Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Information

The fragmentation mechanism of gold nanoparticles in water under femtosecond laser irradiation

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This PDF file includes:

Other supplementary materials for this manuscript:

Supplementary Movies 1–14 can be found at https://doi.org/10.5281/zenodo.5589531

Methods

***In situ* transmission electron microscopy.** Experiments were performed with a modified JEOL 2010F transmission electron microscope.[1] The sample was irradiated *in situ* with femtosecond (515 nm, 200 fs, 10 kHz) or nanosecond laser pulses (532 nm, 0.7 ns, 10 kHz). The laser beams are directed at the sample by means of a mirror mounted above the upper pole piece of the objective lens, so that they propagate almost collinearly with the electron beam and strike the sample at close to normal incidence. The femtosecond and nanosecond laser beams are focused onto the sample, with spot sizes of 30 μm and 34 μm FWHM, respectively, as determined by imaging the beams with a camera placed in a plane conjugate to the sample plane. The reported laser fluences refer to the actual fluence at the sample position and are corrected for losses on optical elements. Liquid samples were imaged with a typical dose rate of 3 electrons/Å^2/s. All movies were recorded with a frame rate of 5 frames/s.

Sample preparation. Gold nanospheres stabilized with polyvinylpyrrolidone were purchased from nanoComposix (5 mg/ml in water). For each liquid cell experiment, 30 μl and 20 μl of suspensions of 15 nm and 50 nm particles, respectively, were freshly mixed and diluted with 1 ml of deionized water. The mixture was centrifuged at 10000 rpm for 10 minutes. The supernatant was then removed, and the particles were resuspended in 1 ml deionized water. This centrifugation and resuspension step was repeated once more, after which a small volume of the resulting suspension was immediately enclosed in a Protochips liquid cell (microwell configuration, with SiN viewing windows of 50 nm and 30 nm thickness for the top and bottom, respectively). Care was taken to avoid evaporation of the thin liquid layer before enclosure.

At the dose rates employed here (typically 3 electrons/Å^2/s), samples prepared with this procedure can be observed for minutes without inducing the nucleation of nanoparticles with the electron beam. If we instead study a nanoparticle suspension that has not been purified or allow the sample to age, we observe that nanoparticles nucleate almost instantaneously.[2] Such electron beam-induced nucleation occurs independently of whether the sample is being irradiated with laser pulses or whether gold nanoparticles are present and is therefore quite distinct from the formation of progeny particles under laser irradiation. Even though both phenomena can be distinguished, we have studied only freshly

prepared samples in which electron beam-induced nucleation did not occur, so as to avoid any ambiguity.

After each experiment, we confirmed the presence of water in the sample by converging the electron beam to observe processes that can only occur in liquid, such as the formation of bubbles,[3] the electron-beam induced etching or growth of the nanoparticles,[2,4] or their movement under the converged electron beam. If none of these phenomena could be observed, the data set was discarded. Note that Supplementary Fig. 1 demonstrates that only nanoparticles in liquid will fragment under femtosecond laser irradiation with the pulse energies employed here, whereas dry particles remain intact. This corroborates the presence of water in our femtosecond laser experiments. Based on the spatial resolution that we obtain, we estimate that the liquid film thickness is typically a few hundred nanometers, close to depth of the microwells of the liquid cell of 170 nm[5].

Gold core silica shell nanoparticles with 20 nm core diameter and 20 nm shell thickness were purchased from NanoComposix and deposited on a multilayer graphene specimen grid (Graphene Supermarket).

Processing of images and movies. Images and movies were corrected for sample drift using phase correlation based image registration.[6] Displacements of the nanoparticles during laser irradiation therefore correspond to actual movements with respect to the liquid cell chip. The 4k×4k movies were binned 4×4. A Gaussian filter was applied to the images in Fig. 2. The frame rate of the supplementary movies corresponds to the actual frame rate of the camera (5 frames/s).

Determination of the angular distributions of progeny particles. Gold core silica shell nanoparticles were irradiated *in situ* with femtosecond laser pulses (100 mJ/cm^2) for about 30 s, after which the sample was imaged to determine the angles at which progeny particles had been ejected. The ejection angles were measured with respect to the horizontal, as indicated in Fig. 3. For the gold particles in water, the angular distribution was obtained from movies recorded during *in situ* irradiation (53 mJ/cm^2). Angles were measured in the movie frame in which a new progeny particle first appeared, so as to give the particles as little time as possible to diffuse to a different location. In order to test whether the presence of previously ejected progeny particles alters the distribution of new progeny particles, we

distinguished cases in which four of fewer progeny particles had been created from cases with a larger number. For either, we found an isotropic distribution within our signal to noise. The same is true for progeny particles created around a parent nanoparticle that formed a dark halo. The angular distribution presented in Fig. 3d comprises all three cases. A total of 250 progeny particles were examined to construct each of the histograms in Fig. 3.

