

Supporting Information

Determination of Nanoscale Mechanical Properties of Polymers via Plasmonic Nanoantennas

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S1. Mechanical numerical simulations

The linear elastic mechanical response of gold nanorods (GNR) in air and polymeric environments was obtained from eigenfrequency and frequency-domain solution of Navier's equation with perfectly matched layers (PML) boundary conditions using the commercially available finite-element methods (FEM) software COMSOL Multiphysics:

$$\frac{E}{2(1+\nu)} \left[\frac{1}{1-2\nu} \nabla(\nabla \cdot \mathbf{u}) + \nabla^2 \mathbf{u} \right] + \mathbf{f} = \rho \frac{\delta^2 \mathbf{u}}{\delta t^2}$$

where $\mathbf{u}$ is the displacement vector, $\mathbf{f}$ the force per unit volume, ρ the material density. Continuity of stress and displacement was considered at all boundaries. A thermal strain (ε_{th}) proportional to the decay temperature induced by the absorption of the pump pulse was employed:

$$\varepsilon_{th} = \alpha(T - T_r)$$

where α is the coefficient of expansion of the nanoparticle, T the lattice temperature and T_r the reference temperature (293.15 K) before pump pulse arrival. To account for internal losses in the nanoparticle due to crystalline defects, we have used an isotropic loss factor $\eta = 0.1$ in the gold domain.¹

S2. Optical response of gold nanorod in air and surrounded by the polymer

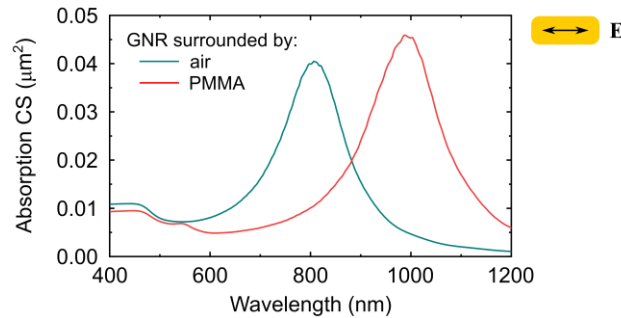


Figure S2. Finite difference time domain simulation (FDTD) for the absorption cross section of gold nanorod surrounded by air and PMMA.

