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The Fragmentation Mechanism of Gold Nanoparticles in Water under Femtosecond Laser Irradiation

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Laser irradiation of plasmonic nanoparticles in liquid is known to generate a plethora of interesting phenomena: laser pulses can reshape the nanoparticles [1], change their size [2] or drive photochemical reactions on their surface [3]. Plasmonic nanoparticles in solution have also been thought to fragment and explode under irradiation with intense laser pulses [4], a behavior that has attracted particular attention in the past 20 years. Fragments of around 2-4 nm in diameter are obtained with this process, providing an easy way to generate particles of these small sizes. However, in the absence of a direct observation method, the mechanism behind this phenomenon is still poorly understood. It has been suggested that the small fragments are the result of surface evaporation and subsequent condensation of the vapor [5,6] Alternatively, for pulses in the femtosecond regime, the idea of a Coulomb explosion has also been brought forth [6]. According to this theory, ultrafast pulses ionize the nanoparticle, which subsequently shatters when the coulombic repulsion exceeds its surface tension[6].

Recently, we have shown that gold nanoparticles embedded in a silica shell fragment under laser irradiation following a different mechanism, namely Coulomb fission [7]. Instead of undergoing an explosion, gold nanoparticles eject individual charged fragments. This finding raised the question whether the same is true in water.

Here, we present a study of the fragmentation mechanism of gold nanoparticles in solution under femtosecond laser irradiation performed *in situ* in a transmission electron microscope (TEM). A schematic of the experimental setup is shown in Fig. 1a: a suspension of commercially available gold nanoparticles in distilled water is encapsulated in a microchip-based liquid cell holder (Protochips Inc.). The suspension is illuminated with femtosecond (515 nm, 200 fs, 10 kHz) laser pulses, and observed in real time with the electron beam.

Laser-irradiated gold nanoparticles eject fragments individually, in a fashion similar to our previous study, ruling out the hypothesis of a Coulomb explosion. This evidence suggests that Coulomb fission is the main fragmentation mechanism for particles in solution.

However, differently from the case of gold nanoparticles in a silica shell, a variety of secondary phenomena were observed in liquid. As shown in Fig.1b-f, the progeny particles themselves undergo Coulomb fission, generating progenies of even smaller size. Furthermore, we observe mass reshuffling among the progenies and the parent particles.

This latter observation, which is independent of the electron beam irradiation, seems to be a form of laser-mediated Ostwald ripening: the bigger particles grow at the expense of smaller ones, which undergo fragmentation and subsequently shrink until they dissolve entirely.

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Our study also rules out the thermal explosion mechanism. Nanoparticles irradiated with nanosecond laser pulses (532 nm, 700 ps, 10 kHz) fragment at very high laser fluences, but undergo explosion instead of fission. The difference between the ejection of progenies suggests that the fragmentation of nanoparticles under femtosecond laser illumination is based on the ultrafast interaction between the laser pulse and the electrons of the plasmonic particle.

In conclusion, our study elucidates the fragmentation mechanism of plasmonic nanoparticle in solution (Fig.1g-k). Using *in situ* electron microscopy we reveal an intricated mechanism that involves multi-step fragmentation and solution-mediated mass reshuffling. Moreover, this study highlights the importance of *in situ* observation to study the different processes occurring during laser irradiation of plasmonic nanoparticles.

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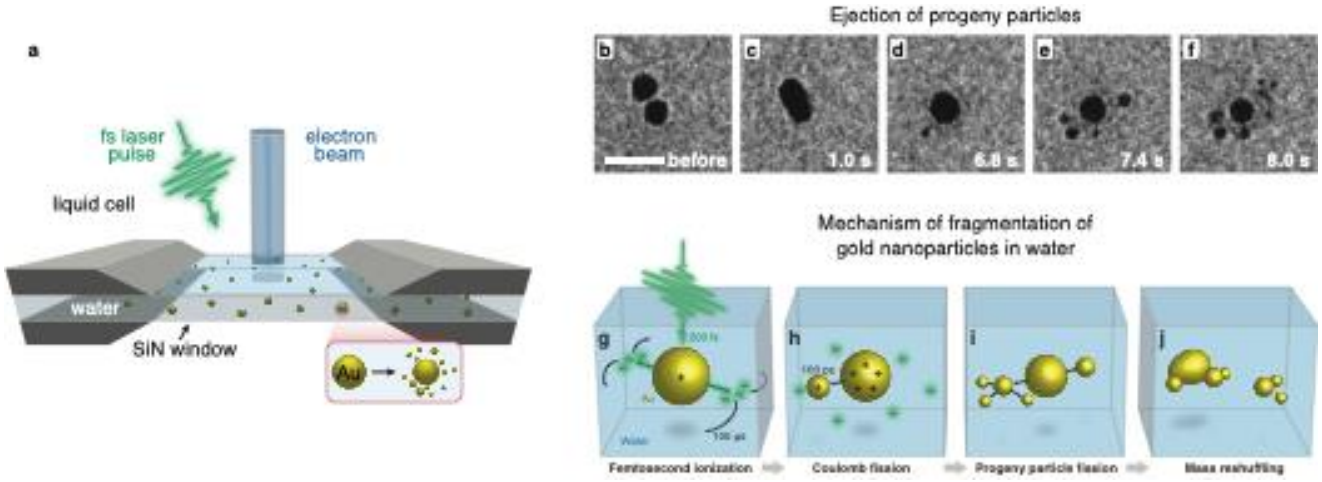

Figure 1. Schematic image of the experiment and direct observation of the fragmentation of gold nanoparticles under femtosecond laser irradiation. a, gold nanoparticles placed in a liquid cell filled with water undergo Coulomb fission under continuous irradiation with femtosecond laser pulses (515 nm, 200 fs). b-f, sequence of images illustrating two nanoparticles fusing into one particle, which emits smaller gold particles of several nanometers in diameter. Over time, more particles are formed. g-j, proposed mechanism of the process. Femtosecond laser pulses ionize the gold particle, and the emitted electrons rapidly diffuse forming a uniformly charged region around the particle. As the result of Coulomb fission, the positively charged melted gold particle ejects a smaller particle in a random direction. During the continuous illumination, redistribution of mass between the main and progeny particles is observed.
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