Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Platinum nanoparticles: a non-toxic, effective and thermally stable alternative plasmonic material for cancer therapy and bioengineering

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Supporting Methods

Finite Element Modeling

To obtain the temperature profile, $T(\mathbf{r})$, the total generated heat, $Q = \int \mathbf{J} \cdot \mathbf{E} = C_{abs} I$ has to be calculated. First the absorption cross section of nanoparticles are calculated based on Mie theory, in which, electric field, $\mathbf{E}(\mathbf{r}, \omega)$ around irradiated nanoparticle was found by numerically solving the electromagnetic wave equation using FEM Multiphysics (COMSOL, Stockholm, Sweden):

$$\nabla \times \mu_r^{-1}(\nabla \times \mathbf{E}(\mathbf{r}, \omega)) - k_0^2[\epsilon_r(\mathbf{r}, \omega) - \frac{i\sigma}{\omega\epsilon_0}]\mathbf{E}(\mathbf{r}, \omega) = 0. \tag{1}$$

Here, μ_r is the relative permeability, $\epsilon_r(\mathbf{r}, \omega)$ is the relative permittivity, k_0 is the free space wave number, and σ is the electrical conductivity. The modeling is based on the fact that the electromagnetic cycle time ($\sim 10^{-15}$ s) is short compared to the thermal time scale ($\sim 10^{-9}$ s, see supporting Figure S1).

In order to calculate the laser intensity at sample plane, I, the electrical field must be given as input. In our simulations, the laser beam is assumed to propagate in the z direction with a Gaussian intensity profile in the x and y directions. The x-component of the electric field (the polarization direction) is therefore written as:

$$\mathbf{E}(x, y, z) = E_0 \frac{w_0}{w(z)} \exp(-\frac{x^2 + y^2}{w(z)^2}) \exp[-i(kz - \eta(z) + k\frac{x^2 + y^2}{2R(z)})]\mathbf{e}_x, \tag{2}$$

where:

$w(z) = w_0\sqrt{1 + (\frac{z}{z_0})^2}$

$$R(z) = z(1 + (\frac{z_0}{z})^2)$$

$$\eta(z) = \arctan(\frac{z}{z_0})$$

$$z_0 = \frac{\pi w_0^2}{\lambda}.$$

In these expressions, w_0 is the beam waist of the laser, measured as in [1], k is the wave number, and z_0 is denoted the Rayleigh range. $\eta(z)$ is the phase change close to the beam waist, the so called Gouy shift. The field propagates like a spherical wave with radius $R(z)$, however, close to the focal point it can be assumed to propagate as a plane wave.

The refractive indices of Pt and Au and their extinction coefficients are deduced from fitting the Brendel-Bormann model to the experimental data [2]. This gives the following values of the refractive indices of Pt, Au and Silica: $n_{Pt} = 3.6$, $n_{Au} = 0.3$, and $n_{Si} = 1.45$, respectively, at $\lambda = 1064$ nm. The extinction coefficients are k_{Pt}=6, k_{Au}=6.6 and k_{Si}=0 at $\lambda = 1064$ nm. The Gaussian beam waist of the laser at the focal plane was set to w_0=850 nm in accordance with the measured experimental value [1].

Calculation of the Photothermal Transduction Efficiency

The photothermal transduction efficiency is the efficacy with which nanoparticles convert absorbed light into thermal energy, it is typically measured for bulk solutions of nanoparticles [3, 4, 5, 6, 7, 8, 9]. In Ref. [3] the analytic calculation of the photothermal transduction efficiency is based on the energy balance of the system:

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = \sum_j Q_j \tag{3}$$

where the left side is the sum of the product of each constituent's mass, m_i, and its corresponding heat capacity, $C_{p,i}$, T is the temperature (in Kelvin), and t is time. The right hand side is the sum of all energy terms, Q_j. Equation 3 is valid when the time it takes for the system to equilibrate internally, i.e., to reach thermal equilibrium within the cuvette, is much smaller than the time it takes to reach thermal equilibrium with the larger surroundings.

