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Formation of Hollow Gold Nanocrystals by Nanosecond Laser Irradiation

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ABSTRACT

The irradiation of spherical gold nanoparticles (AuNPs) with nanosecond laser pulses induces shape transformations yielding nanocrystals with an inner cavity. The concentration of the stabilizing surfactant, the use of moderate pulse fluences, and the size of the irradiated AuNPs determine the efficiency of the process and the nature of the void. Hollow nanocrystals are obtained when molecules from the surrounding medium (e.g., water and organic matter derived from the surfactant) are trapped during laser pulse irradiation. These experimental observations suggest the existence of a subtle balance between the heating and cooling processes experienced by the nanocrystals, which induce their expansion and subsequent recrystallization keeping exogenous matter inside. The described approach provides valuable insight into the mechanism of interaction of pulsed nanosecond laser with AuNPs, along with interesting prospects for the development of hollow plasmonic nanoparticles with potential applications related to gas and liquid storage at the nanoscale.



KEYWORDS: Hollow Gold Nanoparticle • Nanosecond Laser • Surfactant • Formation Mechanism • Nanocavity • Nanocontainer

The development of coherent light pulses during the second half of the 20th century represented a breakthrough in modern science, enabling the study of various phenomena occurring in ultrashort time scales.1–3 For instance, ultrashort laser pulses provided access to the dynamics of bond formation and breaking during chemical reactions⁴ and, together with continuous-wave lasers, they have contributed to the development of novel spectroscopies for the exploration of light–matter interaction phenomena.5,6 With the rise of nanotechnology, pulsed lasers have found application in the synthesis and physicochemical characterization of various nanomaterials, such as metallic nanoparticles, quantum dots, metal oxides, or graphene.7–10 Among them, plasmonic nanoparticles represent certainly one of the most interesting classes of materials, where the use of pulsed lasers has played a pivotal role in nanocrystal reshaping, fragmentation and assembly.11

Gold nanoparticles (AuNPs) have great potential for application in photocatalysis, energy harvesting, photothermal therapy, biosensing, optoelectronics, etc.₁₂₋₁₅ Beyond high chemical stability and low toxicity, their allure stems from the strong interaction with light via the formation of Localized Surface Plasmon Resonances (LSPRs) at the interface between the nanocrystals and their surrounding medium.₁₆ In analogy to investigations on femtochemistry, pulsed lasers have been crucial to disclose the fast electron dynamics responsible for LSPR excitation and relaxation.₁₁ Interestingly, due to the extremely high power intensity of lasers (107–1012 W/cm2), deformation and/or disintegration of the nanocrystals can be readily induced.₁₇₋₂₉ In addition, the pulse duration governs and determines the evolution of the irradiated AuNP shape. For instance, fs pulses deposit energy extremely fast, resulting in a quasi-adiabatic process of laser absorption by the LSPR and a subsequent equilibration with the metal lattice that occurs in a few ps and is controlled by electron–phonon coupling._{17,18,23,25,26,30} Hence, the relaxation processes mainly occur once the laser pulse has terminated. Under such conditions, the temperature may easily exceed the melting point of bulk

gold, triggering nanocrystal reshaping. In the case of ns laser pulses, the amount of energy absorbed by the AuNP is even higher due to the longer pulse duration; however, due to the lower energy deposition rate, the nanocrystal remains excited for a longer period (defined by the pulse duration), and fragmentation (or mass loss) may occur.19,21,25,31,32 In summary, for similar peak lattice temperatures, fs pulses mainly produce reshaping of the irradiated nanocrystals, whereas irradiation with ns pulses leads to fragmentation and size reduction of the nanocrystals.

We report the formation of hollow gold nanostructures produced upon irradiation of spherical gold nanoparticles (AuNPs) with ns laser pulses. Colloidal wet chemistry combined with redox reactions, which relies on complex multistep processes involving Galvanic replacement, has been the most successful approach to produce such nanostructures.³³⁻³⁷ Hence, the protocol described here provides access to the development of simple and direct manufacturing methods for hollow AuNP preparation, and may help fill a knowledge gap regarding the interaction of plasmonic nanoparticles with ultrashort laser pulses. We found that moderate ns laser fluences, combined with suitable colloidal stabilizing agents for AuNPs, induce the formation of nanocrystals with an inner cavity. The experimental observations are further supported by molecular dynamics (MD) simulations, which predict the incorporation of matter in the cavities. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) tomography, performed during in-situ heating experiments, and electron energy loss spectroscopy (EELS) were employed to validate the computational results.

