

Electronic Supporting Information for:

Quenching of nonlinear photoacoustic signal generation in gold nanoparticles through coating

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Experimental Methods

Coated GNP Synthesis.

Citrate-stabilized gold nanospheres of nominally 100 nm in diameter were obtained from BBI solutions (EM.GC100). Before use, the gold nanosphere suspension was shaken and placed in an ultrasound bath for one minute to redisperse any settled nanoparticles. Silica coating of these particles was synthesized in house following the modified Stöber method of Graf et al.¹⁶ Polyvinylpyrrolidone (PVP, Mw 29000), tetraethyl orthosilicate (TEOS), and ethanol were obtained from Aldrich, and ammonium hydroxide solution (25%-26% in water) was obtained from Honeywell Fluka. Filtered and deionized water from a Milli-Q[®] Reference A+ System was used. PVP was dissolved in water with a concentration of 20 mg/mL through ultrasonification of the solution for 15 minutes. PVP was adsorbed onto the surface of the citrate-stabilized uncoated gold nanospheres by mixing 101.7 μ L of the 20 mg/mL PVP solution with 4 mL of the as-purchased uncoated GNP suspension over a period of 24 hours under constant stirring. Excess PVP was then removed through centrifugation (Eppendorf 5804 R, 2500 rpm for 10 minutes) after which the supernatant was removed and the particles were redispersed in water. The centrifugation process was repeated twice, and the remaining particles were dispersed in 2 mL of water. The resulting GNP suspension was mixed with 10 mL ethanol and 0.8 mL of a 100 mM TEOS in ethanol solution. 250 μ L of ammonium hydroxide solution was added to raise the pH. The mixture was stirred for 2.5 hours and the resulting particles were centrifuged (2500 rpm, 10 minutes, repeated three times to remove excess chemicals in the solution) and dispersed in water. The resulting suspension was sonicated 5 minutes in an ultrasound bath after the original synthesis, and again for one minute before each PA experiment. The synthesis process was repeated as described above, to create a second sample of silica-coated GNPs to examine the repeatability of the effect of silica coating on the PA signal. All PA experiments and the imaging of the nanosphere suspensions were carried out within one week of the silica-coated particle synthesis.

GNP Characterization.

Scanning electron microscopy (SEM) imaging (GeminiSEM, Carl Zeiss, Jena, Germany) was used to determine the core gold nanosphere diameter and silica coating thickness for each of the particle suspensions. The purchased citrate-stabilized GNPs were found to have a mean diameter of 100 nm with standard deviation of 10 nm from the SEM imaging, and the silica-coating procedure described above was found to yield a coating thickness of approximately 15 nm. Energy-dispersive X-ray spectroscopy (EDX) spectra of the silica-coated GNPs was also captured with the GeminiSEM device coupled with a Quantax 400 EDX Detector (Bruker, USA). For the EDX measurements, 2 μ L of the suspension was dried on aluminum foil. Dynamic light scattering (DLS) measurements were performed with a Particle Size Analyzer (Litesizer 500, Anton Paar, Graz, Austria) using the high-end batch module (BM10) with measurements carried out at measurement angles of 90° and 175°. For the DLS measurements, the GNPs were dispersed in water by ultrasonification for 10 minutes to obtain concentrations of 0.1 mg/mL, and the samples were filtered through syringe filters with pore diameters of 0.2 μ m before the

measurements. The optical density (OD) spectrum of the suspensions were measured using a UV/Vis Spectrometer (Specord 250 Plus, Analytik Jena AG, Jena, Germany) using a disposable polymethylmethacrylat cuvette with 10 mm optical path length. The overall optical extinction and absorption in the uncoated particle suspensions was measured using an integrating sphere combined with a broadband light source and UV/VIS spectrometer, following the procedure in our previous publication.⁷ The silica coating was assumed not to alter the absorption relative to extinction for the silica-coated GNPs, based on similar measurements from our previous work.¹³

PA Experimental Setup.