One contribution to the right side of equation 3 is the heat (Q_1) dissipated by electron-phonon relaxation of plasmons:

$$Q_1 = P(1 - 10^{-\lambda_L})\eta, \tag{4}$$

where η is the photothermal transduction efficiency, i.e., the efficiency by which light is absorbed and converted to heat. λ_L is given by Beer-Lambert's law and is referred to as the optical density. P is the laser power and Q_0 is the heat dissipated in the cuvette and in the media containing the nanoparticles.

The terms Q_1 and Q_0 add heat to the system and is counteracted by energy loss terms. One type of energy loss term, Q_{cond}, is the energy conducted to the air, the sample holder and other immediate surroundings

$$Q_{cond} \propto \Delta T, \tag{5}$$

where $\Delta T = T - T_{amb}$ and T_{amb} is the ambient temperature. Furthermore, energy is lost through thermal radiation, Q_{rad}, given by Stefan-Boltzmann's law

$$Q_{rad} \propto T^4 - T_{amb}^4 \tag{6}$$

For large T, i.e., $T > T_{amb}$, $Q_{rad}/\Delta T$ varies only little with respect to ΔT. Hence, for ΔT less than 10 °K, we can approximate $Q_{rad}/\Delta T$ with a constant value (the variation is less than 5% [3]). Therefore, the sum of the energy loss terms, Q_{ext} can be written

$$Q_{ext} = Q_{cond} + Q_{rad}, Q_{ext} \propto \Delta T. \tag{7}$$

Hence, Q_{ext} can also be written as

$$Q_{ext} = hA(T_{max} - T_{amb}), \tag{8}$$

where h is a heat-transfer coefficient and A is the relevant projected surface area for radiative heat transfer.

Using the definitions given above equation 3 can be written

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_1 + Q_0 - Q_{ext} \tag{9}$$

We define a typical time constant, τ, characterizing the system as

$$\tau := \frac{\sum_i m_i C_{p,i}}{hA}. \tag{10}$$

τ can be extracted by measuring the response of the system as it reaches thermal equilibrium with the surroundings after the laser is turned off. After the laser is turned off $Q_1 = Q_0 = 0$ and equation 9 reduces to

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = -Q_{ext}. \tag{11}$$

A dimensionless driving force, θ, can be defined as

$$\theta := \frac{T_{amb} - T}{T_{amb} - T_{max}}, \tag{12}$$

where T_{max} is the maximum steady state temperature reached during laser irradiation. Substituting τ and θ into equation 11 yields

$$\frac{d\theta}{dt} = -\frac{\theta}{\tau}. \tag{13}$$

And integrating the expression gives

$$\int \frac{1}{\theta} d\theta = -\frac{1}{\tau} \int dt. \tag{14}$$

Using the initial condition that $\theta = 1$ for $t = 0$ one obtains

$$\log \theta = -\frac{t}{\tau}. \tag{15}$$

It is well-established that a reasonable way to compare the the photothermal efficiency, η, for different nanoparticle samples is to have a fixed λ_L [9, 8, 4, 6]. For the nanoparticles tested here we used $\lambda_L = 0.14$ and from a plot of $\log \theta$ versus t we found τ accordingly to equation 15. To calculate $\sum_i m_i C_{p,i}$, we measured the mass of the cuvette to be $m_1 = 2.20$ g and it has $C_{p,1} = 1.4$ J/gK. The solution is considered to be aqueous [9] with $m_2 = 1$ g and $C_{p,2} = 4.184$

J/gK. Using τ and equation 10 we then calculated the experimental factor hA for each sample.

From a control experiment, where a cuvette with (only) water is exposed to the laser, hA is obtained. With this knowledge Q_0 for samples containing nanoparticles can be obtained as

$$Q_0 = hA(T_{max} - T_{amb}). \tag{16}$$

By rearranging equation 9 and inserting equations 4 and 8 the following expression is obtained for calculating the photothermal transduction efficiency:

$$\eta = \frac{hA(T_{max} - T_{amb}) - Q_0}{P(1 - 10^{\lambda_L})}. \tag{17}$$

In the experiments we used a laser power of P=4.35 W and measured the values of T, T_{max}, and T_{amb}.

