

Electronic Supplementary Information

Opto-Thermophoretic Separation and Trapping of Plasmonic Nanoparticles

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S1. Optical setup

Figure S1 shows an optical setup. An inverted optical microscope (IX73, Olympus) was used to acquire optical micrographs under dark field illumination using a CMOS camera (Zyla 5.5, Andor Technology, Northern Ireland). A microscope objective (50 × , NA = 0.55, Olympus) was used for observation. Scattering spectra of optically trapped Au NSs were measured with a fiber-coupled spectrometer (SD-2000, Ocean Optics). A continuous near-infrared laser with $\lambda = 1475$ nm (FPLB1475, FiberLabs Inc., Fujimino, Japan) was used for simultaneous induction of optical trapping and thermophoresis. To vary laser spot diameter at the focal plane of the objective, an inter-lens distance of a pair of plano-convex lenses was changed; note that the focal plane was fixed at an interface between the upper coverslip and the colloidal solution.

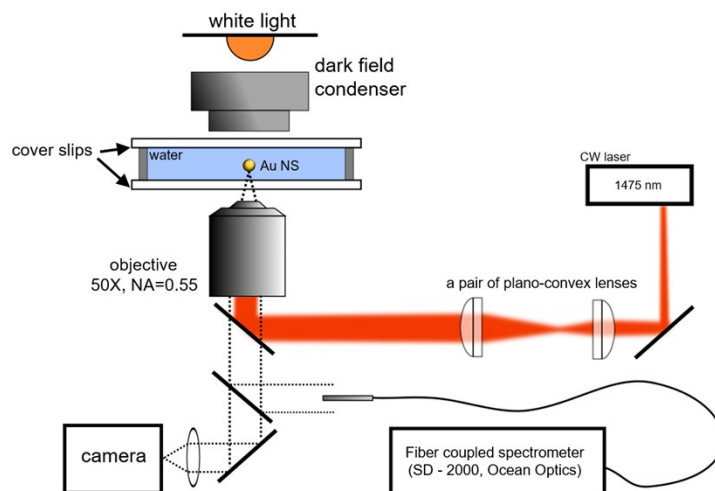


Figure S1. Optical setup.

S2. Photoluminescent image of a focused laser

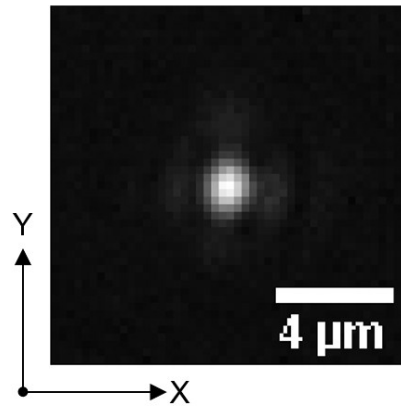


Figure S2. Photoluminescent image of a thin film consisting of microspheres of IR phosphor (IRSPG-5G, LDP LLC) under irradiation with a focused NIR laser.