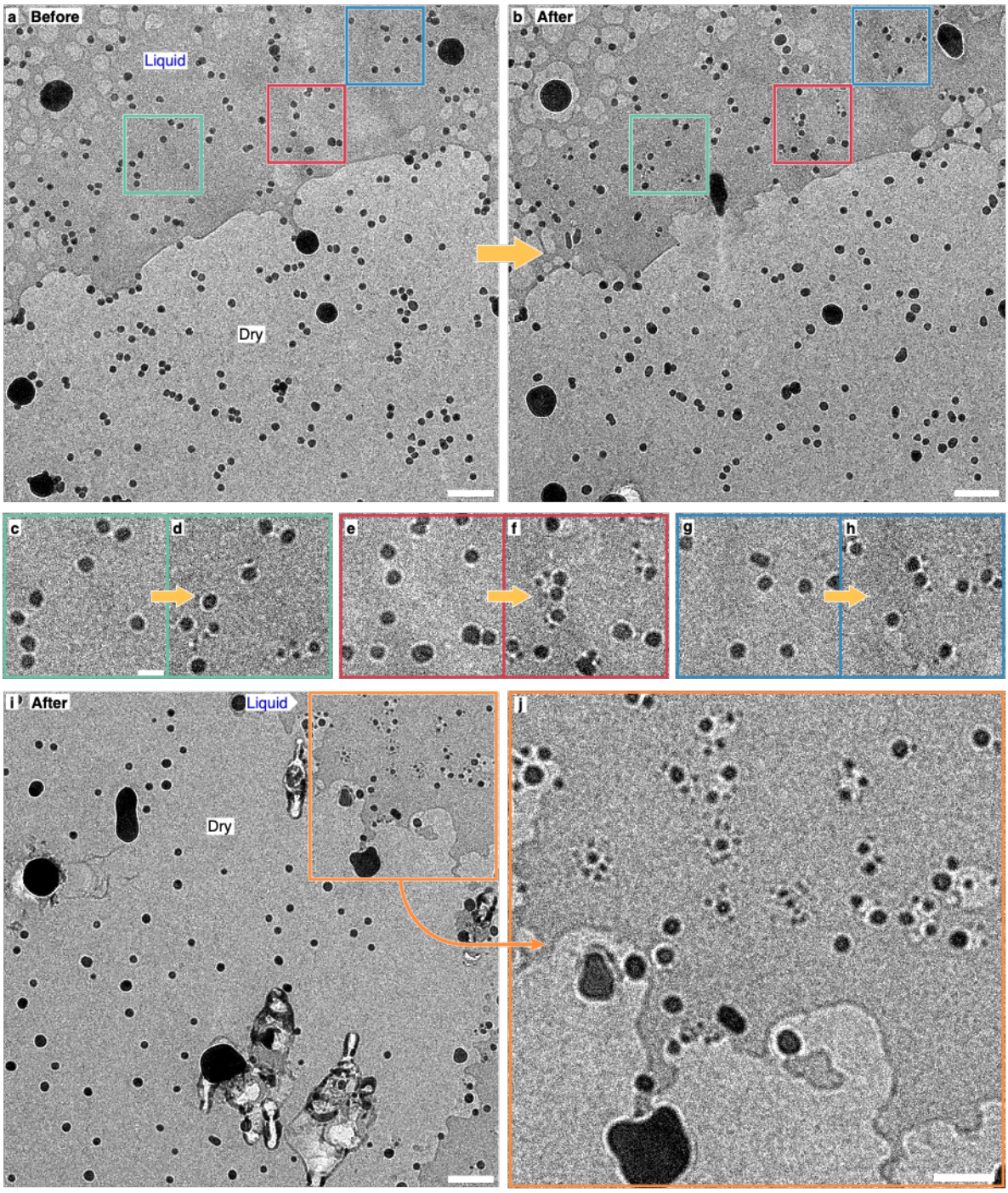


Figure S1. In partially dry samples, only particles in patches of water undergo fragmentation under femtosecond laser irradiation. (a,b) Micrographs of a partially dry sample before (a) and after laser irradiation (b, about 10 s irradiation with a fluence of 53 mJ/cm^2). While in the dry area, some particles have fused together or have deformed, only the area covered in water shows fragmented particles. The different behavior is likely a consequence of the difference in absorption cross section of the gold

nanoparticles, which is about 3 times larger in liquid than in vacuum.[7] Scale bars, 100 nm. (c-h) Details of the areas marked with colored squares in (a) and (b). Scale bar, 25 nm. (i) Another partially dry sample after femtosecond laser irradiation (about 10 s, 53 mJ/cm^2). Fragmentation has occurred only in the area covered in water (top right and bottom right). In parts of the dry area, the window of the liquid cell chip has been damaged by the hot nanoparticles. This effect occurs only for gold particles on a dry substrate and can only be induced through femtosecond laser irradiation. It also prevents us from using higher laser powers to induce fragmentation of the dry nanoparticles. Scale bar, 100 nm. (j) Detail of the area marked with a square in (i). Scale bar, 50 nm.