We used a custom-built backwards mode PA sensor to record time-resolved PA signals generated from excitation by the second harmonic of an Nd:YAG laser (Contium Surelite 10-I, 532 nm wavelength, 5 ns pulse width FWHM, 10 Hz). The details of this sensor have been described in a previous work.⁷ Briefly, the PA illumination is directed through a glass prism, above which is an acoustically coupled sample holder made of clear silicon that holds a free-sitting 300 μL volume of the GNP sample. The generated PA signal is recorded with a custom-made broadband piezoelectric poly(vinylidene) fluoride (PVDF)-based sensor (25- μm -thick) mounted on the prism on the same side of the sample as the illumination (see Figure 2c). The signal from the acoustic sensor was amplified using a current amplifier (Gain 50 kV/A, Bandwidth: 100 MHz, FEMTO) and then recorded with a digital oscilloscope (Keysight InfiniiVision 3000 X-Series 500 MHz, set with 10 averages) through which it was saved by an in-house developed LabVIEW program. The PA signal amplitude was defined as the positive peak PA amplitude in time. A portion of the laser beam upstream of the PA sensor was diverted with a beam splitter into a pyroelectric energy probe (Ophir, PE25BF-C) and monitored in the in-house developed LabVIEW program via a Smart Head to USB Interface (Ophir). Each measurement repetition includes the PA signal measured with five different excitation fluence values at the sample surface between 2 and 10 mJ/cm^2 . A new measurement repetition involved a new sample pipetted on the PA sensor. Three measurement repetitions were carried out for each of the synthesized coated GNP samples (six in total for the coated GNP), whereas five measurement repetitions were carried out each for the uncoated GNP and the liquid dye.

Linearity Assessment

For assessing the linearity of the PA signal amplitude as a function of fluence, two methods were used as described in Schrof et al.²¹ Method I involves a linear fit of the form

$$p(\Phi) = a\Phi \quad (1)$$

where p is the PA signal amplitude, a is the linear coefficient, and Φ is the PA excitation fluence. The coefficient of determination R^2 to the linear fit is used to assess linearity. Method II involves a second order (quadratic) polynomial fit of the form

$$p(\Phi) = a_2\Phi^2 + a_1\Phi \quad (2)$$

where a_2 is the second-order coefficient and a_1 is the first-order coefficient. In this case, the second-order coefficient is used to assess linearity.

Supporting Figures

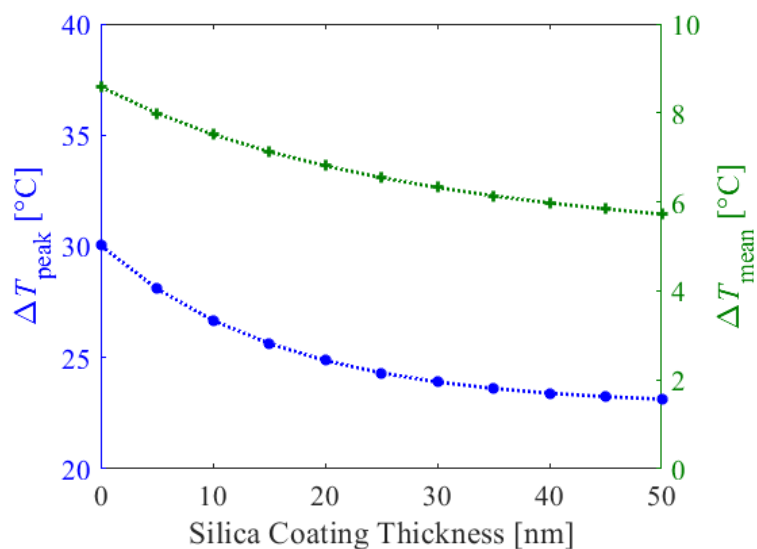


Figure S1. Theoretical modeling of the temperature at the particle-water interface after PA excitation of a silica-coated GNP in water assuming an excitation fluence 1 mJ/cm², pulse width 5 ns, wavelength 532 nm, and initial temperature 20 °C. The peak temperature (left axis) and mean temperature over the first 40 ns after excitation (right axis) are calculated as a function of coating thickness.

