



Light–heat conversion dynamics in highly diversified water-dispersed hydrophobic nanocrystal assemblies

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We investigate, with a combination of ultrafast optical spectroscopy and semiclassical modeling, the photothermal properties of various water-soluble nanocrystal assemblies. Broadband pump–probe experiments with ~100-fs time resolution in the visible and near infrared reveal a complex scenario for their transient optical response that is dictated by their hybrid composition at the nanoscale, comprising metallic (Au) or semiconducting (Fe₃O₄) nanostructures and a matrix of organic ligands. We track the whole chain of energy flow that starts from light absorption by the individual nanocrystals and subsequent excitation of out-of-equilibrium carriers followed by the electron–phonon equilibration, occurring in a few picoseconds, and then by the heat release to the matrix on the 100-ps timescale. Two-dimensional finite-element method electromagnetic simulations of the composite nanostructure and multitemperature modeling of the energy flow dynamics enable us to identify the key mechanism presiding over the light–heat conversion in these kinds of nanomaterials. We demonstrate that hybrid (organic–inorganic) nanocrystal assemblies can operate as efficient nanoheaters by exploiting the high absorption from the individual nanocrystals, enabled by the dilution of the inorganic phase that is followed by a relatively fast heating of the embedding organic matrix, occurring on the 100-ps timescale.

supracrystals | photothermal properties | hot carriers | nanocrystal assemblies | pump–probe spectroscopy

The last decade has witnessed an explosive growth of interest in the photothermal properties of nanostructures, for both fundamental and applied aspects (e.g., ref. 1 and references therein). A striking application is photothermal therapy for cancer, in which light, following irradiation of nanocrystals (NCs), is converted to cytotoxic heat to selectively kill cancer cells and minimize the invasive injury to normal tissues (2–7). Another notable example of the high impact of nanoparticles' photothermal properties is represented by the demonstration of novel solar photodevices for water vapor generation (8, 9) and direct sunlight-driven desalination (10).

Most of the studies in the field deal with Au nanoparticles. The development of novel and possibly more effective photothermal agents requires the understanding of the energy flow upon optical excitation of the nanostructure. For plasmonic NCs, this is well known to be governed by a cascade of dynamic relaxation processes, namely electron–electron scattering, electron–phonon scattering (and subsequent dephasing of acoustic vibrations), and phonon–phonon scattering, the latter culminating in the heat transfer from each nanoparticle to its microenvironment (11). However, unexpected and novel reactions of the medium upon light irradiation and subsequent electron relaxation have been observed in more complex systems (12–14): The combination of multiple scattering processes induces formation of either steam or a liquid vapor phase within a reduced volume even when

the temperature of the bulk fluid volume remains far below its boiling point. Furthermore, hot-electron–induced photodissociation of H₂ was demonstrated by Au nanoparticles supported on SiO₂. These recent data clearly indicate that the heat release mechanisms in composite nanomaterials are far from being fully understood and several open questions remain. This is particularly true for NC assemblies, as the interaction between NCs and the heat transfer through molecular linkers can, in principle, strongly change the thermal properties of these nanostructures and, subsequently, the dynamics of the photothermal energy conversion (1).

NC assemblies have attracted increasing interest in the past few years (see, e.g., ref. 15 for an overview). Advances in colloidal synthesis have enabled the manufacturing of NCs with uniform size, shape, chemical composition, and crystallinity, which in turn allowed their self-assembly in 3D ordered structures. Such assemblies, with a well-defined lattice configuration [e.g., face-centered cubic (fcc), body-centered cubic (bcc), etc.], are similar to atoms in crystals and are thus referred to as supracrystals (16). Depending on the experimental conditions, amorphous 3D aggregates can also be produced (17). The growth mechanism of these assemblies involves several factors (18) leading

Significance

Metal and semiconductor nanoparticles have been widely exploited in research, because of their striking capability to concentrate light energy at the nanoscale and convert it to heat at ultrahigh speed. However, most nanoparticles are made of homogeneous materials, which limits the possibility to engineer their photothermal properties. Additional degrees of freedom are provided by nanoassemblies: periodically arranged nanocrystals of few nanometers in size embedded into an organic matrix. Here we display a specific mechanism presiding over the light–heat ultrafast conversion in a highly diversified family of nanoassemblies, which is intimately related to their hybrid composition at the nanoscale. The exceptional photothermal properties of nanocrystal assemblies open prospects in nanomedicine (photothermal therapy) and energy harvesting.

