal diffusion length R_{th} is extracted. The thermal diffusivity α is calculated via:

$$\alpha = \pi f R_{\text{th}}^2. \tag{I}$$

In Figures 2 E and F from the main text the thermal diffusivity is extracted by scaling the numerical data to the experiments. Therefore, the measured phase delay is plotted against f and the numerically calculated phase delay is plotted against $1/R_{\text{th}}^2$. The scaling factor that minimizes the deviation between experiment and numerical calculation is α/π.

References

[1] M. Selmke and F. Cichos. Energy Redistribution Signatures in Transmission Microscopy of Rayleigh- and Mie-particles. *J. Opt. Soc. Am. A*, 31(11):2370–2384, 2014.

[2] Markus Selmke, Marco Braun, and Frank Cichos. Photothermal single-particle microscopy: Detection of a nanolens. *ACS Nano*, 6(3):2741–2749, 2012.

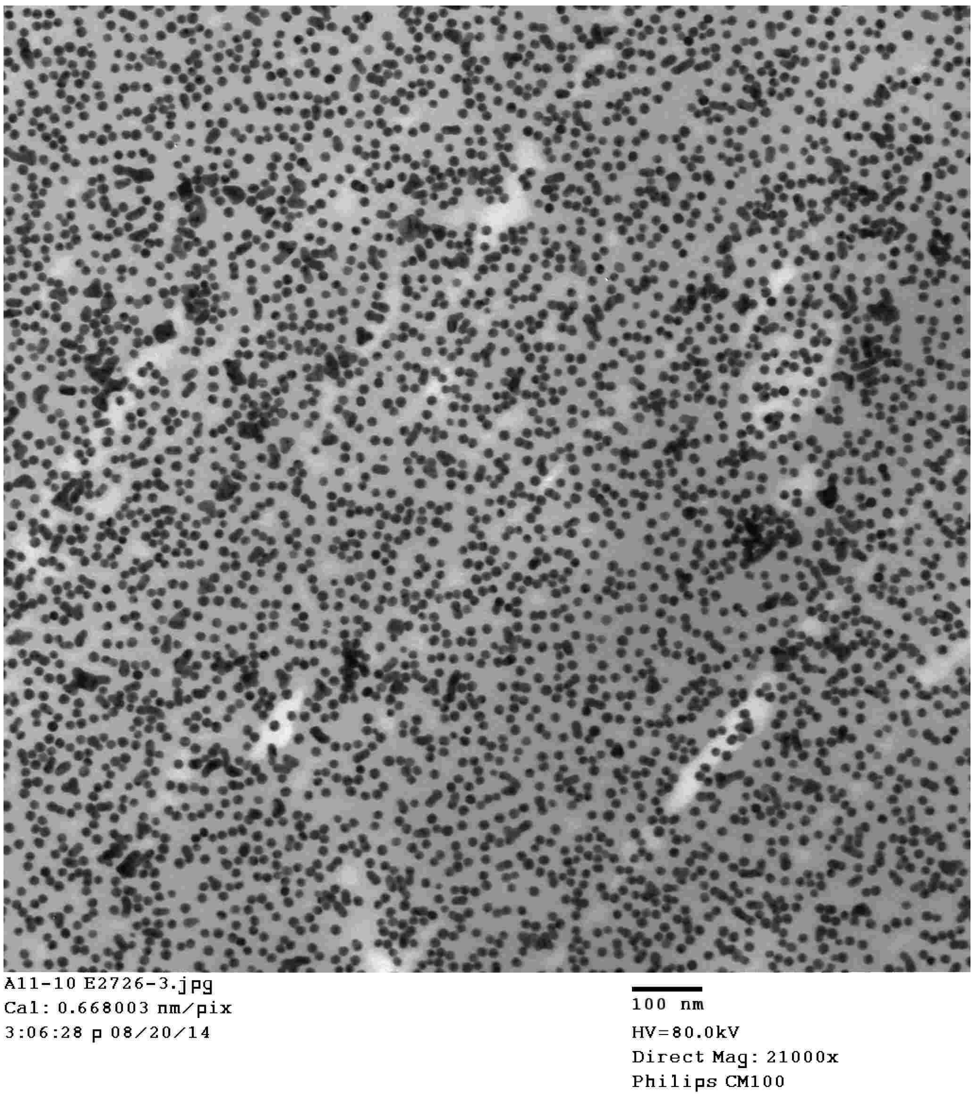

Figure S2: Transmission electron micrograph of gold nanoparticles with 5 nm in radius. Kindly supplied by Nanopartz Inc.