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ABSTRACT
The accurate determination of the photothermal response of nanomaterials represents an essential aspect in many fields, such as nanomedicine. Specifically, photothermal cancer therapies rely on the precise knowledge of the light-to-heat transfer properties of plasmonic nanoparticles to achieve the desired temperature-induced effects in biological tissues. In this work, we present a novel method for the quantification of the photothermal effect exhibited by nanoparticles in aqueous dispersions. By combining the spatial and temporal thermal dynamics acquired at terahertz frequencies, the photothermal conversion efficiency associated with the geometry of the plasmonic nanoparticles can be retrieved in a noncontact and noninvasive manner. The proposed technique can be extended to the characterization of all those nanomaterials which feature a temperature-dependent variation of the refractive index in the terahertz regime.

I. INTRODUCTION
Nowadays, nanotechnology has breached the barriers of laboratories to enter our daily lives, finding applications in a vast variety of fields including chemistry, energy, biology, and medicine, to name a few. Among them, plasmonic nanoparticles still represent an active and fast-growing research area driven by their strong and easily tunable response to external electromagnetic fields. Especially in the biomedical domain, nanoparticles have long been touted to present promising opportunities as nanosized photothermal agents to gain localized control over heat generation and distribution in living tissues. In nanotechnology-enabled therapeutic modalities, such as photothermal therapy of skin carcinomas, near-infrared (NIR) laser illumination is combined with plasmonic nanoparticles to achieve a strong enhancement of the localized heating effect that originates from the excitation of the nanoparticles’ localized surface plasmon resonance (LSPR). The optimization of the nanomaterial’s properties and morphology is essential to tune the LSPR wavelength.
and ensure the efficient light-to-heat transfer required to achieve the desired temperature-induced effects in biological tissues. For example, hyperthermia occurs at ~40°C, protein denaturation at ~60°C, vaporization, and thermal decomposition (ablation) at ~100°C. Despite the extreme interest of plasmonic heating in photothermal therapies, there are still difficulties in linking the geometry and morphology of nanoparticles with the resulting macroscopic thermal dynamics, especially with regard to the accurate quantification of the light-to-heat conversion efficiency.

Thus far, the most widespread method for measuring light-induced temperature changes in nanoparticle dispersions employs thermistor-based probes that rely on physical contact with the sample. In addition, in order to guarantee a homogeneous temperature distribution, a magnetic stirrer is commonly used. However, this method does not allow to instantaneously and reliably measure thermal dynamics within the illuminating laser spot. Moreover, it requires direct contact, thus potentially damaging and/or contaminating the sample, as well as altering the measurement itself. Recently, a simple and fast method to determine the photothermal conversion efficiency of nanoparticles has been reported based on the use of an integrating sphere. However, this method does not reveal the local absolute value of temperature and requires the sample to be placed into the integrating sphere, which in turn might hamper its broader applicability in real-world environments. More sophisticated methods such as infrared thermometry and thermography rely on detecting the infrared radiation emitted by an object to infer its temperature. Although they offer noncontact and nondestructive detection capabilities, these methods can only measure surface temperatures within a direct line-of-sight. A completely different approach, namely, nanothermometry, relies instead on measuring changes in the luminescent properties of nanosized probes to extract local temperatures with submicrometric spatial resolution. Even though this method is highly sensitive, it requires the injection of luminescent nanoparticles, which can potentially contaminate the sample and still cannot be used to measure the temperature when the sample is obstructed or beyond the line-of-sight.

To overcome these drawbacks, we have developed a novel method to characterize the photothermal properties of nanoparticulate dispersions by combining spatial and temporal information recorded via terahertz time-domain spectroscopy (THz-TDS) in reflection geometry. On the one hand, terahertz radiation (frequency range from 0.1 to 10 THz) enables noncontact and noninvasive sensing beyond the line-of-sight since many dielectric nonpolar materials (such as plastics and fabrics) are transparent in this frequency range. Moreover, aqueous solutions experience a significant temperature-dependent refractive index change in the terahertz regime, especially with regard to the accurate quantification of the light-to-heat conversion efficiency.