The effect of laser irradiation conditions (e.g., pulse duration, pulse frequency, fluence, etc.) on AuNPs was intensively investigated in the first decade of the 21_{st} century, but the importance of the stabilizing agent to control the cooling dynamics has only recently been recognized.^{24,26,38} Among the wide variety of capping ligands, hexadecytrimethyl ammonium halides (CTAX, X = Cl and Br) are probably the most interesting ones. For instance, the

homogeneity of gold nanorods reshaped using the energy deposited on their LSPR by fs laser pulses strongly depends on the surfactant concentration.²⁴ Surfactant micelles have been proposed to act as heat insulators, and their ability to tune the cooling rate of the AuNPs has been related to variations in the number of molecules adsorbed on their surface, which is determined by their concentration in solution. Furthermore, CTAX molecules also play an important role in the synthesis of anisotropic nanocrystals due to their ability to stabilize certain crystallographic facets and control the nanocrystal morphology.^{39–42} Therefore, we expected that surfactant aggregates could also play a significant role in the formation and stabilization of characteristic structures during the fragmentation of gold nanocrystals under ns pulsed laser irradiation.

The first evidence supporting our hypothesis was obtained when 20 nm gold nanospheres dispersed in 25 mM aqueous CTAC solution (i.e., the surfactant used for their synthesis)⁴³ were irradiated with 8 ns laser pulses at a wavelength of 532 nm and repetition rate of 10 Hz (Figures 1 and S1, see Supplementary Material for details). After 3 min at a fluence of 0.2 J/cm2, the extinction band of the starting 20 nm AuNP colloid broadened, suggesting fragmentation and size reduction of the nanocrystals (Figure 1A). Analysis of the AuNP morphology by electron microscopy confirmed the reduction of the size from 21 ± 1 to 16 ± 2 nm, together with the broadening of the particle size distribution (Figures 1B,C and S1). Moreover, the presence of defects (grain and twin boundaries) was observed in the corresponding annular dark-field (ADF)-STEM and high-resolution HAADF-STEM images (Figures 1D–G and S2). Statistical analysis of these images revealed an increase of 58% in the number of defects after laser irradiation, as described in the Supplementary Material. The most interesting finding was the observation that 17% of the AuNPs presented a low-density region, suggesting the presence of a cavity (red arrows in Figure 1C). However, since STEM images correspond to 2D projections of 3D objects, HAADF-STEM tomography was used to confirm the formation of cavities

inside the nanocrystals (Figure 1H).44-46 Quantification of the 3D morphology of 14 particles with cavities revealed an average size of 14 ± 4 nm, where the average cavity size was found to be 4 ± 2 nm; the average distance between the surface of the AuNP and the closest edge of the cavity was 3 ± 1 nm.



Figure 1. Irradiation of 20 nm AuNPs for 3 min with 8 ns laser pulses at a wavelength of 532 nm, a fluence of 0.2 J/cm2, and a repetition rate of 10 Hz. (A) Normalized optical density spectra of AuNPs before (black) and after (red) irradiation. (B and C) Low-magnification ADF-STEM images of AuNPs before and after irradiation, respectively. The red arrows indicate examples of likely AuNPs containing a cavity. (D–G) High-resolution HAADF-STEM images displaying the atomic structure of particles with a grain boundary (D) or twin planes and cavities (E–G). The blue arrows point to twin planes. (H) Volume rendering of the reconstructed 3D structure revealing the presence of a cavity inside a AuNP. Scale bars are 50 nm (B and C), 4 nm (D), 3 nm (E), and 4 nm (F–G).

Next, we investigated the role of laser fluence on the origin of such hollow nanostructures. The morphology and dimensions of 20 nm AuNPs remained almost unaltered under irradiation with a reduced fluence of 0.1 J/cm₂, as revealed by TEM analysis (Figures 2A and S3A). In contrast, when the pulse fluence was increased to 0.3 J/cm₂, more fragmented species were obtained, along with a notable size reduction (13.5 \pm 2 nm; Figures 2B and S3B). In both cases, the formation of nanostructures with cavities was not observed, suggesting that the range of pulse fluences that induce the formation of hollow AuNPs is rather narrow.47