S3. Histograms of the X- and Y-positions

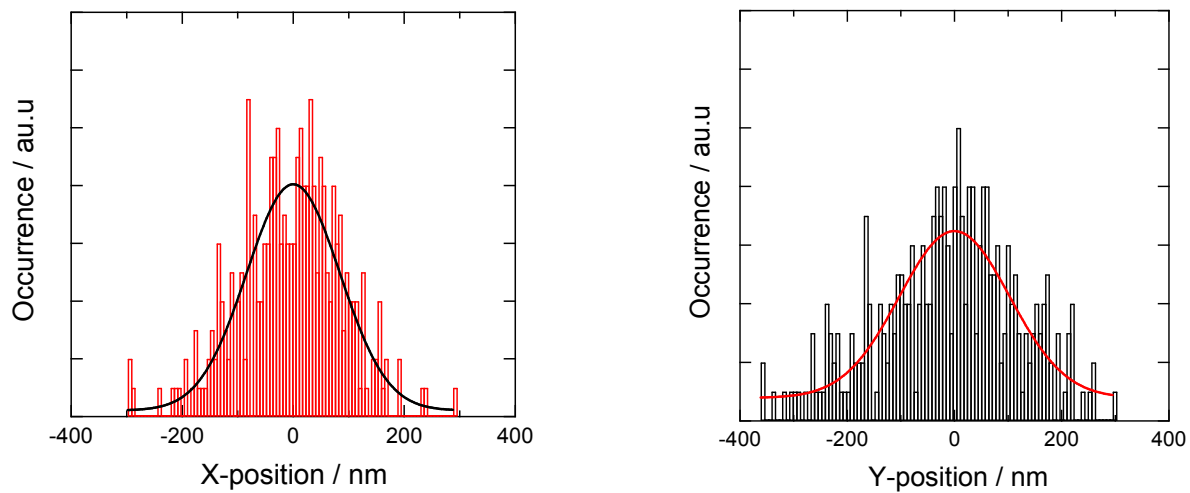


Figure S3. Histograms of the X - and Y -position for the time trajectory. The solid lines are the curves obtained by the analysis with a Gauss function.

S4. Temperature estimation of the laser spot

We calculated temperature of the laser spot in water on the basis of steady-state heat conduction theory. In the following calculation, we consider only the laser heating of water, and neglected the presence of a trapped Au NS in the laser spot; a volume of a single Au NS as a heat source is negligibly small as compare to the laser focal volume in the present condition. Hence, this problem can be considered as an 1D radial heat conduction in a homogeneous medium. The analytical solution is given by¹

$$T(r) = \frac{Q}{4\pi kr} + T_{\infty}$$

where r is the radial coordinate [m], k [$\text{W m}^{-1}\text{K}^{-1}$] thermal conductivity of water, T_{∞} [K] room temperature, a [m] radius of the laser spot, and Q [W] input energy in the laser spot. The Q can be determined from a laser power density, a focal volume of the laser, and an absorption coefficient of water at a wavelength of 1475 nm. The k , T_{∞} , r , and the absorption coefficient are 0.59 [$\text{W m}^{-1}\text{K}^{-1}$], 293 [K], 0.85 [μm], and 2123 [m^{-1}],² respectively: note that the $r = 0.85$ [μm] is the laser spot radius. Figure S3 shows the temperature as a function of laser power density. As can be seen, the temperature is 336 K (43 K as ΔT) at a power density of 4.3×10^5 W cm^{-2} .

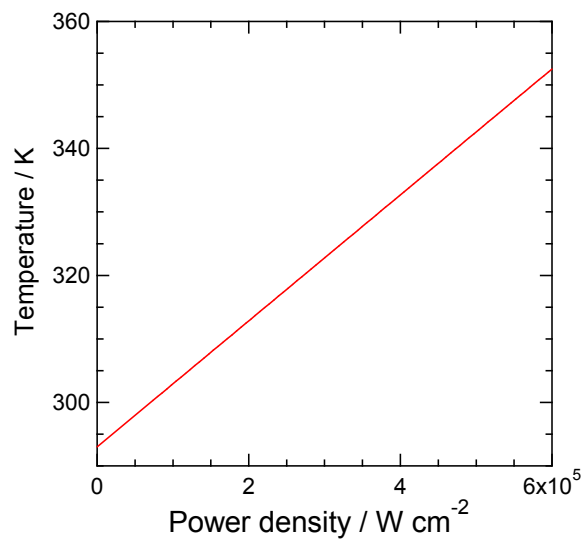


Figure S4. Calculated temperature of the laser spot as a function of power density.