On the other hand, its low photon energy ensures the physicochemical integrity of a sample without influencing the temperature measurement. Moreover, aqueous solutions experience a significant temperature-dependent refractive index change in the terahertz regime, which in turn enables accurate temperature detection. In a pioneering work, the temperature transient of a gold nanoparticle dispersion upon the NIR pulsed laser illumination was measured using THz-TDS in transmission geometry, which requires a very high power terahertz source and a very thin sample path due to the extreme absorption of terahertz radiation in water; in addition, THz-TDS in transmission geometry does not allow temperature measurements directly at the cuvette/dispersion interface. As a benchmark to validate our method, we used three types of commercially available water-based gold nanorod (GNR) dispersions featuring particle diameters of 10 nm, 25 nm, and 50 nm. They feature the same LSPR frequency within the first biological window (i.e., the range of wavelengths between 700 and 950 nm where light deeply penetrates biological tissues). In our study, using a standard polyethylene (PE) cuvette, we combined terahertz temperature time transients and thermal imaging to retrieve the size-dependent photothermal conversion efficiency, as well as the molar heating rate (MHR), of the three GNR dispersions. Our results are in good agreement with equivalent measurements carried out using conventional methods as well as with our analytical predictions, thus validating the effectiveness of our technique for the photothermal characterization of GNRs.

II. THEORETICAL MODELING

To calculate the photothermal conversion efficiency and the MHR, a macroscopic model of collective particle heating was employed to describe heat generation and dissipation of the GNR dispersion inside a conventional cuvette. Under NIR illumination, the change in temperature $T$ is described by the energy balance equation,

$$\sum_i m_i C_i \frac{dT}{dt} = E_{\text{abs}} - E_{\text{loss}},$$

(1)

where $E_{\text{abs}}$ is the heat induced by the absorption of the nanoparticles, $E_{\text{loss}}$ is the heat dissipated through the surrounding medium, $t$ is the time, $m_i$ and $C_i$ are the mass and specific heat capacities of each element $i$ comprising the entire physical system (i.e., GNRs, deionized water, and PE cuvette). For the three GNR dispersions investigated in our study, the mass of the actual GNRs was insignificant in comparison with the mass of the solvent (3 g) and the PE cuvette (2.5 g). Moreover, the heat capacity of gold (0.129 Jg$^{-1}$K$^{-1}$) is also much smaller than that of water (4.18 Jg$^{-1}$K$^{-1}$) and PE (1.33 Jg$^{-1}$K$^{-1}$). Thus, the mass and heat capacity of the entire GNR dispersion can be assumed to be the one of water. The absorption and dissipation energy in Eq. (1) can be expressed as follows:

$$E_{\text{abs}} = P(1 - 10^{-A_i}) \eta,$$

(2)

$$E_{\text{loss}} = hS[T(t) - T_0],$$

(3)

where $P$ denotes the incident NIR continuous-wave laser power employed to photoexcite the plasmon resonance of the GNR, $A_i$ is the absorbance value of the GNRs at the excitation wavelength of the laser, $\eta$ is the photothermal conversion efficiency, $h$ is the heat transfer coefficient, $S$ is the surface covered by the GNR dispersion, and $T_0$ is the ambient temperature. Then, Eq. (1) can be rewritten as follows:

$$\frac{dT}{dt} = \frac{P(1 - 10^{-A_i}) \eta}{\sum_i m_i C_i} - \frac{hS}{\sum_i m_i C_i} [T(t) - T_0].$$

(4)

From here, the two constants $A$ and $B$ are defined as

$$A = \frac{P(1 - 10^{-A_i}) \eta}{\sum_i m_i C_i},$$

(5)

$$B = \frac{hS}{\sum_i m_i C_i},$$

(6)
where $A$ is the rate of energy absorption and $B$ is the rate of heat dissipation, which allow for a simpler form of Eq. (4) given by

$$\frac{dT}{dt} = A - B[T(t) - T_0].$$  \hspace{1cm} (7)

By integrating Eq. (7) from 0 to $t$, the temperature transient for an arbitrary initial temperature value $T_{initial}$ results as

$$T(t) = T_0 + \frac{A}{B}(1 - e^{-Bt}) + (T_{initial} - T_0)e^{-Bt}. \hspace{1cm} (8)$$