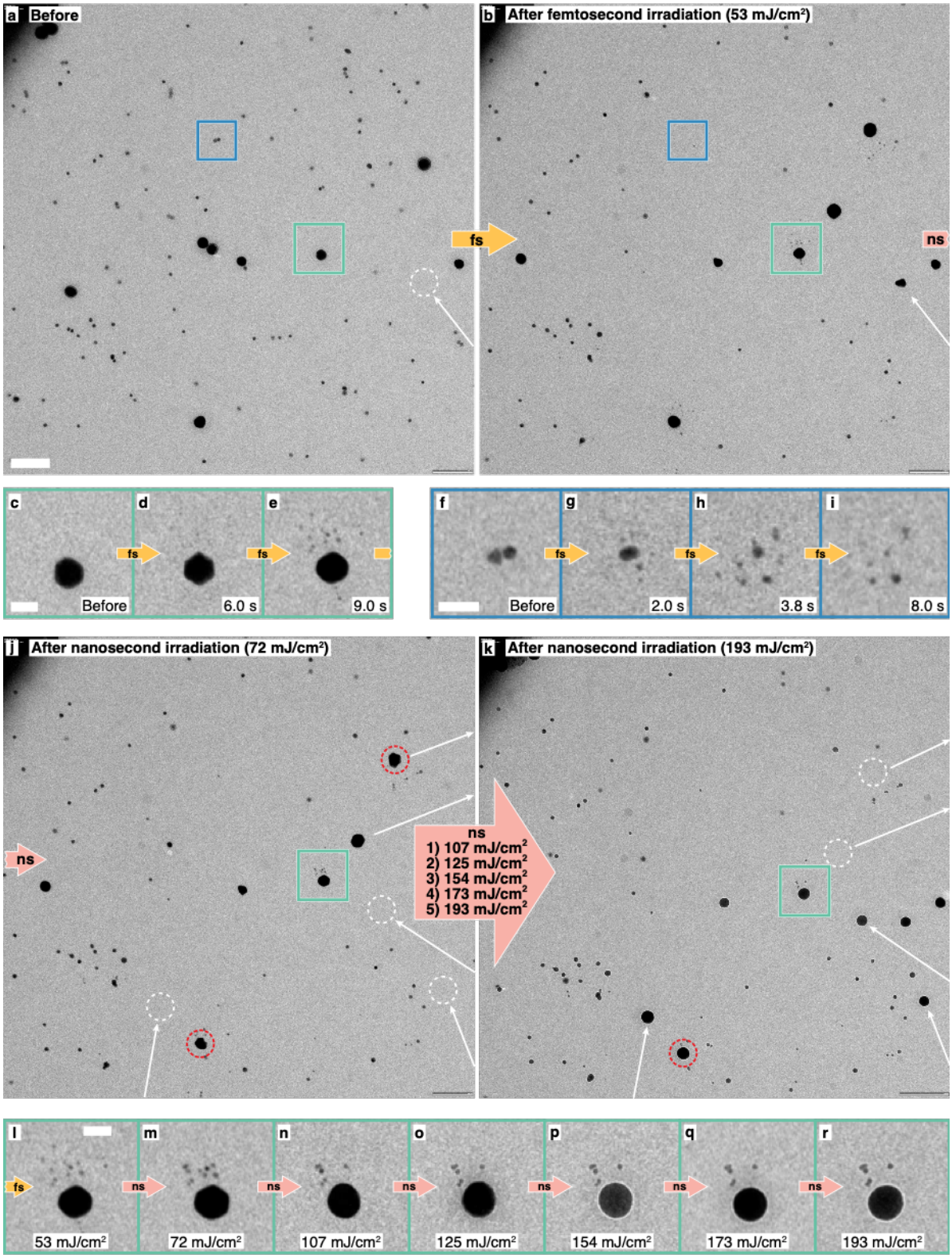


Figure S2. Gold nanoparticles in water fragment under femtosecond laser irradiation, whereas they do not fragment under nanosecond laser irradiation with up to 4.5 times the fluence. (a,b) Femtosecond laser irradiation (9.8 s, 53 mJ/cm^2) causes several particles to fragment (Supplementary Movie 7). A

particle appearing in the field of view during irradiation is marked with a white circle and arrow. Scale bar, 200 nm. (c-e, f-i) Image sequences illustrate the fragmentation of nanoparticles in the areas marked with squares in (a,b). The time stamps of the micrographs refer to the time elapsed since the beginning of laser irradiation. Scale bars, 50 nm. (j) Subsequent irradiation with nanosecond laser pulses (72 mJ/cm^2, 20.2 s) does not induce any further fragmentation, although some particles undergo shape changes (red circles), indicating that they melt at least partially under these conditions (Supplementary Movie 8). (k) Irradiation with nanosecond pulses of increasing fluence (107 mJ/cm^2 for 15.6 s, 125 mJ/cm^2 for 16.6 s, 154 mJ/cm^2 for 17.8 s, 173 mJ/cm^2 for 12 s, and 193 mJ/cm^2 for 12.6 s) does not induce fragmentation either. Supplementary Movie 9 shows the particles under irradiation with a fluence of 193 mJ/cm^2. At even higher fluences, the liquid cell chip tends to break. (l-r) Detail of the area marked with a green square in (a,b) and (j,k). The 50 nm diameter nanoparticle in (l) has ejected several progeny particles under femtosecond laser irradiation. Subsequent exposure to nanosecond laser pulses of increasing fluence causes the particles to undergo shape changes and fuse with each other, but does not induce further fragmentation (m-r). Scale bar, 50 nm.