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Supporting Table and Figures

	C_{abs} ($\times10^{-14}$ m^2)	C_{scat} ($\times10^{-14}$ m^2)	C_{ext} ($\times10^{-14}$ m^2)
Pt70	0.07	0.004	0.074
Pt50	0.02	0.0003	0.02
Pt30	0.004	0.00006	0.004
AuNS	0.43	1.6	2.03
Au70	0.008	0.005	0.013
Au50	0.003	0.0003	0.003
Au30	0.0005	0.00004	0.0005

Table S1. Calculated absorption (C_{abs}), scattering (C_{scat}) and extinction (C_{ext}) cross sections at 1064 nm for platinum and gold nanoparticles with diameters of 30 nm (Pt30, Au30), 50 nm (Pt50, Au50) and 70 nm (Pt70 and Au70), and for 150 nm gold nanoshells (AuNS).

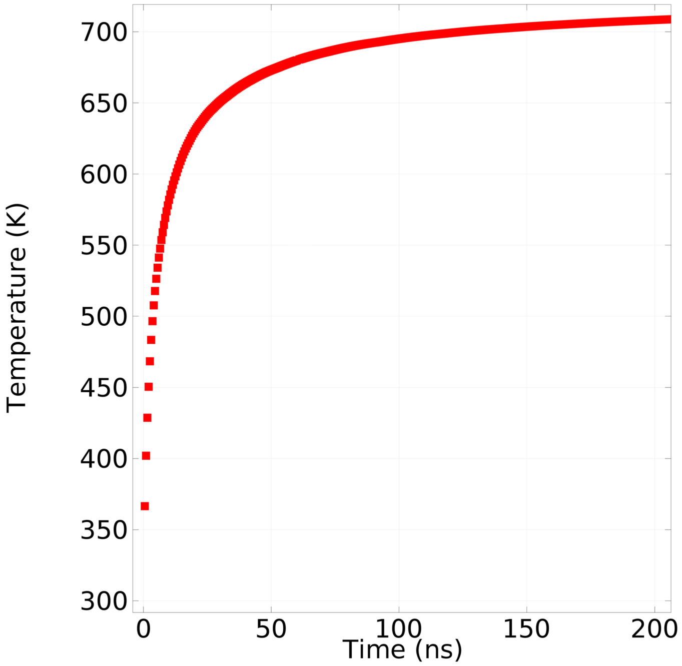

Fig. S1. The surface temperature of an irradiated 70 nm platinum nanoparticle calculated by finite element modeling. The laser power is 375 mW and steady-state is reached after ∼100 ns.