S3. Complex part of the shear modulus G

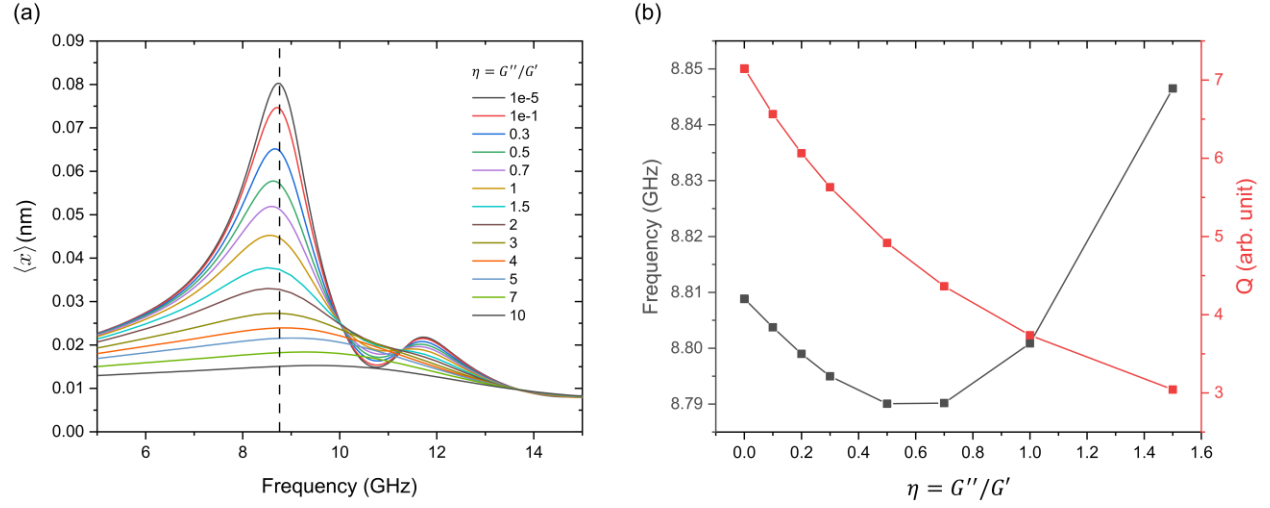


Figure S3. Simulations for complex shear modulus. (a) Simulated frequency-domain spectrum for different values of $\eta = G''/G'$, the ratio between the imaginary and real part of G , associated with the viscous and elastic properties of the polymer, respectively. (b) Frequency and Q factor of the extensional mode as a function of η .

S4. Temperature calculations-simulations

In order to study the process of light absorption and conversion into thermal energy in the time domain, we solve the heat diffusion equations in the GNR and medium domains with the corresponding boundary conditions. If the system is initially at temperature T_r absorbs light, the temperature increase T above T_r at the position r and time t is given by:

$$\begin{cases} \rho_{\text{Au}} c_{\text{Au}} \partial_t T(r, t) = \kappa_{\text{Au}} \nabla^2 T(r, t) + p(r, t) & \text{for } r \in \text{GNR} \\ \rho_{\text{m}} c_{\text{m}} \partial_t T(r, t) = \kappa_{\text{m}} \nabla^2 T(r, t) & \text{for } r \notin \text{GNR} \\ \kappa_{\text{m}} \partial_{\perp} T(s^+, t) = \kappa_{\text{Au}} \partial_{\perp} T(s^-, t) \\ T(s^+, t) = T(s^-, t) \end{cases}$$

where the Au and m subscripts refer to gold and medium and s^+ and s^- refer to the outer and inner parts of the interface position. The first boundary condition (third line in the equation) ensures heat flux conservation at the GNR interface. No interface resistivity due to molecular coating is considered.

The heat power density $p(r, t)$ is the heat power dissipated in the GNR (or the absorbed energy) per unit of volume (V_{GNR} is the GNR volume). In the case of femtosecond-pulsed illumination, the heat power depends on the irradiance $I(t)$ and is calculated as:

$$p(r, t) = \frac{\sigma_{\text{abs}} I(t)}{V_{\text{GNR}}}$$

where σ_{abs} is the absorption cross section of the GNR.

The GNR is uniformly illuminated at a wavelength λ .

This set of equations has no analytical solution and we solved it numerically using a finite difference scheme, with a regular spatiotemporal discretization in a cubic box of 300 nm side with the GNR centered at the origin. Constant room temperature was imposed on the boundary of the box.

