The irradiation of gold nanorod colloids with a femtosecond laser can be tuned to induce controlled nanorod reshaping, yielding colloids with exceptionally narrow localized surface plasmon resonance bands. The process relies on a regime characterized by a gentle multishot reduction of the aspect ratio, whereas the rod shape and volume are barely affected. Successful reshaping can only occur within a narrow window of the heat dissipation rate: Low cooling rates lead to drastic morphological changes, and fast cooling has nearly no effect. Hence, a delicate balance must be achieved between irradiation fluence and surface density of the surfactant on the nanorods. This perfection process is appealing because it provides a simple, fast, reproducible, and scalable route toward gold nanorods with an optical response of exceptional quality, near the theoretical limit.

**PLASMONIC MATERIALS**

**Femtosecond laser reshaping yields gold nanorods with ultranarrow surface plasmon resonances**

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The irradiation of gold nanorod colloids with a femtosecond laser can be tuned to induce controlled nanorod reshaping, yielding colloids with exceptionally narrow localized surface plasmon resonance bands. The process relies on a regime characterized by a gentle multishot reduction of the aspect ratio, whereas the rod shape and volume are barely affected. Successful reshaping can only occur within a narrow window of the heat dissipation rate: Low cooling rates lead to drastic morphological changes, and fast cooling has nearly no effect. Hence, a delicate balance must be achieved between irradiation fluence and surface density of the surfactant on the nanorods. This perfection process is appealing because it provides a simple, fast, reproducible, and scalable route toward gold nanorods with an optical response of exceptional quality, near the theoretical limit.
single particle with the average dimensions [FWHM = 30 nm (0.07 eV)] (Fig. 1A and fig. S5). Complete suppression of non-reshaped particles was achieved by irradiation of nanorods with a longitudinal LSPR band centered at 770 nm (fig. S6).

Maintaining the CTAB concentration around the cmc was crucial, as reflected in the optical changes of colloids irradiated above the cmc (Fig. 1D and fig. S7). At high CTAB concentrations (>5.0 mM), several LSPR bands appeared, indicative of nonhomogeneous reshaping of the nanorods. MD simulations were carried out to visualize CTAB adsorption on the Au(100) surface, typically exposed at nanorod lateral facets (29). We performed quantum calculations at the level of second-order Møller-Plesset perturbation theory to improve the current state-of-the-art CTA+ force field (fig. S8) (30). Using this new model, we assessed the stability of preassembled CTAB bilayers from isothermal-isobaric MD simulations (28). Contrary to previous assumptions (31), our simulations indicate that CTAB does not absorb as a uniform bilayer (fig. S9 and movie S1). The packing required to achieve enough molecular cohesion is not compensated by the entropy loss necessary to stretch the hydrocarbon tails within the layer. Hence, the system evolves spontaneously into a relatively compact heterogeneous distribution of adsorbed micelles (30).

Therefore, we studied the adsorption of fully grown micelles from solution on the surface of gold at different surfactant concentrations by tuning the size of the micelles (Fig. 1E and fig. S10) (30, 31). At the cmc, with an aggregation number of 60 (32), we observed partial coverage of the substrate by a small micelle, in which a large number of water molecules were in close contact with the gold surface (31). Above the cmc, the surfactant surface density increased through the formation of larger micelles, which considerably reduced the proximity between water molecules and the nanorod. We conclude from this analysis that the degree of surfactant coverage is likely one of the reasons behind the unsuccessful reported reshaping attempts in which nanorods were irradiated in as-synthesized conditions (fig. S7) (24, 27, 33).

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**Fig. 1. Preparation of gold nanorod colloids with ultranarrow LSPRs by femtosecond laser–controlled reshaping.** (A) Experimental (symbols) and fitted (lines) optical density spectra of colloids (stabilized at the cmc of CTAB), before (red) and after (blue) irradiation with 800-nm 50-fs laser pulses (represented by the red vertical band) and a fluence of 3.2 J/m² for 1 hour. The normalized spectrum (optical density of 0.15 at 400 nm) of the purified irradiated colloid (green) nearly matches that calculated for a single particle (black). The inset shows the aspect ratio probability densities derived from the optical fits. (B and C) Representative TEM images of reshaped nanorods at different magnifications. (D) Optical density spectra of non-irradiated colloids (red) and irradiated colloids stabilized at CTAB concentrations of 1.0 mM (blue) and 5.0 mM (cyan). (E) Snapshots from MD simulations of CTA+ (blue sticks) at and above the cmc on an Au(100) surface (red spheres). Bromide ions and water molecules are represented by green spheres and red sticks, respectively.