Figure 2. TEM analysis, showing the effect of pulse fluence, surfactant concentration, and particle size on the formation of AuNPs with cavities. (A,B) AuNPs obtained after exposure of 20 nm AuNPs in 25 mM CTAC to 0.1 J/cm₂(A) and 0.3 J/cm₂(B) laser pulses. (C,D) AuNPs resulting from irradiation of 20 nm AuNPs with 0.2 J/cm₂ pulses in the presence of 1 mM (C) and 100 mM (D) CTAC. (E,F) Effect of irradiation with 0.2 J/cm₂ pulses on 10 nm (E) and 40 nm (F) AuNPs suspended in a 25 mM CTAC solution. Red arrows point to particles with cavities, which are magnified in the inset. (G–J) Low and high magnification images of nanostructures produced upon irradiation of 40 nm AuNPs

in the presence of 1 mM CTAC. Black arrows below the images indicate the direction of magnitude increment. Scale bars: 100 nm (A–G) and 20 nm (F inset, H–J).

In addition to pulse fluence effects, the concentration of surfactant has been shown to influence the transfer of absorbed energy to the surroundings.²⁴ We observed here that the surfactant concentration had a strong effect on the fragmentation process. When the CTAC concentration was reduced to its corresponding critical micelle concentration (1.0 mM), two well-defined size populations of 6 ± 2 nm and 18 ± 3 nm were obtained upon irradiation of 20 nm AuNPs with 0.2 J/cm² pulses (Figures 2C and S4), but hollow nanostructures were not produced. However, considering the nature of the process, which may involve melting of the AuNPs, we found particularly relevant the irregular shape displayed by a fraction of the products (Figure S4). Upon increasing the CTAC concentration to 25 and 100 mM (Figures 1B and 2D), this effect was suppressed and cavities were formed again.

Nevertheless, the greatest impact on the nanocrystal morphology and cavity formation was found when varying the size of the irradiated AuNPs. Whereas 10 nm AuNPs (10 ± 1 nm) remained largely unaffected by the laser pulses (0.2 J/cm_2), 40 nm AuNPs evolved into a large number of fragmented nanostructures, some of them containing large cavities of up to 20 nm (Figures 2E,F, S5 and S6). In particular, irradiation of 40 nm AuNPs at low surfactant concentrations (i.e., the optimal conditions to induce fragmentation) favors the formation of products having irregular shapes and large cavities (Figure 2G-J). As a result of the laser excitation, the plasmonic band of the 40 nm AuNPs colloid broadened and a significant increase of the absorption in the NIR range was observed (i.e., larger than that of the irradiated 20 nm AuNPs, Figure S7). The effect of the particle size is likely related to two effects. First, bigger particles remain hot for longer periods of time because the heat release rate depends on the surface-to-volume ratio, which is proportional to 1/R.48 Second, the mechanism behind cavity formation may involve stretching of the AuNP and/or material loss. Hence, larger AuNPs are less affected by the leakage of atoms and better suited to reassemble and also to support larger cavities, as we see in the experiments.

The most intriguing question that arises is the mechanism behind the formation of a cavity inside the particles. It has been predicted by numerical calculations that, under irradiation with fs laser pulses, a AuNP expands and an inner cavity is created; if the fluence is high enough, the nanocrystal is stretched until some gaps are formed in the wall, after which the AuNP may eventually fragment.29 Additionally, it has been recently shown that, during irradiation with ps laser pulses, heterogeneous melting occurs at the surface, followed by eccentric density fluctuations deep inside the nanocrystal, which are directionally correlated to the polarization of the incident laser.49 We hypothesize that, during expansion, some matter can enter inside the particle through the gaps in the wall, and then remain trapped when it is cooled down. Examples of this matter can be any phase of the solvent – due to the high (and unknown) temperatures and pressures involved, it is hard to say whether the trapped water molecules are liquid, steam or a supercritical fluid – and/or surfactant molecules (or their fragments). In this case, this mechanism may be specific to ns laser pulses because with fs pulses the AuNP cools down too fast (in the few-hundred-ps time scale), hampering the uptake of matter within the nanocrystal. The presence of matter trapped in the cavity is indicative of this formation mechanism; for this reason, we investigated whether the cavities are empty or filled with matter. In the former case, heating of the AuNPs should favor the diffusion of gold atoms to fill the cavity,50 whereas the presence of matter should help stabilizing the cavity.