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electron microscopy (TEM) image of individual assemblies shown in Fig. 1 *B–D* indicates a local ordering of the NCs. This is confirmed by the TEM image obtained after deposition of a drop of the colloidal solution (Fig. 1*E*), which shows that the Au NCs are well ordered in a compact hexagonal network.

The linear optical response of Au clustered structures dispersed in aqueous solution was characterized by extinction measurements with a standard spectrophotometer. The measured absorbance (Fig. 1*F*) exhibits a pronounced peak around 600 nm, which, according to a previous study (26), is ascribable to a photonic (i.e., collective) mode of the assembly, since its spectral position scales linearly with supracrystal size.

To investigate the energy flow upon light irradiation, we performed pump–probe experiments with ultrashort laser pulses. A 100-fs pump pulse at 400-nm wavelength, generated by frequency doubling the output of an amplified Ti:sapphire laser system (27), is used to excite the sample. A broad-band laser pulse focused on the sample at a given time delay t with respect to the pump pulse is used to dynamically probe the transient optical response. The differential transmission ($\Delta T/T$) spectra are recorded as a function of t and the probe wavelength λ . The results are shown in Fig. 2 *A* and *B* for visible and near-infrared probing, respectively. On the initial timescale of 10 ps, the transient signal resembles the typical $\Delta T/T$ map recorded for plasmonic nanoparticles [spheres (28) or rods (29, 30), for example]. In particular, the map cross-sections at early time delays (black and red traces in Fig. 2*A*, *Bottom*) show the characteristic transient spectra of isolated NCs which are dominated by shift and broadening of the plasmonic resonances (30). Moreover, these spectra exhibit a decay constant of a few picoseconds (Fig. 2*A*) that is the timescale of electron–phonon scattering in noble metals (31). See also Fig. 3*A* for the dynamics at selected probe wavelengths for delay times up to 10 ps. This demonstrates that in the ultrafast optical response the Au assemblies keep the fingerprint of their building blocks (26). However, on the longer timescales, the $\Delta T/T$ of Au clustered structures exhibits very distinct features which, to the best of our knowledge, have not been reported in any metallic nanostructure: Instead of a monotonic decrease over time, we observe the buildup of a positive signal which is red shifted by about 100 nm (blue and magenta traces in Fig. 2*A* and *B*, *Bottom*) compared with the early spectra. The temporal dynamics at selected probe wavelengths, reported in Fig. 3*B*, detail the onset of this broadband transient signal within about 100–150 ps. To ascertain that the observed buildup is a phenomenon that cannot be ascribed to mechanical oscillations [which, in Au NCs, are well known to have a strong impact on the ultrafast optical response on this timescale (11)], we performed pump–probe measurements on the nanosecond timescale. The results, reported in Fig. 3*C*, confirm that after the buildup the signal remains constant on the nanosecond timescale. However, we see a clear-cut fingerprint of mechanical oscillations with an oscillation period $T_{osc} \sim 300$ ps. We assign that oscillation to a breathing mode of the whole assembly by assuming an average speed of sound v_s of the order of 1 km/s (i.e., $T_{osc} \simeq 2D/v_s$, with $D = 160$ nm), which makes sense considering the hybrid metal–organic composition (v_s in bulk gold being about 3.2 km/s). Finally, note that this transient signal was not observed in dry Co assemblies deposited on highly oriented pyrolytic graphite (HOPG) substrate (32).

To understand the origin of the observed optical features and, in particular, of the unexpected transient optical response on the 100-ps timescale, we developed a model to simulate the optical experiments. A 2D model of the supracrystal, based on the morphology detailed in Fig. 1*A*, is reported in Fig. 4*A*. Finite-element method (FEM) electromagnetic simulations retrieve the same wavelength position as in the experiment for the extinction