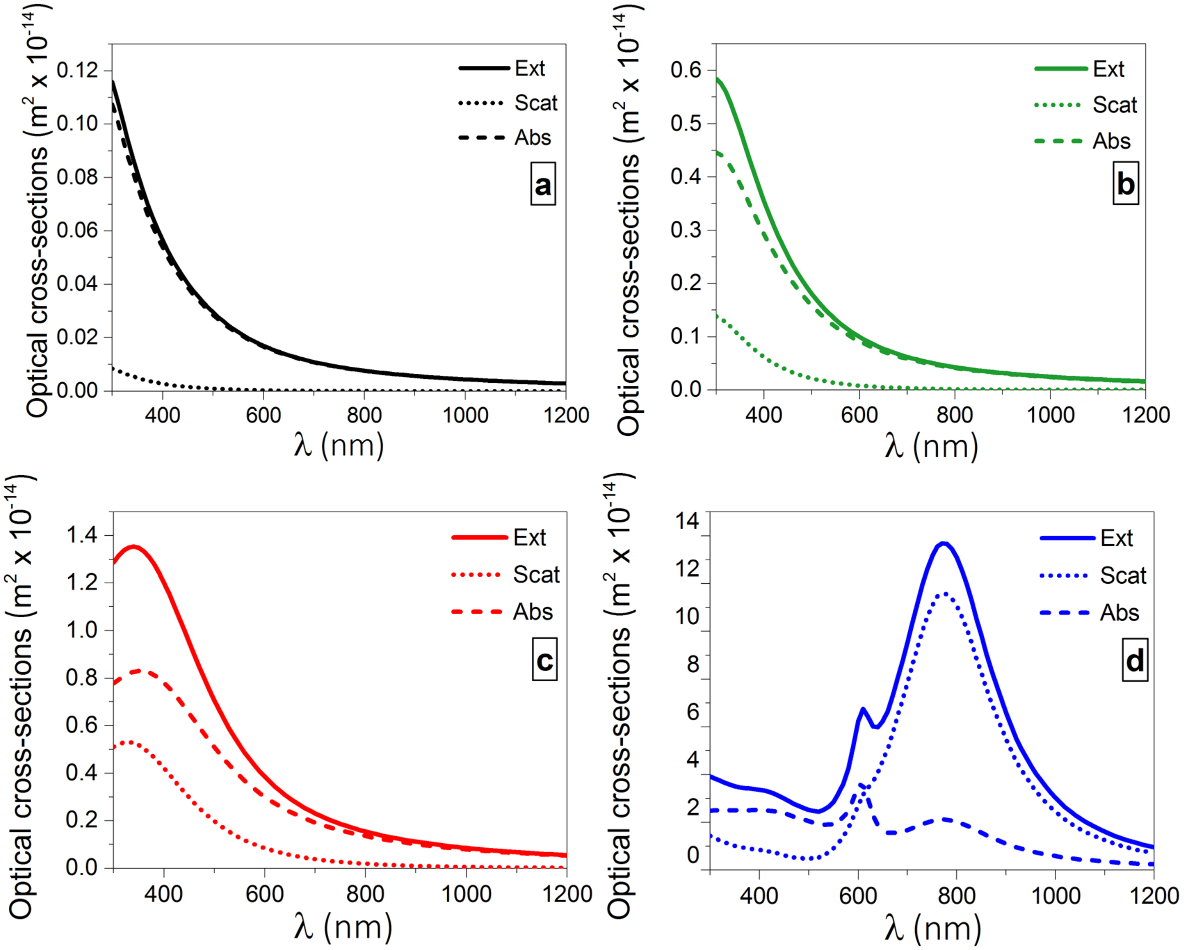

Fig. S2. Optical characteristics of platinum nanoparticles and gold nanoshells. Calculated extinction (full line), scattering (dotted line), and absorption (dashed line) cross sections as a function of wavelength for Pt30 (a, black), a Pt50 (b, green), Pt70 (c, red), and a 150 nm AuNS (d, blue).

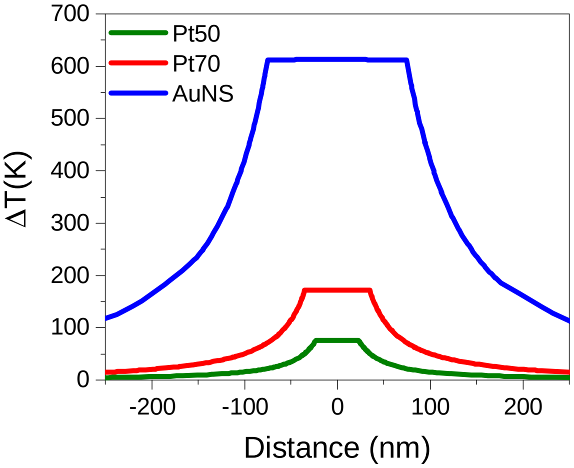

Fig. S3. The temperature profiles around an irradiated gold nanoshell (AuNS, blue), an irradiated 70 nm platinum nanoparticle (Pt70, red), and an irradiated 50 nm PtNP (Pt50, green) using a laser power of 85 mW.