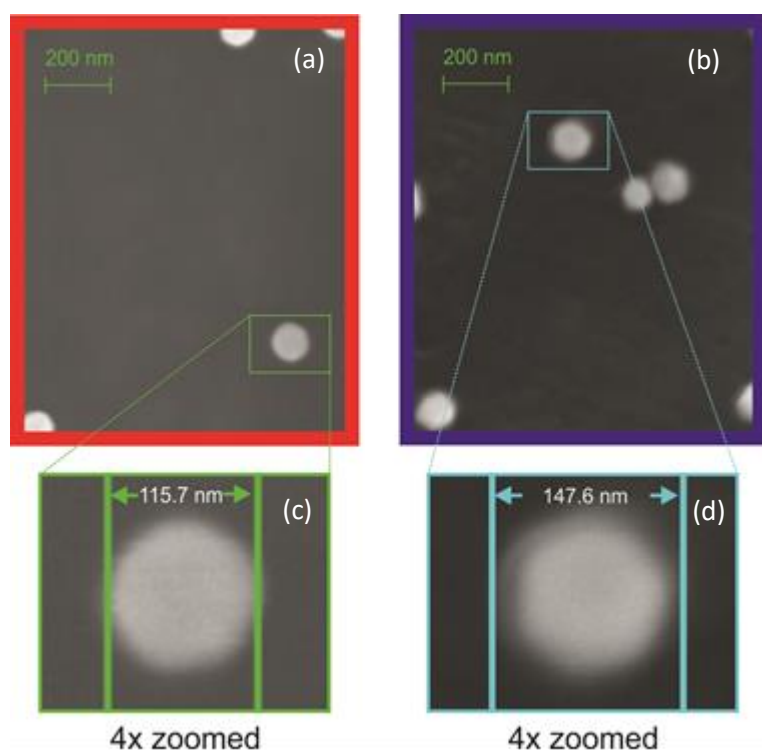


Figure S2. Scanning electron microscopy (SEM) images of the gold nanoparticles. (a) Uncoated GNP. (b) Coated GNP. (c) and (d) are expanded versions of (a) and (b), respectively.

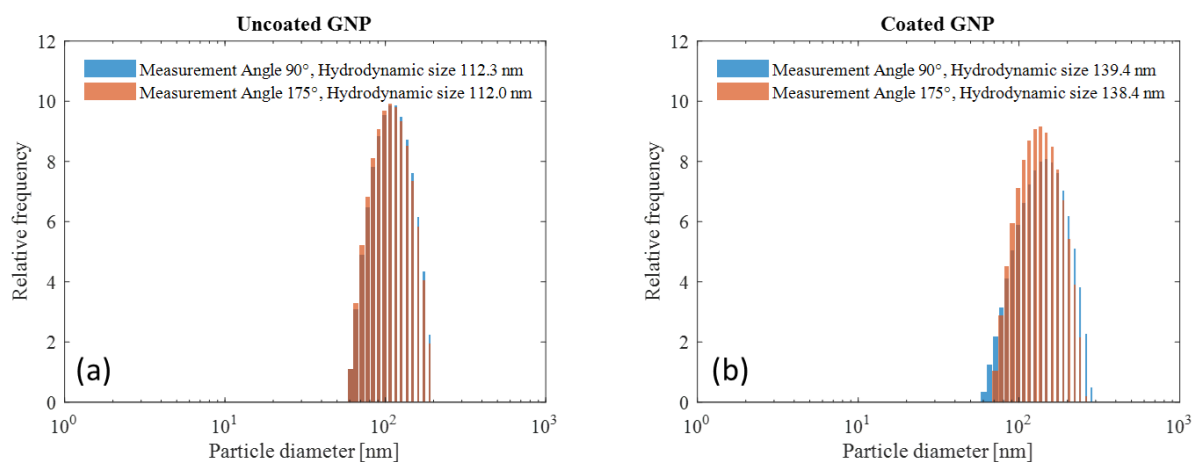


Figure S3. Dynamic light scattering (DLS) measurements of particle size distribution of the (a) uncoated GNPs and (b) coated GNPs.