In order to retrieve the photothermal conversion efficiency $\eta$, it is necessary to measure the temperature variation of the GNR dispersions as a function of time during both the photothermal heating (under laser excitation, $A \neq 0$ and $T_{initial} = T_0$) and the subsequent cooling ($A = 0$ and $T_{initial} > T_0$). By fitting the experimental curve with Eq. (8), the values of $A$ and $B$ can be extracted and used to calculate the experimental photothermal conversion efficiency $\eta$,

$$\eta = \frac{A \sum m_i C_i}{P(1 - 10^{-At})}. \hspace{1cm} (9)$$

The $MHR$, which is defined as the initial rate of change in temperature divided by the molar concentration, has been recently introduced to evaluate the photothermal properties of nanoparticles in the biomedical realm. The $MHR$ is computed by using the following equation:

$$MHR = \frac{A}{c}, \hspace{1cm} (10)$$

where $A$, the rate of energy absorption, also represents the initial rate of variation in temperature (i.e., the time derivative evaluated at $t = 0$) and corresponds to the heating speed of the GNR dispersion, while $c$ denotes its molar concentration (molarity). Theoretically, the rate of energy absorption $A$ might be estimated by simply taking the time derivative at $t = 0$; however, retrieving the overall temperature transients gives a more reliable set of data for the accurate extraction of $A$.

III. SAMPLES AND EXPERIMENTAL SETUP

We aimed at comparing three types of GNR dispersions (commercially available from Nanopartz\textsuperscript{Tm}) to determine the particle size that yields the highest light-to-heat conversion performance $\eta$ and $MHR$ under plasmonic excitation at 786 nm. A standard macro-PE cuvette ($12.5 \times 12.5 \times 45 \text{mm}^3$) was loaded with the dispersions, as shown in Fig. 1. All three types of GNR dispersions are capped with hexadecyl-trimethyl-ammonium bromide (CTAB) ligands. Figures 1(a)–1(c) show the representative TEM images of the three samples. The average diameter × length of the three types of GNRs is equal to 10 nm × 41 nm, 25 nm × 90 nm, and 50 nm × 150 nm, and we refer to them as GNR10, GNR25, and GNR50, respectively. The coefficient of variation for the size monodispersity was determined to be less than 10%. The dispersions were purified of any reactive chemicals, and the CTAB concentration was kept to less than 5 mM. The absorbance spectra (accounting for scattering and absorption effects) of the different GNR dispersions were measured using UV/VIS/NIR spectroscopy, as illustrated in Fig. 1(d). It is noteworthy to mention that the GNR25 batch shows the highest absorbance at the LSPR frequency. A detailed summary of the physico-optical properties of the three types of GNR dispersions is provided in Table S1 in the supplementary material.

The THz-TDS system utilized in this study is based on two photoconductive antennas (PCAs) (Tera8-1 from Menlo Systems),...
made of low-temperature-grown gallium arsenide (LT-GaAs) with a gap size of 5 μm, as either terahertz transmitter or detector. Photocarriers within the PCA substrate are excited by a laser source (775 nm wavelength, FemtoFiber smart from Toptica) featuring 100-fs-long pulses at 100 MHz repetition rate. The emitted terahertz pulse is guided by four polymethylpentene (TPX) lenses (BATOP Optoelectronics) to realize a reflection scheme with a ∼1.5 mm focusing spot size. The sample cuvette is placed onto the focal plane of the lens. The angle of incidence is 45° with respect to the normal axis of the cuvette. The power spectrum of the emitted terahertz pulses peaks at about 0.3 THz and exceeds 3 THz in bandwidth, resulting in a signal-to-noise ratio of 419 and a dynamic range of 60 dB (evaluated using the method in Ref. 26). A 50-mm translational stage (T-LSM050A from Zaber) is used to delay the probe with respect to the pump beam in order to read out a single terahertz waveform within a scanning time of 10 s. The scan speed of the delay line was set to 0.5 mm/s. The sample cuvette was mounted on a motorized translation stage enabling pixel-by-pixel terahertz raster-scans.

IV. RESULTS AND DISCUSSION

A. Calibration curve for temperature measurements

In order to realize temperature sensing using THz-TDS, it is fundamental to determine the temperature-dependent terahertz reflectivity. To this end, the function relating the amplitude of the reflected terahertz waves to the temperature, i.e., the calibration curve of the terahertz temperature sensing, is established experimentally for each GNR dispersion.