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**Fig. 2. Versatility and robustness of femtosecond laser–controlled preparation of gold nanorod colloids with ultranarrow LSPRs.** (A) Experimental (symbols) and fitted (lines) optical density spectra of colloidal gold nanorods before (blue) and after (purple) irradiation with 750-nm 50-fs laser pulses (3.2 J/m², 1 hour), compared with the spectra of a typical colloid synthesized by the seeded growth method (orange). The inset shows the aspect ratio probability densities derived from optical fits. (B and C) Representative TEM images of nanorods with different aspect ratios (3.9 ± 0.4 and 3.4 ± 0.5) and volumes [(4.0 ± 1.0) × 10³ and (13.0 ± 2.5) × 10³ nm³, respectively]. (D) Representative TEM image of reshaped nanorods obtained from irradiation of a 7:2 mixture of those shown in (B) and (C). (E) Experimental (symbols) and fitted (lines) optical density spectra of the colloidal mixture before (violet) and after two-step irradiation with 800-nm 50-fs laser pulses: 1 hour at 3.2 J/m² (brown) and 1 hour at 3.8 J/m² (green). The inset shows the probability densities of aspect ratios derived from optical fits.
Fig. 3. Monte Carlo simulation of the evolution of a gold nanorod colloid under femtosecond laser irradiation. (A) Schematic representation of the irradiation of a randomly oriented nanorod with respect to the laser wave vector \( \mathbf{k} \). \( E \), electric field. Yellow dashed and solid ovals, position of the nanorod before and after rotation around the Euler angles, respectively. Black dashed ellipse, region of the \( xy \) plane where the rod can be placed by rotation around the \( z \) axis (Euler angle \( \alpha \)). (B and C) Experimental (symbols) and fitted (lines) optical density spectra of colloidal nanorods (stabilized at the cmc of CTAB) for different irradiation times and fluences of 3.2 J/m\(^2\) (B) and 5.1 J/m\(^2\) (C). Irradiation times (represented by different colors) are 0, 5, 10, 15, 25, 40, and 60 min for the fluence of 3.2 J/m\(^2\) and 0, 15, 30, 60, 120, 240, and 600 s for the fluence of 5.1 J/m\(^2\).

We confirmed the versatility of the reshaping process by preparing monodisperse nanorods at different LSPR wavelengths (Fig. 2A and fig. S11). For example, the LSPR band of the colloid resulting from the previous irradiation could be further blueshifted by \( \approx 30 \) nm upon irradiation with a femtosecond laser tuned at 750 nm. Most importantly, the ultranarrow aspect ratio distribution in the colloid (3%) was not affected by the second irradiation. We conclude that this process can be applied to colloids with longitudinal LSPR bands located in any region of the Vis-NIR spectrum, with the only limitation being the availability of femtosecond lasers with an appropriate wavelength.

Efficient reshaping of colloidal precursors with an initially high polydispersity in the aspect ratio (>20%)—obtained by mixing two batches of nanorods with different aspect ratios (3.9 ± 0.4 and 3.4 ± 0.5) and volumes [(4.0 ± 1.0) \times 10^3 and (13.0 ± 2.5) \times 10^3 nm\(^3\), respectively] at a 7:2 ratio (Fig. 2, B and C, and fig. S11)—provides further evidence of the robustness of the method. The mixed colloid displayed a broad band because of the different longitudinal resonances of the individual components (Fig. 2E). Upon irradiation at 800 nm in two steps (1 hour at 3.2 J/m\(^2\) and 1 hour at 3.8 J/m\(^2\)), the final colloid featured an ultranarrow LSPR band centered at 710 nm [the FWHM being reduced from 208 to 43 nm (from 0.36 to 0.11 eV)] and an aspect ratio polydispersity of 3%, whereas the average difference in size between the nanorod populations was maintained (Fig. 2D). The second irradiation step resulted in a substantial reduction in the number of non-reshaped nanorods with LSPRs above 900 nm (aspect ratio > 4.5). Excellent dispersities in the aspect ratio (4%) were also obtained by irradiating nanorods with considerably higher volumes [(9.0 ± 2.0) \times 10^3 nm\(^3\)] (fig. S12). We thus confirmed that femtosecond laser–induced reshaping can be used to narrow the aspect ratio of gold nanorods with arbitrary aspect ratios and volumes. It was somewhat unexpected that larger nanorods could be modified with the same fluence as the smaller ones, because the former scatter more light (20). This implies that the losses are compensated by some mechanism, allowing efficient reshaping with a lower energy per atom.