peak in the simulated absorbance (black curve in Fig. 1*G*). Note that, different from the effective index approximation of ref. 26, the present model fully mimics (even though in 2D) the nanostructuring of the assembly: A square lattice arrangement of Au NCs is embedded in the $C_{18}H_{37}SH$ matrix and surrounded by a thin (3-nm) layer of dipalmitoylphosphatidylcholine (DPPC) (Fig. 4*A*). For comparison, we also performed numerical simulations of a triangular arrangement of NCs with the same density (SI Appendix). The static optical response turned out to be similar to that retrieved from the square lattice configuration (compare solid curves with dashed-dotted curves in Fig. 1*G*). This result indicates that our assemblies behave as metaparticles, rather than finite arrays of NCs, as the collective effects are not dominated by Bragg scattering mechanisms, but rather by the onset of an effective medium, in agreement with the approximations made in ref. 26. Interestingly, despite the thickness of the assembly, the power absorbed per unit volume ρ at the 400-nm excitation wavelength (Fig. 4*B*) is more uniform compared with that in a Au nanosphere of the same diameter. This is due to the higher penetration depth of light in the supracrystal structure (about 60 nm, which is almost four times larger than in bulk Au at the same wavelength) in view of the dilution of the metallic phase. If and how the organic phase in the assembly contributes

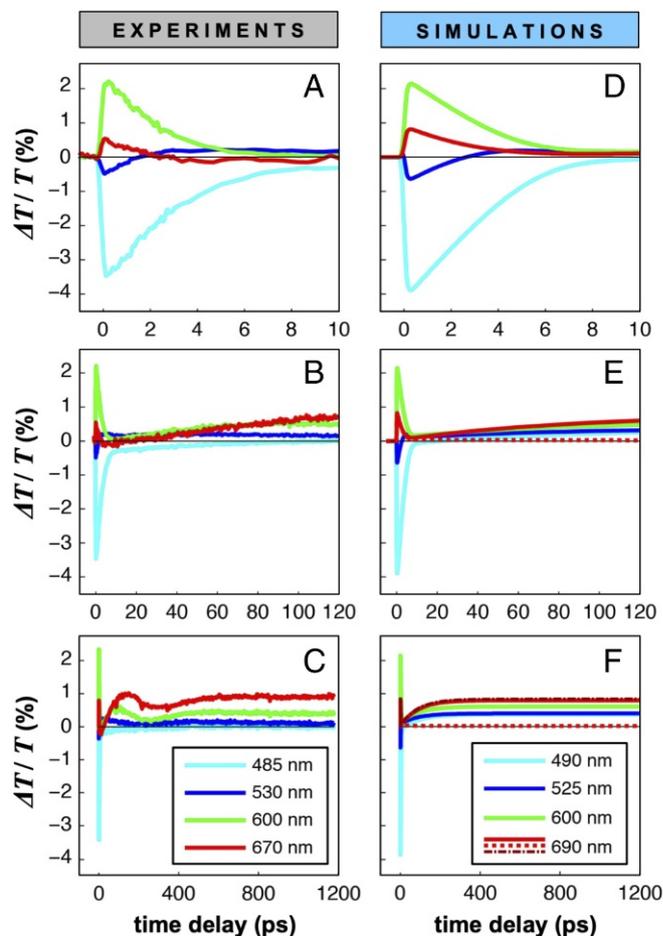


Fig. 3. Measured (*A–C*) and simulated (*D–F*) dynamics of the $\Delta T/T$ signal at selected probe wavelengths, on the three different timescales of energy flow in the Au clustered structures. The dotted curve in *E* and *F* is retrieved without taking into account the thermo-optical effect in the organic matrix, whereas the dashed-dotted curve in *F* is calculated from a triangular lattice model with the same density of NCs as in the square lattice in Fig. 4*A*.

its thermo-optical response turned out to be crucial to provide a consistent interpretation of the nonlinear response of the Au clustered structures. Neglect of this contribution results in a poor agreement with the experiments, both for the spectra (dotted magenta curve in Fig. 2 C and D) and for the dynamics (dotted curves in Fig. 3 E and F), as the model is unable to reproduce the rise of the signal observed on the 100-ps timescale. Note that its prominent contribution to the $\Delta T/T$ is a clear-cut indication of the high temperature increase, of about 15 K according to our simulations (Fig. 4E), attained after the absorption of a single pump pulse at a moderate fluence (2.75 mJ/cm^2). This is made possible by the specific collective regime of photo-temperature generation exploited in the assembly, in agreement with what is reported in a pioneering work by Govorov et al. (38), where it has been theoretically shown that for clusters the photo-temperature is expected to increase fast with the number of NCs. On the contrary, the lattice arrangement seems to play no role, since the simulated traces of the $\Delta T/T$ map retrieved by a triangular configuration (dashed-dotted curves in Figs. 2 C and D and 3F) are almost superposed to the corresponding traces computed from the square configuration (solid curves in Figs. 2 C and D and 3F).