We carried out molecular dynamics simulations to disclose the nature of the cavity and its content (see Supplementary Material for details). First, we studied the dynamics of 20 nm hollow spheres at different temperatures between 300 and 1500 K (Figure 3A). At temperatures of 1200 K and below, no changes were noticed in either the cavity size or its position during the simulation time (around 1 ns). However, at temperatures of 1300 K and above (the melting

point of bulk Au is 1337 K), the cavity size was found to reduce until the nanocrystal collapsed into a solid sphere. Concerning the content of the cavity, we cannot know its precise composition, but we presume that it may contain organic material from the surfactant, water molecules from the medium, or a gas derived therefrom. However, from the point of view of the mechanical behavior of the structure, its state of matter aggregation is more important than its precise composition. Hence, we performed MD simulations for cavities filled with a liquid (water, Figure S8) and a gas (argon, Figure S9). Water is the most likely liquid candidate to exist in the cavity, whereas argon was chosen for the sake of simplicity, considering that noble gases are easier to represent in MD simulations with a simple Lennard-Jones potential.

The cavity was filled with either 5017 molecules of water (i.e., 1 g/cm₃) at a pressure of ca. 105 Pa (i.e., 1 atm) or 200 argon atoms, which translated into a pressure of ca. 5×106 Pa. Such an overpressure in the case of argon was used because, for the size of the cavity, a pressure of 105 Pa was reached with just 4 Ar atoms, indicating that if the filler is a gas it should be at high pressure. The Ar-filled cavity (Figure 3B) showed no changes at temperatures of 1200 K and below, whereas at 1300 K and above it showed no displacement but it did shrink until a pressure of ~ 108 Pa was reached, which rules out the hypothesis of having a compressible gas filling the cavity. On the other hand, the water-filled cavity (Figure 3C) moved towards the outer surface without size reduction and, more importantly, the displacement could already be appreciated at 1200 K (i.e., below the melting point of gold). It should be noted that water travels collectively inside the AuNP, and diffusion of individual molecules was not observed. This collective displacement generates a protrusion in the nanocrystal at times prior to the release. Once the crack occurs, a massive release of water molecules is produced in all directions, followed by collapse of the nanocrystal surface. The AuNP thus heals the gap by closing on itself and producing a flat region with a small pore. The displacement and release of water from the nanocrystal is enhanced by a temperature increase (i.e., the outwards movement is faster at higher temperatures, Figure 3D). A similar behavior was observed for a cavity filled with argon atoms at a pressure of 108 Pa (i.e., containing around 3000 atoms, see Supplementary Material for details). In all cases, the observed migration can be explained by the eccentric location of the cavity, which translates into asymmetric resistance to a sudden expansion of the inner sphere. This effect creates a net force in the direction of the thinner gold wall that displaces the cavity in the same direction.



Figure 3. Summary of MD results. Snapshots of (A) hollow, (B) Ar-filled, and (C) waterfilled gold spheres, as a function of temperature. (D) Snapshots of a water-filled gold sphere heated at 2000 K, as a function of time. The OVITO visualization software was used to generate the snapshots.⁵¹

Experimental proof for the presence of matter inside the cavities was obtained in two ways: directly by spectroscopic means and indirectly by heating hollow particles and imaging the evolution of the cavity (see Supplementary Material for details). Experimental observation of the heating effect on single hollow AuNPs can only be achieved using advanced electron microscopy techniques. The use of advanced TEM holders have enabled the investigation of nanomaterials under controlled environmental conditions, such as elevated temperatures, the presence of gases, liquids and biasing.52-54 Recently, we demonstrated the importance to study heat-induced morphological changes of complex metal nanoparticles by electron tomography.55-57 In the present case, this developed technique allowed us to monitor the evolution of the cavities upon heating in 3D. All experimental details can be found in the Supplementary Material. We observed that the cavity migrated toward the closest outer AuNP surface at temperatures above 1073 K (Figures 4A–E), generating a flat surface region, in good agreement with the MD results (Figure 3C). Meanwhile, statistical observations based on 2D HAADF-STEM images over 56 particles with cavities during the same heating experiment revealed that the cavity disappeared at temperatures beyond the same temperature threshold for 54% of such particles.

Next to the heating experiments, the presence of matter inside the cavity was directly confirmed through the detection of organic species by EELS measurements. Figures 4F–I show the resulting maps for the oxygen, nitrogen, and carbon distributions. Oxygen was mainly present at the surface of the nanocrystal, most likely due to partial oxidation of the surface ligands (Figure 4G). Nitrogen was uniformly distributed over the entire scanned region (Figure 4H), which is not surprising considering that the AuNP was lying on a silicon nitride support. The darker region in the upper right corner of Figure 4H can be attributed to beam damage of the only 5 nm thin support. The signals of both elements, oxygen and nitrogen, did not show any significant enhancement in the region of the cavity. A local increase of the carbon signal,

however, was clearly visible inside the cavity (Figure 4I), indicating the presence of organic compounds. Carbon could also be observed on the surface of the AuNP, due to the presence of CTAC. An especially high concentration of carbon was detected between particles, due to the accumulation of ligand molecules.