We note that we do not observe fragmentation under nanosecond irradiation even though similar fluences have previously been shown to induce fragmentation of particles in bulk water through a thermal evaporation mechanism[8]. Likely, the liquid cell environment allows the particles to dissipate heat more efficiently during the nanosecond laser pulse. The particles therefore reach a lower peak temperature, which reduces evaporation. In bulk water, nanobubbles rapidly form around the hot particle and slow its cooling.[8] In the liquid cell environment, the particle remains in contact with the silicon nitride viewing window, which allows for efficient heat dissipation even when a nanobubble has formed.

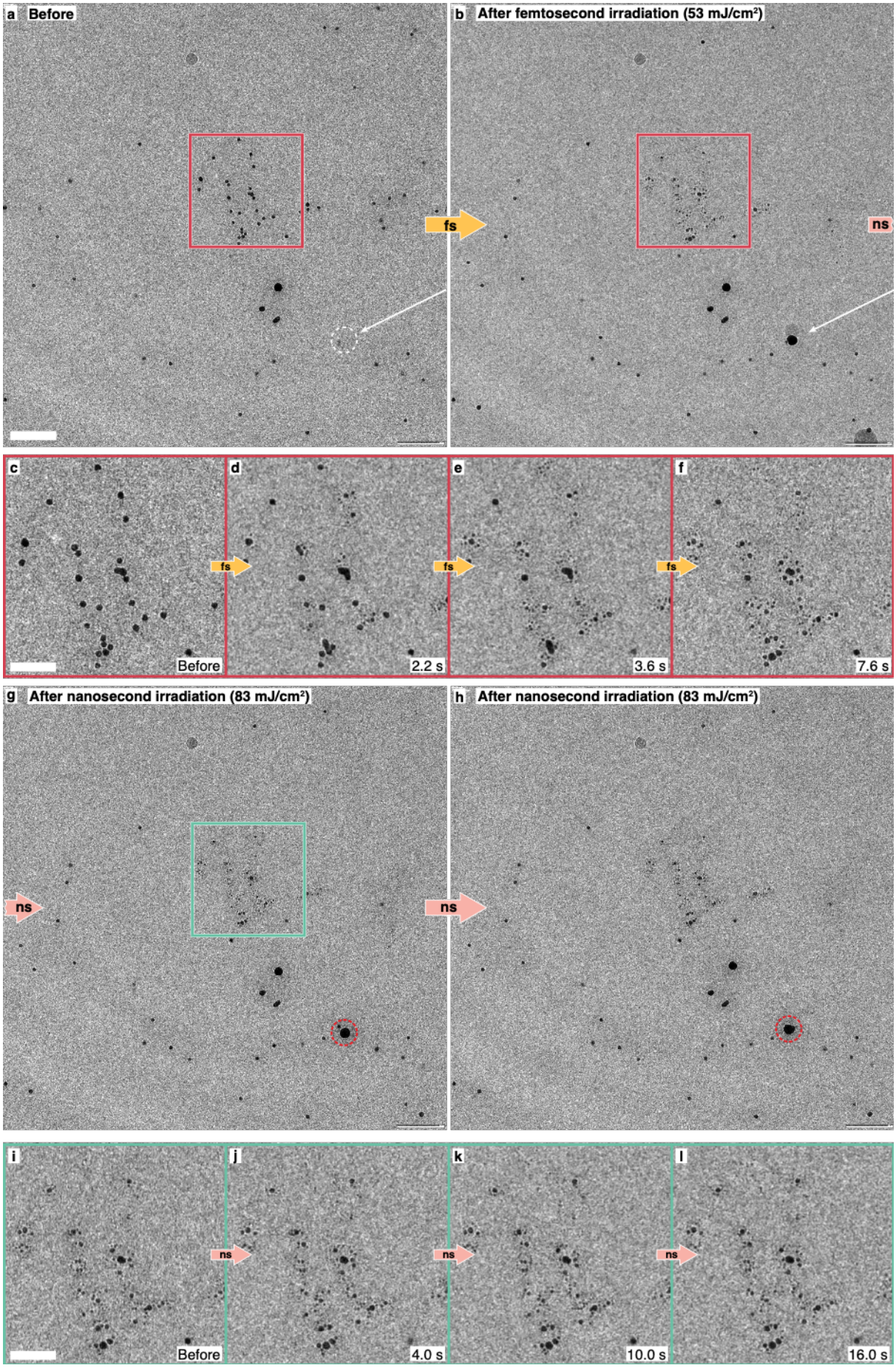
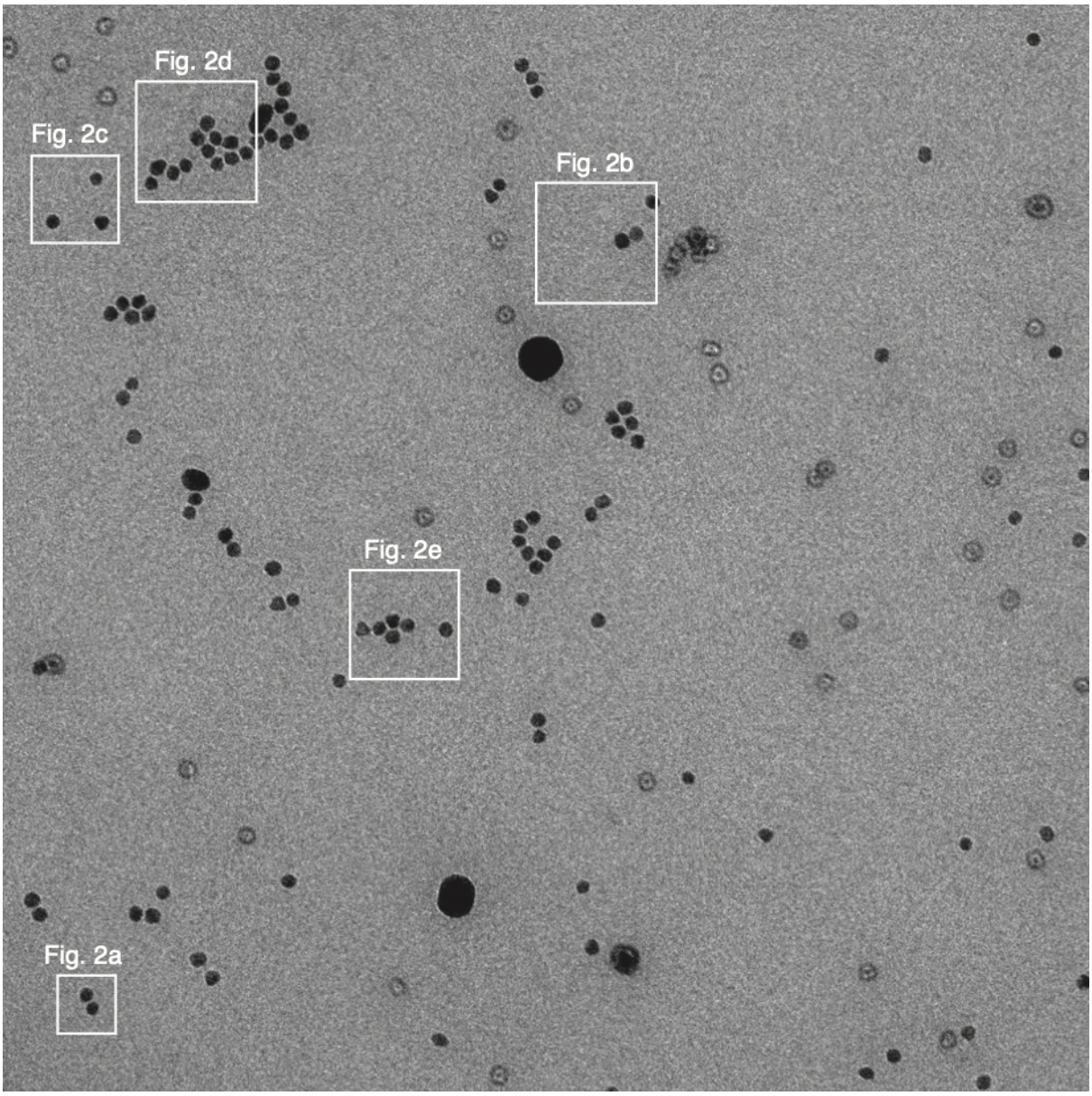
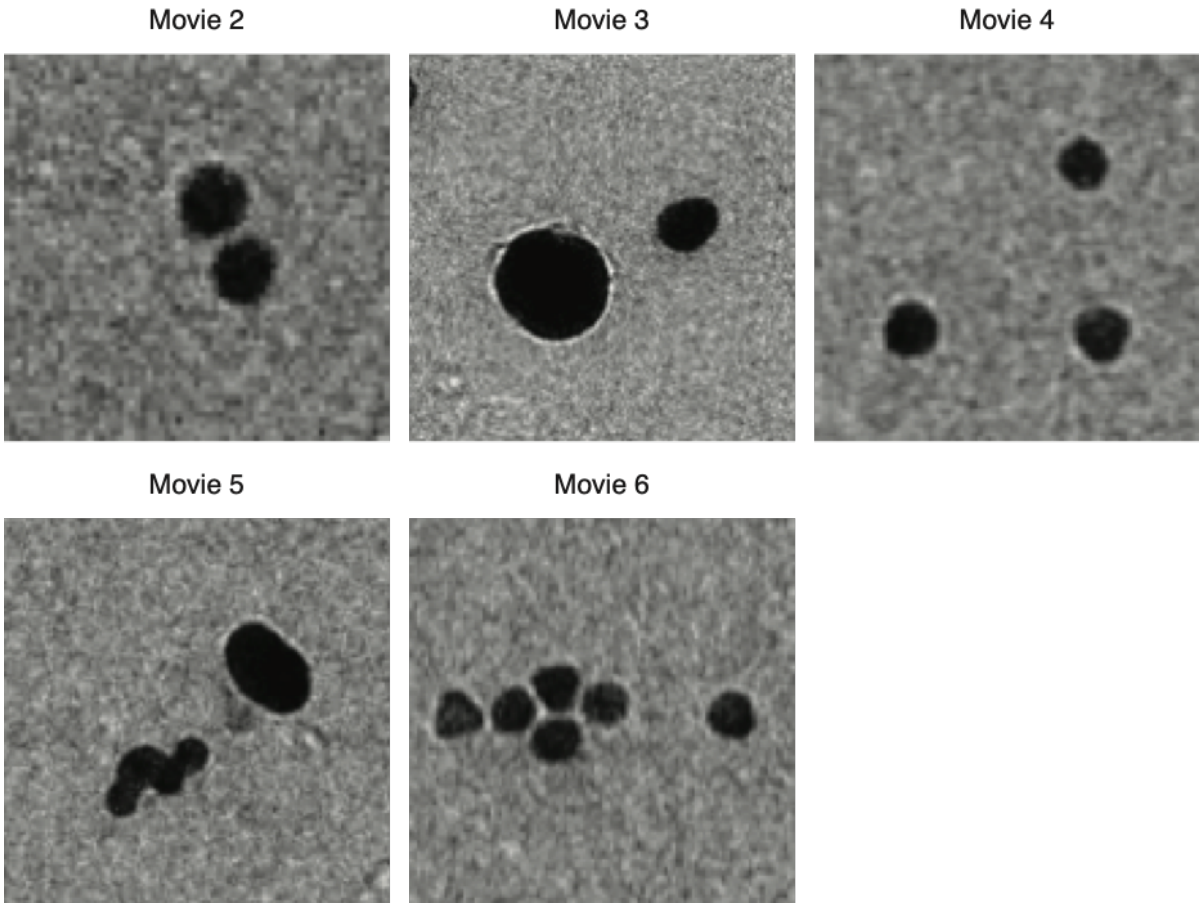