Terahertz temperature measurements were carried out based on the THz-TDS system set in reflection mode. A sealed standard 10-mm path length PE cuvette containing 3 ml of each GNR dispersion was placed in the terahertz focusing spot, as depicted in Fig. 2(a). A continuous-wave NIR laser emitting at 786 nm was employed to excite the sample inside the cuvette. A typical terahertz time trace reflected from the sample is shown in Fig. 2(b). Three terahertz echoes are clearly identified, which correspond to the terahertz reflections from the air/cuvette (1st echo), cuvette/GNR dispersion interfaces (2nd echo), and a second-round reflection.
(3rd echo), respectively. The NIR excitation laser spot (~2 mm diameter) is overlapped with the terahertz focal spot, in order to record the temperature-induced terahertz changes exactly within the heating spot at the interface between the cuvette and the GNR dispersion. The terahertz echo arising from the cuvette/GNR dispersion interface (i.e., the second echo) was utilized to determine the temperature transient during the heating and cooling cycles. The first echo arising from the air/cuvette interface was instead used for self-referencing in the following postprocessing procedure.

A robust temperature measurement relies on an accurate extraction of the amplitude associated with the second terahertz echo, the latter being reflected from the cuvette/sample interface. As shown in Fig. 2(b), the first echo has an enduring signal or “ringing” due to the ambient water vapor, which interferes with the second echo. Therefore, simply ignoring this interference will lead to an inaccurate measurement of the amplitude associated with the second echo. In order to isolate the first and second echoes, a sparsity-based deconvolution method was used to extract the distinct waveforms of the two terahertz reflections, as shown in Fig. 2(b). Moreover, typical THz-TDS systems suffer from amplitude fluctuations and phase drifts, which can impede reliable and precise measurements. However, the fluctuations in amplitude and phase of the first and second terahertz echoes are correlated since they arise from intrinsic system noise. These effects were mitigated by using a self-reference calibration method. Hence, following the amplitude variations extracted from the first terahertz echo, the second is adjusted accordingly. Therefore, combining the deconvolution and the self-reference calibration method, an accurate evaluation of the second terahertz echo peak value can be obtained. Detailed information about the terahertz sparse deconvolution and the self-calibration method can be found in the supplementary material.

To correlate the terahertz response with temperature, calibration experiments were carried out by plasmonic heating of the GNR dispersions at various power densities between 0.95 and 60.4 W/cm². The temperature was recorded by inserting a thermocouple probe close to the heating/sensing spot in the cuvette once the temperature reached the steady-state. The change of amplitude following the increase in temperature was observed by monitoring the terahertz echo reflected from the cuvette/sample interface. This is due to the heat-induced change in the refractive index of the water solution at terahertz frequencies. The temperature was then assigned to the corresponding measured terahertz amplitude, resulting in a linear relationship with a coefficient of determination $R^2$ of ~0.99, shown in Fig. 2(d). The slight difference in the calibration curves might be due to the different dimensions of the GNRs, which lead to small variations in the refractive indices. The slopes of the calibration curves were recorded for each dispersion to directly translate terahertz amplitudes into temperature values. Following this post-processing procedure, a temperature resolution of 1 °C was achieved and a well reproducible measurement can be guaranteed.

B. Quantification of the photothermal effect via THz-TDS

In order to calculate $\eta$ as well as MHR of the three GNR dispersions, transient temperature measurements were carried out for the heating and cooling cycles by using THz-TDS. During the heating cycle, a NIR illumination with a power intensity of 31.8 W/cm² was maintained for 12 min. Thereafter, the laser was switched off, and the temperature decay was recorded for 15 min to acquire the temperature transient of the cooling cycle. Each temperature transient was obtained by recording the peak amplitude of the second terahertz echo (after postprocessing) every 10 s and directly translating it into a temperature value, according to the calibration curves. Figure 3 shows the complete temperature transients of the three GNR dispersions. Their temperature increased under laser illumination and then decreased toward the ambient value after the laser source was switched off, following the trend predicted by Eq. (8).