According to our model, the delayed buildup of the $\Delta T/T$ signal on the few hundred picoseconds timescale is the signature of the final step in the light-heat conversion process that ultimately results in the heating of the matrix of organic ligands. As such, this dynamical feature in the transient optical response is expected to be an intrinsic property of any hybrid assembly of hydrophobic NCs, regardless of the peculiar nature (i.e., plasmonic or not) of their building blocks. To test this hypothesis we considered two other kinds of water-dispersed assemblies, namely ferrite supraparticles and eggs of Au/ferrite (25).

As shown in Fig. 5A, spherical assemblies of ferrite NCs with an average size in the range of 200 nm are produced. The small-angle X-ray diffraction pattern (Fig. 5A, *Inset*) confirms the ordering of ferrite NCs in fcc supracrystals. These structures exhibit a pronounced extinction peak at around 400 nm

(Fig. 5B) which is mostly ascribable to absorption from ferrite NCs. The differential transmission maps are reported in Fig. 5C, with map cross-sections at selected probe wavelengths shown in Fig. 5D. Note that after the exhaustion of the initial dynamics that comprise both positive and negative signals (depending on wavelength) within the first 10 ps, the longer timescale exhibits a $\Delta T/T$ that monotonically increases and reaches its maximum within a few hundred picoseconds. These are precisely the same dynamics observed in Au clustered structures (Fig. 3), the differences in the spectral profiles being related to the different kinds of resonances that dominate the linear extinction of the two kinds of assemblies.

A further evidence of the peculiarity of this mechanism is provided by Au/ferrite eggs. A TEM image of the sample (Fig. 5E) shows formation of binary core $(\text{Fe}_3\text{O}_4)\text{Au}_{13}$ supracrystals trapped into a ferrite colloidosome. The linear extinction spectrum (Fig. 5F) is characterized by a shallow peak at around 580 nm, ascribable to the plasmonic resonance of the Au NCs. Actually, the $\Delta T/T$ map (Fig. 5G) resembles the one reported for Au clustered structures, both on the short timescale and on the long one (Fig. 2A), indicating that the plasmonic resonance from the metallic phase dominates on the absorption from the semiconducting nanostructures. Also for this structure we observe that the heating of the assembly takes place on the few hundred picoseconds timescale (Fig. 5H).

Conclusions and Perspectives

In this paper we have investigated the photothermal properties of water-soluble hybrid nanoassemblies: Au clustered structures, ferrite supracrystals, and Au/ferrite eggs. An extensive experimental and theoretical investigation of the transient optical response of these assemblies was performed with the aim of tracking the energy flow in these kinds of nanomaterials following photoexcitation. Our results indicate that Au clustered structures exhibit very peculiar features, never observed in Au NCs or even larger (polycrystalline) gold nanoparticles or Co assemblies deposited on HOPG substrate (32). In particular we show that (i) due to the dilution of the metallic phase, the