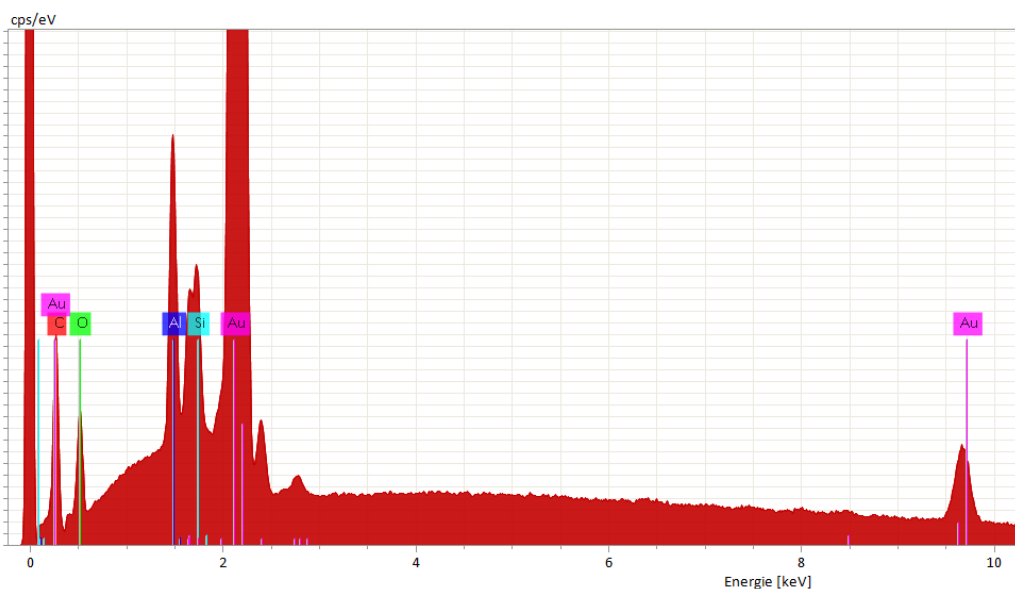


Figure S4. Energy-dispersive X-ray spectroscopy (EDX) spectra of the silica-coated GNPs dried on an aluminum foil sample holder. From the EDX spectra, the main elements seen are gold (Au), silica (Si) and oxygen (O) from the silica coating (SiO_2), and aluminum (Al) from the sample holder.

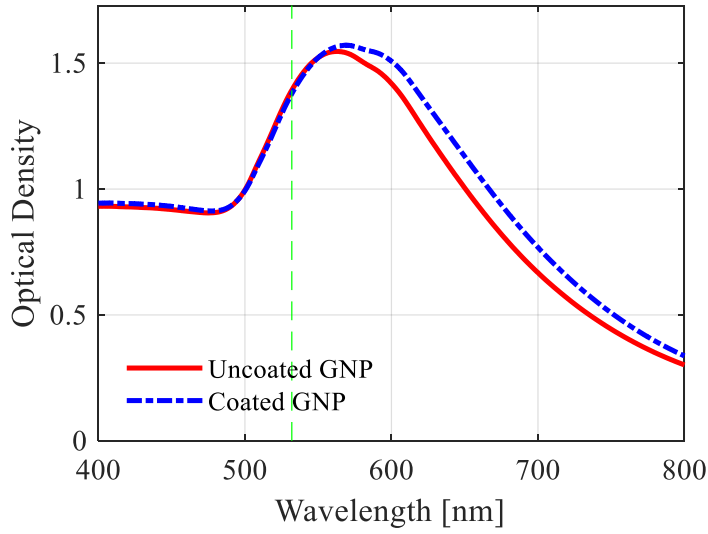


Figure S5. Optical density (OD) spectra of the uncoated GNP and coated GNP suspensions measured in a 10 mm path length cuvette. The dotted green line represents the PA excitation wavelength of 532 nm. Both suspensions were diluted to an identical OD 1.4 at 532 nm.