![FIG. 3. Typical temperature transients measured by THz-TDS. For each GNR dispersion, a constant NIR illumination was maintained for 12 min to acquire the heating curve, and then the laser was switched off to obtain the cooling curve.](image)

After heating for 12 min, GNR10 and GNR25 reached a similar steady-state temperature of ~53 °C, while the temperature of GNR50 increased to ~45 °C. The fluctuations in the measurements of the temperature transients might be associated with thermal drifts in the system and surrounding environment. The impact of the fluctuations was mitigated by fitting the experimental data with our theoretical model.

To evaluate the photothermal conversion efficiency $\eta$ of the GNR dispersions, the rate of energy absorption $A$ and the rate of heat dissipation $B$ were extracted by fitting the experimental temperature transients with Eq. (8). The rate of heat dissipation $B$ between the GNRs and the external environment can be determined from the cooling cycle of the temperature transients. The theoretical model for the temperature transient of the heat dissipation can be found by setting $A = 0$ and $T_{\text{initial}} = T_{\text{max}}$ in Eq. (8), $T(t) = T_0 + (T_{\text{max}} - T_0)e^{-Bt}$, where $T_{\text{max}}$ is the maximum temperature achieved during photothermal heating. Based on this equation, a linear relationship is identified between $\ln[(T(t) - T_0)/(T_{\text{max}} - T_0)]$ and time $t$. The heat dissipation rate $B$ can be determined from the slope of this curve. It indicates a first-order decay as the heated system reaches equilibrium with the surrounding medium. By fitting the experimental data with this linear model, the parameter $B$ for each GNR dispersion was determined to be around $3.0 \times 10^{-3}$ s⁻¹. The fitting results for the cooling curves are shown in Figs. 4(a1)–4(c1). The heat dissipation rate does not depend on the GNR dimensions, as shown in Eq. (6). Once the heat dissipation rate $B$ is retrieved, the energy absorption rate $A$ can be obtained by fitting the heating cycles of the temperature transients...
FIG. 4. Extraction of the heat dissipation rate $B$ and the energy absorption rate $A$ by fitting the experimental data (symbols) with Eq. (8) for each GNR dispersion. The fitting results (solid lines) for the cooling cycle are shown in (a1), (b1), and (c1), while the fitting results (solid lines) for the heating cycle are accordingly shown in (a2), (b2), and (c2).

It is important to note that, since no magnetic stirrer was employed in the cuvette, only a fraction of the total mass was affected by the photothermal heating. This led to a nonuniform temperature distribution inside the sealed PE cuvette, which must be accounted for by determining the effectively heated mass of the sample during laser excitation. To this end, terahertz thermal imaging based on raster-scans with spatial resolution of 0.25 mm was performed along the entire front and back sides of the cuvette prior to heating, as well as after having reached the steady-state temperature level. In this case, the sample cuvette was mounted on a motorized

FIG. 5. Thermal images for GNR10 obtained via THz raster-scans, showing the temperature distribution following plasmonic heating. (a) Photograph of the front surface of the cuvette with the illumination spot marked in red. Thermal images of the temperature distribution $\Delta T$ (relative to the ambient value) of (b) the front window and (c) the back window of the cuvette.
X-Y translation stage in order to facilitate the terahertz raster-scans. The NIR beam was fixed to the center of the cuvette [as shown in Fig. 5(a)] during the imaging process (i.e., both the NIR beam and the cuvette were moving across the terahertz beam). The resulting terahertz thermal image maps the temperature distribution at the internal cuvette/GNR dispersion interface when the heating cycle reaches the steady-state. For the GNR10 dispersion, the terahertz thermal images acquired from both the front and back window of the cuvette are shown in Fig. 5, exhibiting the temperature variation ($\Delta T$) at the steady-state with respect to the initial ambient value. The image acquisition is essential to estimate the effective mass of the GNR dispersion. We underline that neither the temperature transients nor their spatial distributions lead to the determination of the photothermal conversion efficiency of the GNRs, but only their mutual correlation. The terahertz thermal images from the front and back window of the cuvette display a similar temperature distribution and clearly reveal that the GNR10 dispersion close to the cuvette bottom was not heated to the same temperature as that at the cuvette top due to heat convection. Therefore, the effective mass of the heated GNR dispersion in the cuvette can be calculated by the following equation:

$$m_{\text{eff}} = \frac{\iint T(x,y) \, dx \, dy}{S_c} m_{\text{sol}},$$

where $T(x,y)$ is the normalized temperature distribution of the front surface, $dx$ and $dy$ are the dimensions associated with one pixel of the terahertz image, $S_c$ is the area of the cuvette surface, and $m_{\text{sol}}$ is the entire mass of the GNR dispersion in the cuvette (3.0 g). By taking an average of the values achieved from the front and back windows, the effective mass of the GNR10 dispersion was determined to be 1.74 g. Moreover, the effective mass of the PE cuvette was taken into account as $(m_{\text{eff}}/m_{\text{sol}}) \times m_{\text{cuv}} = 0.9$ g, where $m_{\text{cuv}}$ accounts for the mass of the cuvette surrounding the GNR dispersion.

Therefore, by combining the temperature transients and the thermal images achieved via THz-TDS, the photothermal conversion efficiencies of the three GNR dispersions were calculated, as shown in Fig. 6(a) (red bars), without the need of stirring the sample. Using the known particle concentration (see Table S1 in the supplementary material) together with the retrieved energy absorption rate $A$, the MHR was also calculated based on Eq. (10) and illustrated in Fig. 6(a) (orange bars). It is worth noticing the high values of $\eta$ achieved with these GNRs, especially with the sample containing the particles with the smallest volume [see Fig. 6(a)]. In particular, the GNR10 sample achieves a $\eta$ of 90%, a value similar to other reports for comparable gold nanostructures. Furthermore, Fig. 6(a) clearly shows that $\eta$ and MHR follow an opposite trend with respect to the increasing average volume of the GNRs. Whereas $\eta$ is highest for...

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**FIG. 6.** (a) Experimentally achieved photothermal conversion efficiencies $\eta$ (red bars) and the MHR (orange bars) of the GNR dispersions with a particle diameter of 10 nm, 25 nm, and 50 nm, respectively. Additionally, we present the values (pink bars) of the photothermal conversion efficiencies $\eta$ estimated from the theoretical interaction cross sections calculated for the GNRs. (b) Schematic diagram illustrating the main properties underlying the data in panel (a): the increase in overall extinction per particle and increasing relevance of scattering as the nanoparticles increase in volume. (c) Theoretical extinction cross sections of the three GNRs, along with a representation for the relative weight of the scattering cross section over the total extinction. (d) Theoretical estimation of $\eta$, obtained with Eq. (12) by using the calculated cross sections and the absorption coefficient of water, also presented in this panel. Choosing wavelengths outside the absorption lines of water is key to achieve controlled localized heat delivery.
the GNRs with the smallest diameter, the MHR is maximum for the largest ones. These results follow the behavior that is expected for plasmonic resonators, supporting the reliability of our method and also illustrating the role of the electromagnetic response of the GNRs in the heating process, for which a schematic depiction of some relevant properties can be found in Fig. 6(b). First, the interaction cross sections of a plasmonic nanoparticle do increase with its polarizability, which in turn scales with the volume of the particle. Figure 6(c) shows the theoretical results for the extinction (sum of absorption $\sigma_{\text{abs}}$ and scattering $\sigma_{\text{scat}}$) cross sections corresponding to the GNRs used in the experiments. Importantly, it is the increase in their absorption cross sections that leads to a larger amount of energy absorbed in each particle, thus driving the positive trend for the MHR shown in Fig. 6(a). It is relevant to recall that the GNR samples have a comparable optical density, meaning that the GNR50 sample has a significantly lower particle number concentration than the GNR10.