Under the selected experimental conditions (constant laser fluence and LSPR matching the laser wavelength), the energy deposited on one nanorod by a laser pulse is mainly determined by two factors: (i) the absorption cross section \( \sigma_{abs} \) at the laser wavelength, which ultimately depends on the nanorod aspect ratio, and (ii) the orientation of the nanorod with respect to the laser polarization (Fig. 3A). Thus, it proved difficult to determine the exact amount of energy deposited during a single shot, because the nanorods are randomly aligned in solution during irradiation, and the polydispersity in the aspect ratio translates into different values of \( \sigma_{abs} \). Hence, obtaining explicit equations for the aspect ratio variation as a function of irradiation fluence became impossible. We developed a MC code that could precisely determine the amount of energy deposited by each laser pulse on an arbitrary nanorod in the solution (Fig. 3 and figs. S13 to S16) (28). The only unknown quantity was the variation of the aspect ratio as a function of the energy, which depended on the initial aspect ratio (\( \rho_0 \)) because nanorods with a lower anisotropy would be more thermodynamically stable (23). We thus used the assumption, subsequently confirmed by MD simulations, that the normalized variation of the aspect ratio, \( \Delta = (\rho_0 - \rho)/(\rho_0 - 1) \), was independent of \( \rho_0 \).

We first determined the aspect ratio distribution in the colloids as a function of the number of laser pulses from a fit of the optical density spectra of gold nanorods, measured in situ during irradiation. This procedure was
Fig. 4. MD simulations of gold nanorod evolution upon excitation with a laser pulse. (A) Normalized variation of the aspect ratio as a function of the energy deposited on the electronic system by the laser pulse (red line, obtained from MC simulations) and the energy transferred to the lattice (symbols, yielded by MD simulations). Agreement between the curves was obtained for an efficiency of energy transfer to the lattice of \( \eta = 0.75 \). (B) Effect on aspect ratio of thermal insulation, represented by two different heat transfer time constants, \( \tau = 60 \) ps and \( \tau = 350 \) ps (CTAB at the cmc).

The mechanism behind gentle nanorod reshaping thus relies on two effects: (i) the strong dependence of the energy absorbed by the nanorod on its aspect ratio (Fig. 3D), and (ii) the lower thermodynamic stability of the nanorods with larger aspect ratios (38). Nanorods with an LSPR band in resonance with the laser pulse, absorb much more energy. As their aspect ratio is reduced, the amount of energy absorbed is concomitantly decreased until it is not sufficient for reshaping. Additionally, nanorods with larger elongations undergo a faster reshaping (i.e., the variation of aspect ratio for a single pulse is larger), owing to their lower thermodynamic stability. Thus, they were modified even when the energy absorbed would not affect nanorods with lower aspect ratios. The synergy between these two effects results in an increased concentration of nanorods with similar aspect ratios.

To better understand nanorod deformation, we performed MD simulations on full gold nanorods with aspect ratios of 3.25, 3.33, and 3.87, excited at different energies, up to \(-0.5 \) eV/atom (Fig. 4 and fig. S17). When energy was deposited on a nanorod by a femtosecond laser pulse, its temperature increased up to a certain value (for example, up to \(1900\) K for \(0.5\) eV/atom in \(5.8 \times 10^7\) atoms) within an ultrashort time, typically below 10 ps (fig. S18 (39)). Additionally, whereas it has been reported that the time constant of heat transfer from gold nanorods to water is \(\tau \sim 60\) ps (35), CTAB capping molecules at concentrations around the cmc acted as a thermal barrier for water, dramatically reducing the dissipation of heat (\(\tau \sim 350\) ps) (36).

The difference between heating and cooling time scales—related to electron-phonon and phonon-phonon coupling at the nanorod surface, respectively—rendered the temperature increase nearly independent of its thermal environment. Nonetheless, heat dissipation into the surrounding medium depended strongly on the environment (36). Hence, thermal insulation determined the observed differences in the evolution of nanorod colloids under different irradiation conditions. For the MD simulations, we included only the nanoparticles, ignoring the presence of the surfactant, because (i) CTAB was difficult to simulate at this temperature range (up to \(1900\) K with the existing potentials, and (ii) CTAB molecules were most likely decomposed by the laser pulse and subsequently replaced by “fresh” molecules in a colloidal equilibrium process (37)).