References

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S5. Estimation of thermophoretic force and natural convection

In this section, we try to estimate the magnitude of thermophoretic force F_T . Thermophoretic velocity v_T in the x -direction is phenomenologically described as $v_T = -D_T(dT/dx)$ [1], where D_T is a thermophoretic mobility. In experiments, the magnitude of D_T is usually reported to be within a range $|D_T| = 1$ to $10 \mu\text{m}^2 \text{s}^{-1} \text{K}^{-1}$ [2]. It should be remarked that the values of dT/dx in experiments are estimated from the temperature distribution of fluids away from the particle.

If we consider the steady motion of particle is driven by thermophoretic force F_T in the x -direction, the counterbalance between F_T and the Stokes drag force $F_d = 3\pi d\eta v_T$ exerted by surrounding fluid leads to the relation $F_T = 3\pi d\eta v_T = -3\pi d\eta D_T(dT/dx)$, where $\eta = 6.81 \times 10^{-4} \text{ Pa} \cdot \text{s}$ is the viscosity of a solution at temperature 311 K (see, Fig. 6(c)). The value of $dT/dx = (T_{high} - T_{low})/d$ can be estimated from the numerical simulation presented in the main text, and that of D_T is set to $10 \mu\text{m}^2 \text{s}^{-1} \text{K}^{-1}$, which is within the range of Ref. [2]. The results are shown in Table S1. It is found that the magnitude of the thermophoretic force less than 1 fN seems to be too weak to induce the motion. In fact, the thermophoretic velocity observed in our experiment is the order of $1 \mu\text{m} \text{s}^{-1}$, and one or two orders of magnitude larger than the estimation in Table S1. We consider that the underestimation is attributed to the following two factors: i) the overestimation of the thermal conductivity of gold shells, and ii) the evaluation of dT/dx . For the former, as already mentioned in the main text, the gold shells could have a small thermal conductivity compared with that of the bulk. This might result in the underestimation of F_T of 30 to 50 %. For the latter, recall that the experiments of previous studies use the values of dT/dx away from the particle and not those on the surface of particle. In the present study, the temperature gradient in water around the surface of the Au NS is the order of $5 \times 10^5 \text{ K m}^{-1}$. As this value is two order of magnitude larger

than that shown in Table S1, one can expect two orders of magnitude greater F_T for the Au NSs. These values are the same order as references, e.g. Ref. [3].

However, as reported in the literatures [4, 5], the small temperature gradient at the surface of metal nanoparticles plays an important role for suppression of the thermophoresis. Judging from our calculations and the facts, rigorous estimation of the thermophoretic force acting on metallic core-shell nanoparticles is difficult and far beyond the scope of this study.

It should be noted that the effect of thermal convection in our setup is considered to be negligibly small. In the previous study [6], the magnitude of thermal convection was estimated to be at most $0.01 \mu\text{m s}^{-1}$ using the numerical simulation, where the size of the localized temperature increase was about 60 K, the corresponding temperature gradient was about $5 \times 10^5 \text{ K m}^{-1}$, and the channel height was 17 μm . While the temperature gradient of Ref. [6] was almost same with that in this research, the channel height in Ref. [6] was larger than that of the present study, that is, the magnitude of thermal convection in the present study can be estimated to be smaller than that in Ref. [6]. Therefore, the thermal convection in the present study is less than $0.01 \mu\text{m s}^{-1}$, which leads to the drag force $3.6 \times 10^{-2} \text{ fN}$.

Table S1. Estimation of thermophoretic force using the values of dT/dx on the surface of particle.

d [nm]	d_{core} [nm]	$T_{\text{high}}-T_{\text{low}}$ [mK]	$-dT/dx$ [K m ⁻¹]	v_T [$\mu\text{m s}^{-1}$]	F_T [fN]
240	160	0.99	4.14×10^3	4.14×10^{-2}	0.13
240	180	1.36	5.66×10^3	5.66×10^{-2}	0.17
240	200	2.09	8.69×10^3	8.69×10^{-2}	0.27
240	220	4.21	1.75×10^4	1.75×10^{-1}	0.54

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