At the same time, as the size of a plasmonic nanoparticle increases, the amount of energy scattered by the particle (i.e., events that do not deposit energy locally and, therefore, do not contribute to the heating process) relatively to its total extinction increases as well. Figure 6(c) also shows this ratio for the different sizes of GNRs considered. This is a general property of light-matter interaction and arises from the different dependence of absorption and scattering on the polarizability of the nanoparticles, which are linear and quadratic, respectively. Therefore, the dominance of scattering over absorption in the larger GNRs, depicted in Fig. 6(c), justifies the decreasing trend of $\eta$ as a function of the GNR size. To further underline this point, Fig. 6(a) also includes an estimation of the $\eta$ values (pink bars) obtained solely from the theoretical interaction cross sections calculated for the GNRs. As one can observe, the model presents the same trend as that of the experimental data. These values were computed using the following expression:

$$\eta = \frac{Q_{\text{solution}} - Q_{\text{solvent}}}{P_{\text{extinction}}} = e^{-\mu_{\text{water}} L} - e^{-\left(\sigma_{\text{abs,water}} + \sigma_{\text{scat,water}}\right) L} \cdot \frac{1}{1 - e^{-\sigma_{\text{water}} L}}.$$  \hspace{1cm} (12)

Here, $Q_{\text{solution}}$ and $Q_{\text{solvent}}$ stand for the heat input in the aqueous solution and water, respectively, $\mu_{\text{water}}$ is the linear attenuation coefficient of water, and $n_{\text{G}}$ is the GNR density. $P_{\text{extinction}}$ is the power extinguished by the GNRs and $L$ denotes the total sample thickness. Importantly, the heating effect arising from the absorption of light by water is negligible at the wavelength used in this experiment (786 nm), but it will significantly reduce the efficiency of any phototherm heating at longer wavelengths. To illustrate this point, Fig. 6(d) includes the full spectrum of photothermal conversion efficiency for the studied GNRs, again using computational results and Eq. (12), alongside the spectrum of water absorption. More details on the methodology followed to obtain all the theoretical results are presented in the Appendix.

V. CONCLUSION

We have introduced a novel method implemented in a typical THz-TDS system that can be used for a noncontact and noninvasive characterization of the photothermal effect associated with plasmonically heated nanoparticles. Photothermal conversion efficiencies $\eta$ as well as MHRs of three types of GNR dispersions have been quantified by combining the temperature transients in time and thermal images in space recorded at terahertz frequencies. In the light of recent developments of compact and affordable THz-TDS systems with fast imaging capabilities, this work may pave the way to simplify and improve the automation of the thermal characterization process of nanomaterials within confined aqueous based systems and offers an appealing alternative to more invasive conventional methods.

SUPPLEMENTARY MATERIAL

See the supplementary material for more information. In particular, this section contains a table listing the physical and chemical parameters of the investigated GNR dispersions as well as the terahertz sparse deconvolution and the self-calibration method. One figure is also included to prove the effectiveness of the proposed signal processing method.

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APPENDIX: THEORETICAL SIMULATIONS

The theoretical results presented in Fig. 6 were obtained from full electromagnetic simulations. The interaction cross sections of the GNRs were calculated using a commercial package, COMSOL Multiphysics, implementing numerical solvers in a finite-element method (FEM) approach. The noninteracting GNRs were modeled with the same geometries as the experimental samples, considered to be surrounded by a homogeneous medium of dielectric index $n = 1.33$, and under continuous plane wave illumination. The sizes of the GNRs were chosen so that they presented the same LSPR in water as the samples under investigation, while fixing the same nominal experimental diameter, resulting in an aspect ratio of 4.10, 3.65, and 2.90 for the batches of samples labeled as GNR10, GNR25, and GNR50, respectively. Given the anisotropy of these particles, the
cross sections reported in this paper were computed as the average over six combinations of linear polarization and incidence directions of light over the GNRs, reproducing the effect of a randomly oriented ensemble of nanoparticles illuminated by an unpolarized light source. The GNRs were described using the experimental permittivity of gold and broadened with respect to the bulk parameters using the Drude model, where the plasma frequency and damping rate, \( \omega_p \) and \( \Gamma \), of gold were set to 8.9 eV and 0.076 eV\(^{-1} \), respectively,

\[
\varepsilon_{\text{broad}} = \varepsilon_{\text{experimental}} - \varepsilon_{\text{Drude}} + \varepsilon_{\text{Drude, broad}} \\
= \frac{\omega_p^2}{\omega^2} \left( \frac{1}{\omega^2 + i2\Gamma} - \frac{1}{\omega^2 + i\omega} \right). \tag{A1}
\]

Finally, the theoretical \( \eta \) of the different GNR dispersions were calculated using Eq. (12) and the interaction cross sections computed as described above. The values are displayed in Fig. 6(a) (pink bars).

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