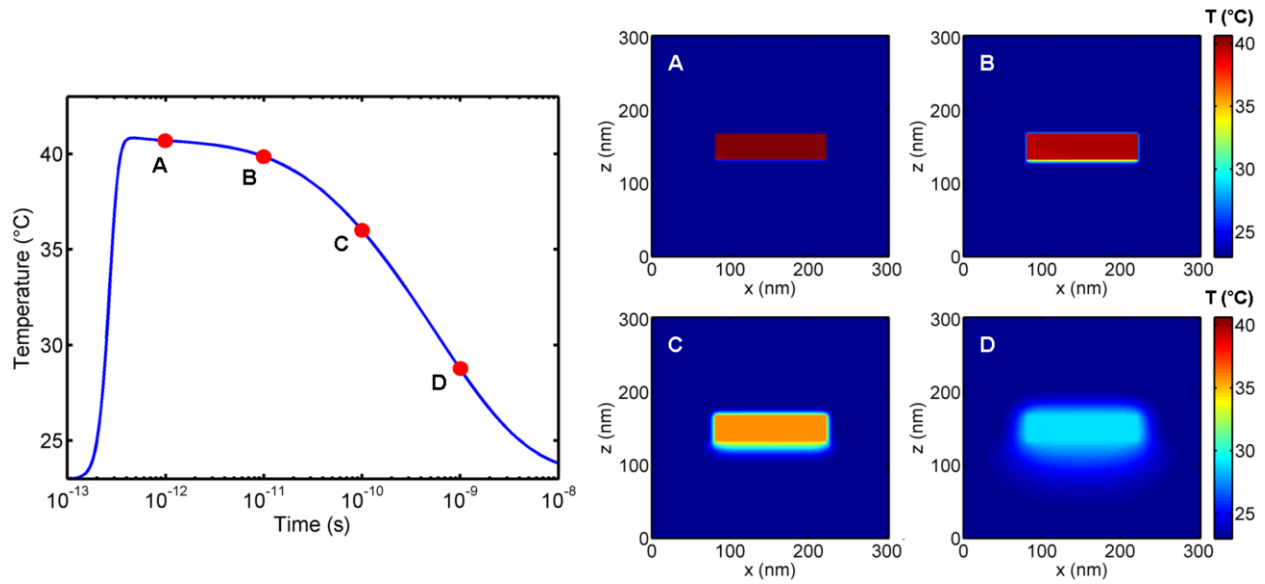


Figure S4.1. Temperature evolution of GNR with nominal dimensions (see Figure 1a) surrounded by PMMA during and after the absorption of an ultrashort pulse of $0.07 \text{ mW } \mu\text{m}^{-2}$ at 400 nm. Right panels show temperature maps in a plane parallel to the x -axis and perpendicular to the substrate at times (A) 0.001 ns, (B) 0.01 ns, (C) 0.1 ns and (D) 1 ns after the pulse arrival, marked as red dots in curves.

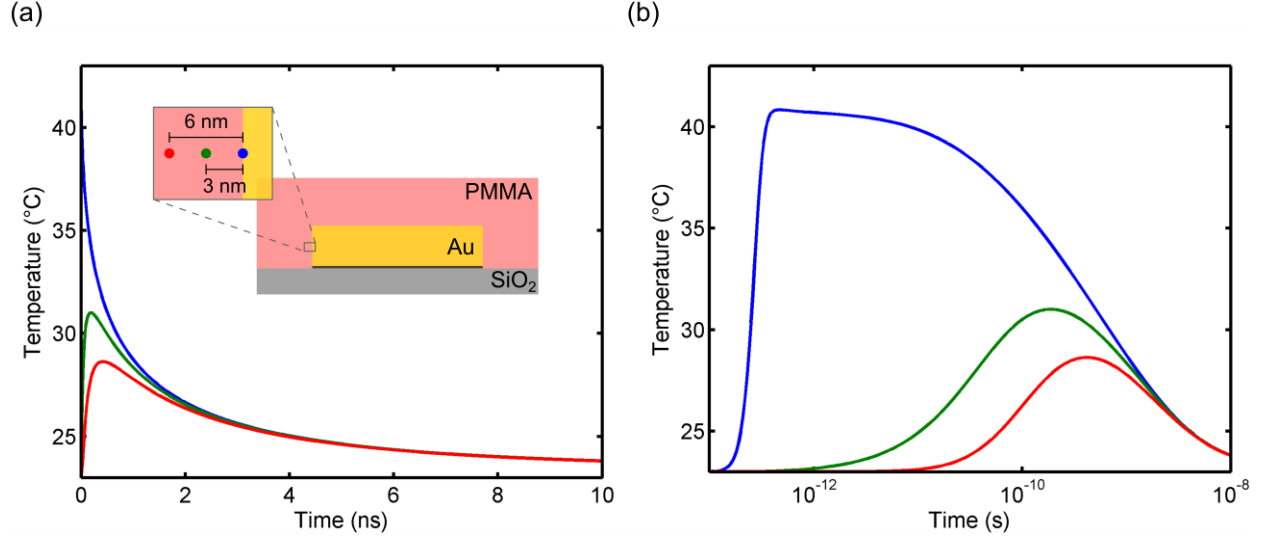


Figure S4.2. (a) Temperature evolution on the surface of a GNR (blue) and on the surrounding PMMA at 3 nm (green) and 6 nm (red) away during and after the absorption of a light pulse of $0.07 \text{ mW } \mu\text{m}^{-2}$ at 400 nm. (b) The same as before in semi-logarithmic scale.