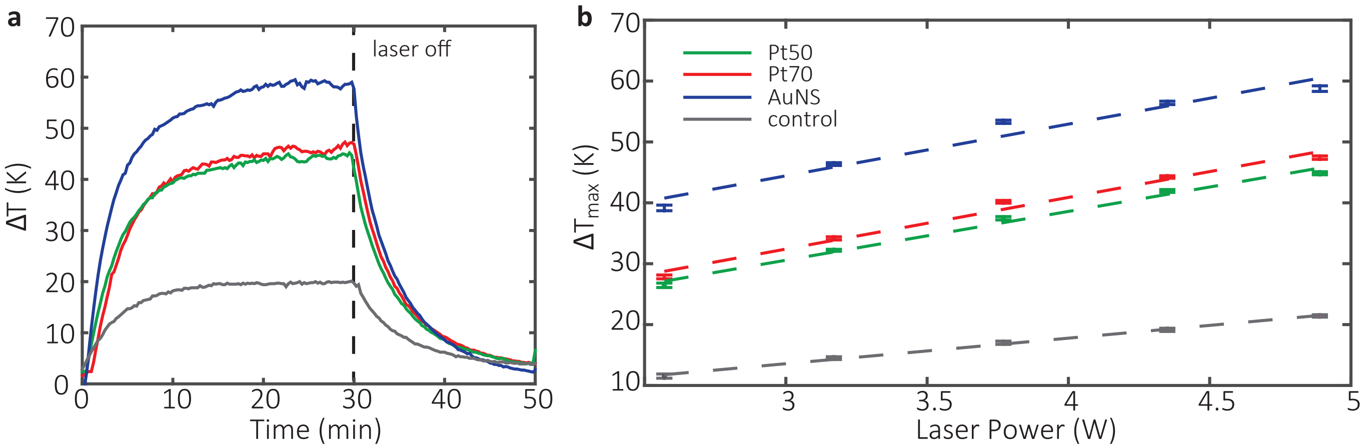

Fig. S4. Temperature increase of nanoparticle bulk solutions which are density matched. (a) The bulk temperature during 30 min of irradiation and 20 minutes of cooling (no laser irradiation). Samples with gold nanoshells (AuNSs) are denoted by a blue line, 70 nm platinum nanoparticles (Pt70) with a red line, 50 nm platinum nanoparticles (Pt50) with a green line and the gray line denotes a control with only the solvent (millipore water). The sampling rate is 4 per minute. The vertical punctuated line indicates where the laser is turned off. The laser power was P =4.32 W. After $\sim$ 20 min of irradiation, the temperature increase reached a maximum steady-state value designated ΔT_{max}. (b) ΔT_{max} as a function of laser power. The hardly visible error bars denote standard deviations over 2.5 minutes with a sampling rate of 4/min. The dashed lines are linear fits to the data points, same color code as (a).

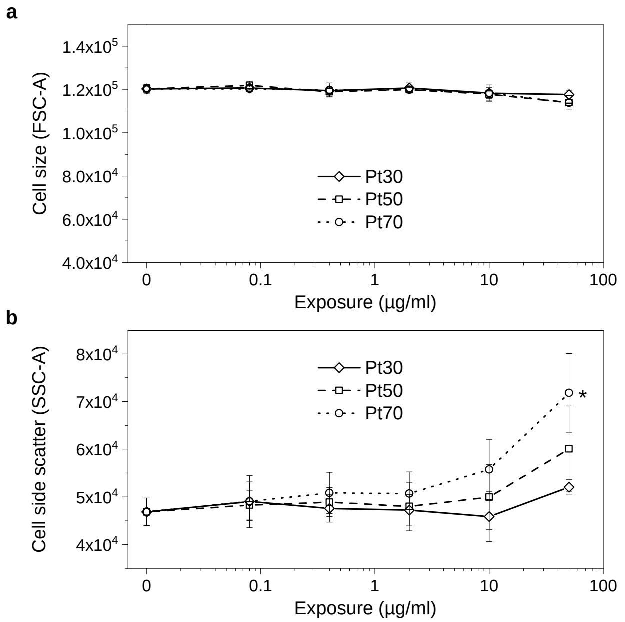

Fig. S5. Additional flow cytometry data. Human SK-OV-3 cancer cells after 24 hours of exposure to platinum nanoparticles (PtNPs). Effects on cell size (a) and cell side scatter (b) after exposure to 30 nm PtNPs (tiltet squares, solid line), 50 nm PtNPs (squares, dashed line) and 70 nm PtNPs (circles, dotted line). Error bars represent one standard deviation, n = 3, *significantly different from groups 0-2 μg/ml ($P<0.005$) and 10 μg/ml ($P<0.05$).