HAADF-STEM and EELS results during in-situ heating thus confirmed the presence of matter inside hollow AuNPs, as an essential element to generate a stable cavity inside the AuNP and avoid its collapse. The displacement of the cavity toward the AuNP surface at high temperature can be explained by isotropic expansion of matter inside the void, which experiences anisotropic resistance from the surrounding gold, as predicted by MD simulations. Since most cavities were found to be somewhat eccentric (i.e., nonhomogeneous wall thickness), the distribution of Au atoms around them is not the same in all directions. Therefore, under expansion of the matter in the cavity, they contribute with a nonzero force acting in the direction of the thinner wall and facilitating the migration of the cavity.



Figure 4. (A–E) Volume rendering of the 3D morphology of a AuNP with a cavity during in-situ heating at the indicated temperature, for 5 min. (F) Scanned region for EELS measurements. (G–I) Mapping of oxygen, nitrogen, and carbon in the scanned region, respectively.

We therefore hypothesize that, transformation into hollow AuNPs by ns pulsed irradiation can be mediated by melting of the gold nanocrystal. Subsequent expansion and stretching of the resulting liquid droplets would result in formation of gaps and, at high enough energies, in an explosion, thereby releasing some fragments (Figure 5). Under rather specific conditions, such as those investigated in this study, the explosion can be counteracted and a small amount of water (probably as a supercritical fluid, due to the high temperatures and pressures involved) and organic matter (derived from surfactant molecules) would enter the AuNPs through the gaps created during expansion, and remain trapped during the cooling process (recrystallization). In this way, in addition to the small fragmented AuNPs typically observed in ns laser pulse experiments, some hollow AuNPs would also be produced (Figure 5).



Figure 5. Proposed mechanism for the fragmentation and formation of hollow AuNPs by ns laser pulses. Excitation with ns pulses may lead to melting of the AuNP. The expansion and stretching of liquid droplets produce gaps and induce the release of fragments by explosion. During the cooling process under specific conditions, the explosion can be counteracted by the penetration of some water molecules and organic matter (derived from surfactant molecules) in the AuNP, thereby stabilizing the cavity.

In summary, we have demonstrated that the effect of ns laser pulses on AuNPs can be controlled by a rational interplay between pulse fluence and surfactant concentration. Indeed, the formation of hollow nanostructures has been observed only under certain specific conditions. We additionally found that the presence of matter trapped inside the cavity is crucial to stabilize the hollow nanostructure, which was confirmed by a combination of MD simulations and advanced electron microscopy. MD simulations of the heating process carried out on water- or gas-filled nanospheres revealed the migration of the cavity toward the outer surface. On the other hand, heating of nanostructures containing empty cavities (or filled with a gas at low pressure) would lead to the total (or partial, until the gas reaches a high enough pressure) collapse of the whole structure. Notably, in-situ heating experiments during characterization of the hollow AuNPs by HAADF-STEM tomography revealed a similar behavior to that predicted by MD for water-filled AuNPs. Isotropic expansion of the embedded atoms resulted in an anisotropic distribution of the stress, resulting in the displacement of the inner cavity toward the particle surface. Additional support to this hypothesis was obtained by EELS analysis, which revealed the presence of carbon inside the cavities.

This work offers valuable insight to elucidate the interaction dynamics of plasmonic AuNPs with ns laser pulses and the mechanism behind their fragmentation at high fluences. The possibility of entrapping matter from the surrounding medium during thermal expansion of AuNPs may be the first step toward the development of novel methods for the preparation of hollow nanostructures in high yield. The trapped matter can be subsequently released either by means of conventional heating or by irradiation with ultrashort laser pulses, with potential applications, for example, in controlled gas and liquid storage and delivery. Moreover, the high temperatures attained during the formation of hollow AuNPs upon excitation with ns pulse lasers may allow new advances in catalysis, whereby unconventional reaction conditions may be achieved by local heating within the nanocavities.

ASSOCIATED CONTENT

Synthetic details and characterization techniques, ns laser irradiation experiments, MD simulations description and representative movies, HAADF-STEM tomography and EELS experiments can be found in the Supporting Information. "This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>."

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