S5. Numerical calculations employing the Dupaix-Boyce model

The Dupaix-Boyce constitutive model describes the strong temperature dependence of the elastic moduli with the temperature, i.e. the stress-strain behavior, connecting the glassy and the rubbery states through the glass transition.² Within the framework of this model, the resistance of the material to the imposed deformation is represented by two mechanisms in parallel: a resistance due to intermolecular interactions, and a resistance due to the stretching and reorientation of the underlying molecular network. This model is expressed as:

$$G(T) = \frac{1}{2}(G_g + G_r) - \frac{1}{2}(G_g - G_r) \tanh \left[\frac{5}{\Delta T}(T - T_g) \right] + X_g(T - T_g),$$

where G_g and G_r are the shear modulus at the glassy and rubbery state respectively, ΔT is related to the width of the transition and X_g is the slope in the glassy and rubbery regions. Figure S5a illustrates the meaning of each parameter in the model curve of this latest equation. Numerical calculations employing the Dupaix-Boyce model are able to accurately reproduce the observed experimental behavior, as shown in Figure S5b for an antenna of dimensions $141 \times 61 \times 35 \text{ nm}$, whose numerically calculated extensional mode frequency in air (8.24 GHz) matches the

experimental bare resonance (shown as a horizontal dashed line). The parameters used for the annealed-PMMA glass transition were $G_g = 1800$ MPa, $G_r = 750$ MPa, $T_g = 74^\circ\text{C}$, $\Delta T = 40^\circ\text{C}$ and $X_g = -2$ MPa K⁻¹.

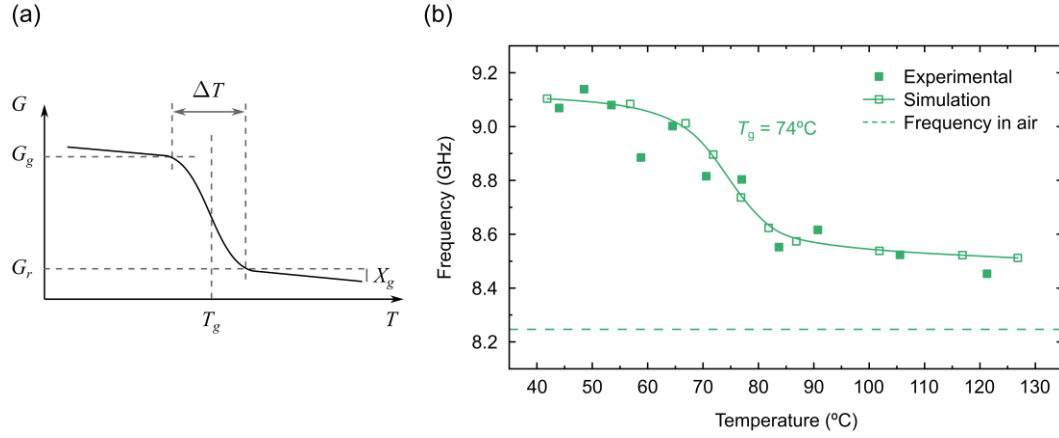


Figure S5. (a) Illustration of parameters involved in the Dupaix-Boyce model for the dependence of the shear modulus G of an amorphous polymer with temperature through the glass transition. (b) Comparison between experimental results and numerical calculations employing the Dupaix-Boyce model. Experimental bare resonance is shown as a horizontal dashed line.

References

- (1) O'Brien, K.; Lanzillotti-Kimura, N. D.; Rho, J.; Suchowski, H.; Yin, X.; Zhang, X. Ultrafast acousto-plasmonic control and sensing in complex nanostructures. *Nat. Commun.* **2014**, *5*, 4042.
- (2) Dupaix, R. B.; Boyce, M. C. Constitutive modeling of the finite strain behavior of amorphous polymers in and above the glass transition. *Mech. Mater.* **2007**, *39*, 39–52.