a Before
b After femtosecond irradiation (53 mJ/cm²)
fs
ns
c
d
e
f
fs
fs
fs
Before
2.2 s
3.6 s
7.6 s
g After nanosecond irradiation (83 mJ/cm²)
h After nanosecond irradiation (83 mJ/cm²)
ns
ns
ns
i
j
k
l
ns
ns
ns
Before
4.0 s
10.0 s
16.0 s

Figure S3. Gold nanoparticles in water fragment under femtosecond laser irradiation, whereas they do not fragment under nanosecond laser irradiation at twice the fluence. (a,b) Femtosecond laser irradiation (12.6 s, 53 mJ/cm^2) causes several particles to fragment (Supplementary Movie 10). A particle appearing in the field of view during irradiation is marked with a white circle and arrow. Scale bar, 200 nm. (c-f) An image sequence (Supplementary Movie 11) illustrates the fragmentation of nanoparticles in the area marked with the red square in (a,b). The time stamps of the micrographs refer to the time elapsed since the beginning of laser irradiation. Scale bar, 100 nm. (g,h) Subsequent irradiation with nanosecond laser pulses (83 mJ/cm^2, for 17.2 s and 2 s, in (g) and (h), respectively) does not induce any further fragmentation, although some particles undergo shape changes (red circles), indicating that they melt at least partially under these conditions (Supplementary Movies 12 and 13). (i-l) An image sequence shows that the nanoparticles in the area marked with a green square in (g) remain unchanged under nanosecond laser irradiation (Supplementary Movie 14).

Supplementary Movies



Movie 1. *In situ* observation of the fragmentation of gold nanoparticles in water under femtosecond laser irradiation (Fig. 1d,e of the main text). Laser irradiation was started about 3 s after the beginning of the movie and is evident from a sudden movement of the particles. At the beginning of the movie, a number of particles are visible that are attached to the top window of the liquid cell and therefore appear out of focus. The movie was corrected for drift, which creates the artifacts at the edges of the frame. White squares mark the areas for which details are presented in Fig. 2 of the main text and in Supplementary Movies 2-6.



Movies 2-6. *In situ* observation of the fragmentation of gold nanoparticles in water under femtosecond laser irradiation; details of Supplementary Movie 1, as presented in Fig. 2 of the main text. The movie clips start at the following times with respect to the beginning of Supplementary Movie 1.