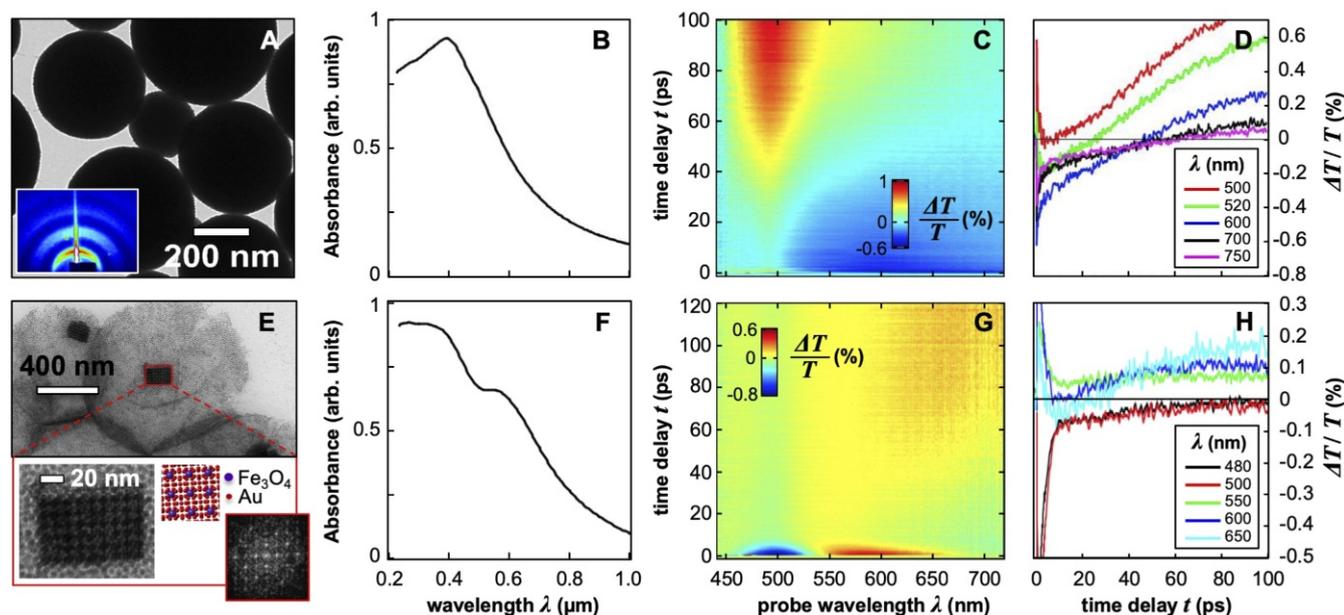


Fig. 5. (A) TEM image of ferrite supraparticles. *Inset* shows the X-ray diffraction spectrum. (B) Linear extinction spectrum of the sample. (C) Measured differential transmission maps $\Delta T/T$. (D) Map cross-sections at selected probe wavelengths (pump fluence of about 10 mJ/cm^2 at 400-nm wavelength). (E–H) Same as A–D but for Au/ferrite eggs. E, *Inset* details the structure of the core with (*Left*) the enlargement of the TEM image in E and (*Right*) the FFT pattern and a sketch of the binary core $(\text{Fe}_3\text{O}_4)\text{Au}_{13}$ supracrystal.

penetration depth of visible light is much greater than in homogeneous metallic nanoparticles of similar size, thus enabling a high average thermal load in the whole assembly; (ii) the organic matrix, even though not directly absorbing, acts as an internal reservoir for efficient accumulation of energy within few hundred picoseconds; (iii) for moderate excitation fluences we estimated a temperature increase in the assemblies that is fully compatible with hyperthermia (7); and (iv) the above features are due to the collective regime of photo-temperature generation enabled by the assembling, since even though our model was validated on Au clustered structures, a similar behavior was experimentally observed with both Fe_3O_4 NCs self-assembled in fcc spherical supracrystals (called supraparticles) and binary supracrystals $[(\text{Fe}_3\text{O}_4)\text{Au}]_{13}$ trapped in colloidosomes. These results provide a clear-cut indication that such hybrid nanostructures can be operated as very efficient nanoheaters, with enhanced biocompatibility due to their larger size, high stability in water, and all of the fingerprints belonging to the NCs used as building blocks.

Materials and Methods

The synthesis of clustered structures has been published recently (25, 26). In brief, Au NCs with $r \simeq 2.75$ nm radius coated with $\text{C}_{18}\text{H}_{37}\text{SH}$ and 5%

size distribution are well dispersed in toluene. To produce shaped Au assemblies, we controlled the supracrystal growth process by subjecting the colloidal solution to a bad solvent for the alkyl chains (39). For a nucleation and growth process time of $t_1 = 10$ h and $t_2 = 8$ min, respectively, we obtained spherical assemblies with an average diameter of 160 ± 50 nm. Kranenburg et al. (24) demonstrated that the best interdigitation process is obtained with long-tail surfactant molecules and large head group surface area. Here the best interdigitation is obtained by using C_{18} alkyl chains as a coating agent of Au NCs and DPPC characterized by two C_{16} chains (SI Appendix). The synthesis of Fe_3O_4 supraparticles was already reported (25), and Au/ferrite eggs are obtained by revisiting the synthesis of ferrite supraparticles. Here 6.5-nm Fe_3O_4 NCs coated with oleic acid and 3.5-nm Au NCs coated with dodecanthiol are dispersed in chloroform containing octadecene, whereas the remaining procedure is unchanged. At the end of the synthesis, the colloidal solution is dispersed in water. See SI Appendix for further details.

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