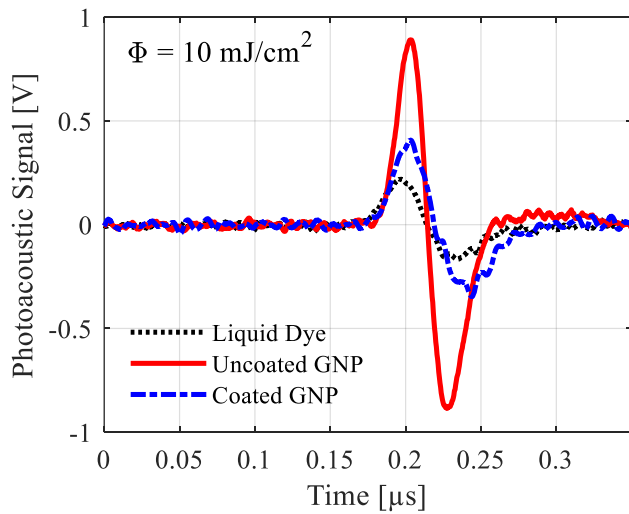


Figure S6. Representative PA signal measurement in time from the uncoated GNP and coated GNP suspension. Also shown for comparison is the PA signal measurement from a homogeneous liquid dye with identical absorption coefficient as the GNP suspensions. The PA signal amplitude is defined as the maximum of the PA signal measurement in time, which is shown near time zero. The excitation fluence for the case shown is 10 mJ/cm².

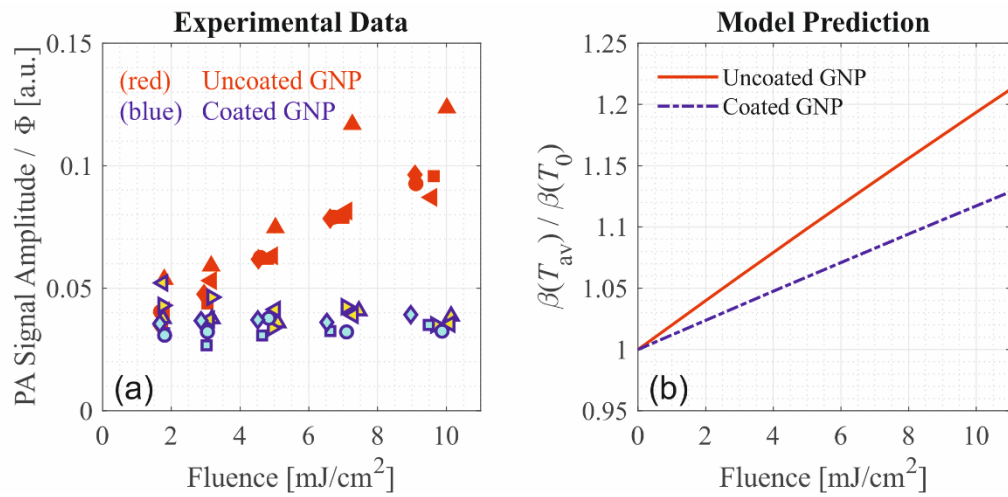


Figure S7. (a) PA signal amplitude divided by the respective fluence for the uncoated and coated GNPs for all measurement repetitions. Different symbol shapes indicate different measurement repetitions. The results from two different independent synthesis of the coated GNP samples are indicated with a different color symbol filling. (b) The thermal expansion coefficient of water at the average temperature attained in the volume surrounding the GNP extending 100 nm from the particle surface as computed by the theoretical model. The volume-averaged temperature is averaged over the first 40 ns after the PA excitation, and the thermal expansion coefficient shown is normalized by the thermal expansion coefficient of water at 20 °C.