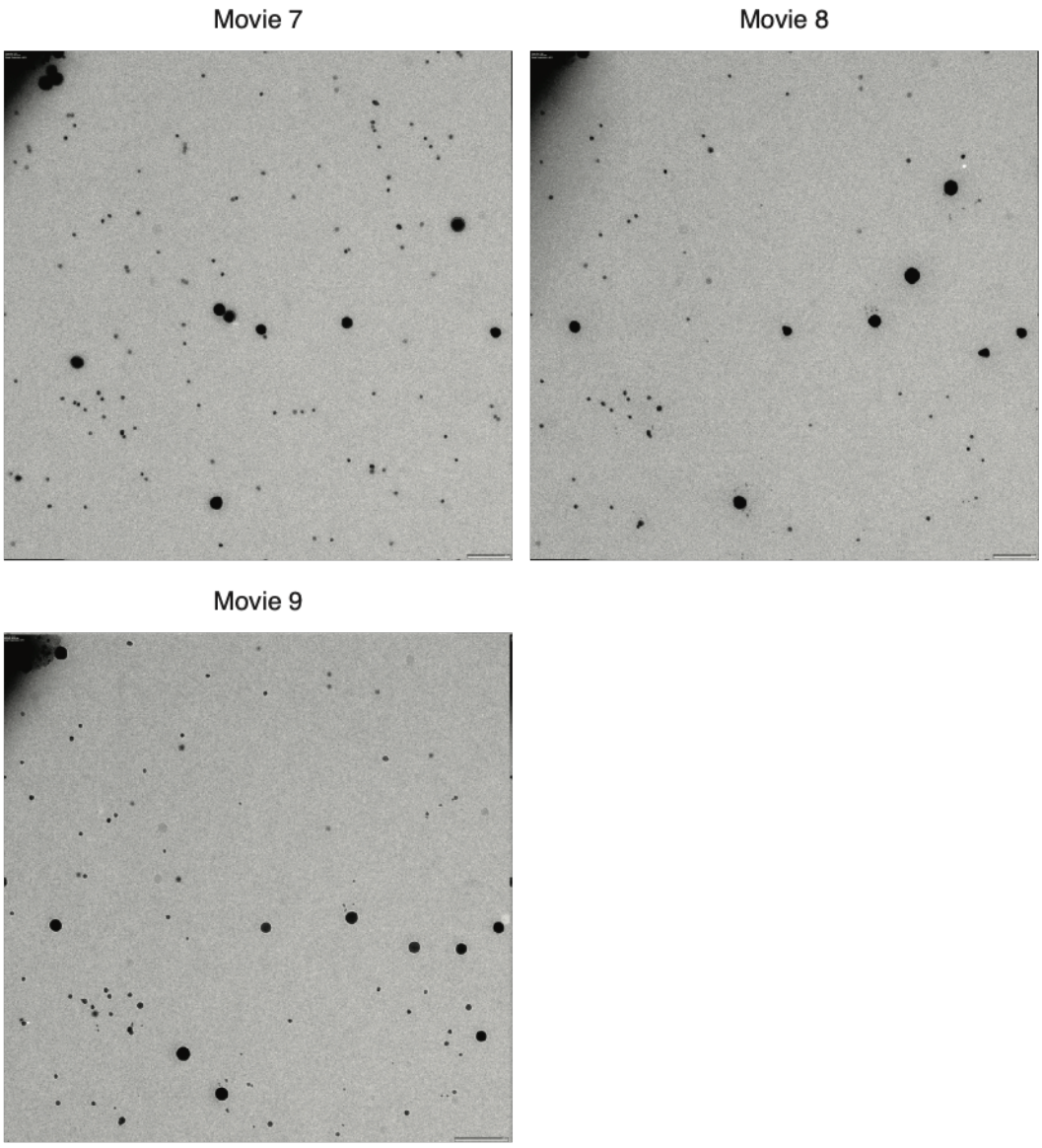
Supplementary Movie 2, 0 s;

Supplementary Movie 3, 15 s;

Supplementary Movie 4, 2 s;

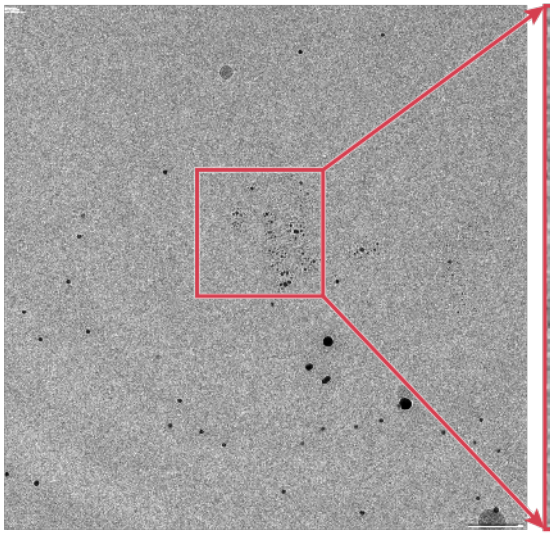
Supplementary Movie 5, 4.4 s;

Supplementary Movie 6, 0 s.