The results from MD simulations (performed with a \(\tau\) of \(350\) ps) are summarized in Fig. 4. If heat was transferred from a nanorod into the surrounding water molecules too quickly (e.g., bare particles immersed in water), either the deformation occurred too slowly or the fraction of heavily modified (or fragmented) nanorods was too high, which made it impossible to identify useful irradiation regimes (Fig. 4B). However, slower cooling allowed for gentle reshaping of the gold nanorods. The effect of the total energy deposited throughout the deformation process is illustrated in Fig. 4A. For low energies (below \(0.3\) eV/atom), deformation was very gentle, and only a multishot process could produce considerable variations in the aspect ratio.

For higher energies, even a single shot led to substantial deformation, so that the rod-like shape was not preserved. At sufficiently high energies (above \(0.45\) eV/atom), the nanorods...
were readily transformed into spheres (Fig. 4C). This finding is not a coincidence, because the melting temperature of gold (~1357 K) could be reached for energies above 0.3 eV/atom (22). The reliability of the MD simulations is reinforced by the prediction of intermediate morphologies that were observed by TEM (Fig. 4D).

The aspect ratio variation predicted by MD simulations followed the same trend as the experimental curve obtained from the MC analysis (Fig. 4A). This result supports the assumption that the deformation of gold nanorods was governed by control over the heat dissipation rate, which was appropriately slowed down in the presence of CTAB at its cmc (Fig. 1). Above the cmc, where lower dissipation rates are expected, the partial formation of non-nanorod-shaped nanoparticles, analogous to those obtained at high energies, was confirmed by TEM (Fig. 4E and fig. S7). This finding means that an increase in CTAB concentration may affect the first region of the $\Delta(E)$ curve, in such a way that nanorod reshaping by a single pulse is more obvious.

The energy absorbed by the plasmon is eventually transferred into the nanocrystal lattice through electron-phonon relaxation processes, increasing the temperature of the nanorods and inducing reshaping mediated by gold atom diffusion (33, 34). There is a ~25% shift between the energy deposited in the electronic (LSPR) and atomic (thermal energy) systems, as determined from the MC and MD simulations, respectively, which implies a conversion efficiency of $\eta = 0.75$ (Fig. 4A).

Heat transfer to the medium during energy deposition into the nanorod atoms can be neglected because the characteristic time for electron-phonon coupling is much shorter than that for phonon-phonon coupling. Moreover, energy can be partly transferred to the surrounding water and surfactant molecules as hot charge carriers (e.g., through plasmon decay into molecular absorbate levels and/or hot electron-hole pair production) during ultrafast energy deposition in the plasmon, on time scales from a few to tens of femtoseconds (37). Although classical models predict that direct charge transfer accounts for only a small fraction of the total energy (38), theoretical and experimental evidence suggests that this fraction can be above 20% in certain plasmonic systems (39, 40). This mechanism for energy loss is particularly important for small nanoparticles (37) and explains the effect observed for particles with larger volumes, which are reshaped with less energy per atom.

Because hot electron production is strongly suppressed for large nanoparticles (37), a larger fraction of the absorbed energy is available for the rod reshaping process, compensating other potential pathways for energy loss (e.g., light scattering).

Although femtosecond laser pulses can be used to selectively reshape gold nanorods, this useful irradiation regime can only be achieved after careful selection of the chemical environment and irradiation fluence. MC and MD simulations revealed that the nanorod modification kinetics depend on two related parameters: the total energy deposited on the nanoparticle and the heat dissipation rate into water. The former parameter can be readily controlled by means of the irradiation fluence, but the same is not true for the latter. Addition of CTAB molecules at the cmc concentration results in a regime characterized by two well-defined regions. At lower energies, the variation of the aspect ratio is sufficiently gentle, which constitutes the basis of our method for the efficient production of nanorod colloids with very narrow aspect ratio distributions. Above a certain energy threshold, the nanorods are drastically modified by a single laser pulse, making controlled modification impossible. Thus, deviation from the cmc concentration renders formation of gold nanorod colloids approaches the theoretical limit, rendering it a highly appealing approach toward improving and expanding the applications of plasmonic nanorods.

REFERENCES AND NOTES

28. See the supplementary materials.

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S18

References (41–66)

Movie S1

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Femtosecond laser reshaping yields gold nanorods with ultranarrow surface plasmon resonances

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Laser-shaping nanoparticles
For many applications of the plasmon resonances of metal nanoparticles, it is necessary to have narrow resonance lines. However, most methods for synthesizing nanoparticles create a distribution of sizes and shapes that broaden the resonance lines. González-Rubio et al. annealed gold nanorods dispersed in an aqueous solution of a surfactant with carefully tuned ultrafast (femtosecond) laser pulses. This approach reshaped the nanoparticles to create a near-uniform distribution with resonance lines nearly as sharp as for a single nanorod.
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