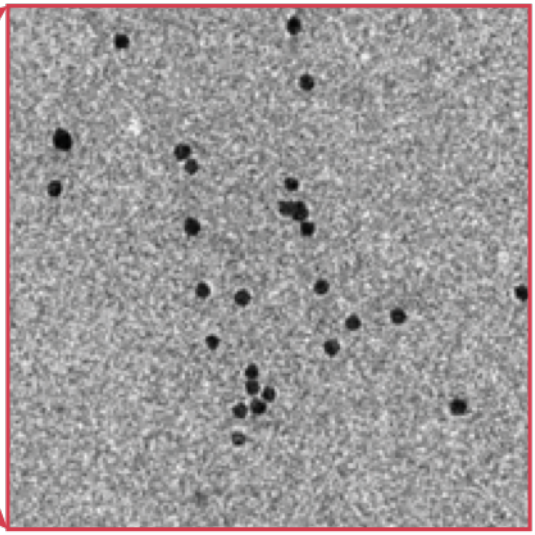


Movies 7-9. Gold nanoparticles in water fragment under femtosecond laser irradiation, whereas they do not fragment under nanosecond laser irradiation with up to 4.5 times the fluence (see Fig. S2). Supplementary Movie 7 shows the fragmentation of particles under femtosecond laser irradiation (53 mJ/cm^2). Subsequent irradiation with nanosecond laser pulses (72 mJ/cm^2, Supplementary Movie 8) does not induce any further fragmentation. Even a fluence of 193 mJ/cm^2 does not fragment the particles (Supplementary Movie 9). In each movie, laser irradiation was started after about 2 s.

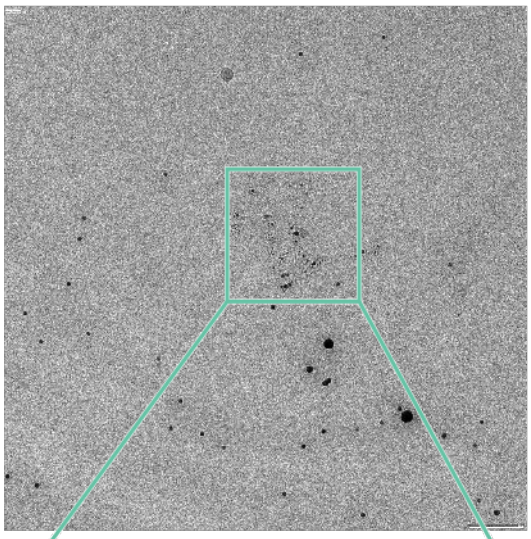
Movie 10



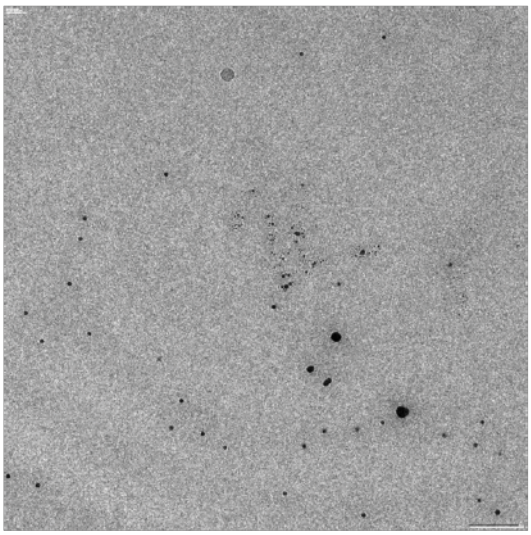
Movie 11



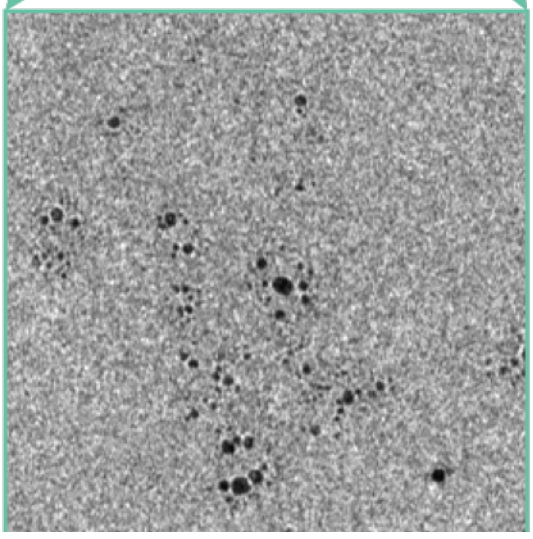
Movie 12



Movie 13



Movie 14



Movies 10-14 | Gold nanoparticles in water fragment under femtosecond laser irradiation, whereas they do not fragment under nanosecond laser irradiation with twice the fluence (see Fig. S3). Supplementary Movie 10 shows the fragmentation of particles under femtosecond laser irradiation (53 mJ/cm^2). Supplementary Movie 11 shows a detail of the region marked with a red square in Supplementary Movie 10. Subsequent irradiation with nanosecond laser pulses (83 mJ/cm^2) does not induce any further fragmentation, as shown in Supplementary Movies 12 and 13. In each movie, laser irradiation was started after about 2 s. Supplementary Movie 14 shows a detail of the region marked with a green square in Supplementary Movie 12.

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