In-Situ Observation of Coulomb Fission of Individual Plasmonic Nanoparticles

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Abstract: Reshaping plasmonic nanoparticles with laser pulses has been extensively researched as a tool for tuning their properties. However, in the absence of direct observations of the processes involved, important mechanistic details have remained elusive. Here, we present an *in-situ* electron microscopy study of one such process that involves Coulomb fission of plasmonic nanoparticles under femtosecond laser irradiation. We observe that gold nanoparticles encapsulated in a silica shell fission by emitting progeny droplets comprised of about 10-500 atoms, with ejection preferentially occurring along the laser polarization direction. Under continued irradiation, the emitted droplets coalesce into a second core within the silica shell, and the system evolves into a dual-core particle. Our findings are consistent with a mechanism in which electrons are preferentially emitted from the gold core along the laser polarization direction. The resulting anisotropic charge distribution in the silica shell then determines the direction in which progeny droplets are ejected. In addition to yielding insights into the mechanism of Coulomb fission in plasmonic nanoparticles, our experiments point towards a facile method for forming surfaces decorated with aligned dual-gold-core silica shell particles.

Keywords: *in-situ* transmission electron microscopy, plasmonic nanoparticles, Coulomb fission, nanoparticle reshaping, single-particle observation, gold-core silica shell particles

Gold nanoparticles have found a plethora of applications in a wide range of fields, including biomedical imaging,[1] sensing,[2,3] cancer therapy,[4,5] gene regulation,[6] catalysis,[7] and optical devices.[8,9] The strong plasmonic absorptions of gold nanoparticles provide a convenient means to reshape them through pulsed laser irradiation[10,11] and thus tune their properties.[12–14] This has given rise to an entire field of research that investigates and exploits a range of mechanisms for laser particle reshaping.[10,11] At low laser fluence, shape transformations are induced through partial or complete melting and subsequent resolidification of the nanoparticles.[15,16] For example, this approach has recently been applied to reshape gold nanorods and improve their monodispersity, thus yielding exceptionally narrow surface plasmon resonances.[14] If higher fluences are employed to heat the particles beyond their boiling point, size reduction occurs through surface evaporation.[17,18] Fragmentation can be achieved through an entirely different set of mechanisms when intense ultrafast laser pulses are used to ionize the nanoparticles. On ultrafast timescales, excited electrons do not have sufficient time to equilibrate with the lattice, which requires about 3 ps (Ref 19), and the particles are ionized through multiphoton and thermionic emission.[20–23] After the laser pulse, the hot electrons equilibrate with the lattice through electron-phonon coupling, which can cause the particle to melt. If the Coulomb repulsion in the resulting charged droplet surpasses its surface tension, *i.e.* if the Rayleigh stability limit is exceeded,[24] Coulomb fission occurs through the emission of highly charged progeny droplets.[25–27] At even higher levels of ionization, Coulomb explosion of the droplet[28,29] or of the solid particle[30] may be induced, which involves the ejection of a large number of charged fragments.

Elucidation of the mechanisms of complex shape transformations that occur during pulsed laser irradiation is frequently a challenge. *Ex-situ* analysis of nanoparticle products usually only provides indirect information about the morphological changes that take place during laser irradiation. While time-resolved spectroscopy[28] and x-ray diffraction[30] can probe the particle evolution on short timescales, they frequently yield only indirect morphological information and thus do not easily permit the elucidation of intricate, multistep processes. In the absence of *in-situ* observations on the single-particle level, a robust understanding of different reshaping mechanisms has thus remained elusive, hampering their application in a deterministic fashion. Questions of an even more fundamental nature remain, for example, regarding

the mechanism of Coulomb fission, which for the smallest droplets has been predicted to occur through ion emission rather than ejection of progeny droplets.[31,32]

Here, we present an *in-situ* electron microscopy study of Coulomb fission of plasmonic nanoparticles. We observe that under intense femtosecond laser irradiation, gold nanoparticles encapsulated in a silica shell fission through emission of small progeny droplets comprised of about 10-500 atoms. Interestingly, the ejection of these progeny droplets preferentially occurs along the direction of the laser polarization. We find that the droplets emitted from successive fission events accumulate within the silica shell and coalesce into a second core, so that a dual-core particle is formed. Not only do our observations provide insights into the mechanism of Coulomb fission of plasmonic nanoparticles, but they also suggest a straightforward laser-based approach for creating surfaces decorated with aligned dual-gold-core silica shell nanoparticles.

Results and Discussion

The experiments reported here were performed with a modified JEOL 2200FS transmission electron microscope, operating at an accelerating voltage of 160 kV. Silica-coated gold nanoparticles with a 20 ± 3 nm diameter core and a 20 ± 5 nm thick shell (suspended in ethanol, available from NanoComposix) were deposited onto an electron microscopy specimen grid (multilayer graphene on 2000 mesh copper) and were irradiated *in-situ* either with femtosecond (515 nm, 240 fs, 20 kHz) or nanosecond laser pulses (532 nm, 1 ns, 20 kHz). This is achieved with the help of an aluminum mirror that is mounted above the upper pole piece of the objective lens and that reflects the laser beams onto the sample such that they propagate almost collinearly with the electron beam. The excitation wavelengths are close to the predicted absorption maximum at 533 nm of the nanoparticles.[33] In order to obtain the laser fluence, the laser spot size was determined *in-situ* with the knife edge method.

Figure 1a shows a micrograph of a typical sample. After irradiation with 10^6 femtosecond laser pulses (Fig. 1b), many of the cores have fragmented into two equally-sized gold particles that appear to be connected by a void in the silica shell. The newly formed dual-cores are roughly aligned along the polarization direction of the laser (as indicated by the double-headed arrow). Here, we determine the laser

polarization direction *in-situ* by illuminating a gold nanoparticle with an ultrafast optical pulse and imaging the scattered near-fields with photon-induced near-field electron microscopy[34] (Fig. 1c). Briefly, the ultrafast laser pulse striking the gold particle is spatially and temporally overlapped with an ultrafast electron pulse. Under such conditions, electrons that interact with the near-fields of the particle gain or lose energy in multiples of the photon energy. The energy-filtered micrograph of Fig. 1c, which is formed only with electrons that have gained energy, therefore maps the dipolar near-fields of the particle and allows us to accurately determine the laser polarization direction.[35] We find that femtosecond laser irradiation of the gold-core silica shell particles predominantly leads to the formation of two equally-sized gold cores. However, approximately 2% of particles feature three, four, or even five cores of different sizes arranged in varying configurations (Fig. 1d-f).

We quantify the degree of alignment of the dual-core particles as well as their yield as a function of laser fluence. For core-shell nanoparticles that were irradiated with $6 \cdot 10^6$ ultrafast laser pulses, we obtain a fairly broad angular distribution at a fluence of 22 mJ/cm^2 (Fig. 2a). At almost twice the fluence (39 mJ/cm^2, Fig. 2b), the distribution markedly narrows and peaks around 37°, the angle of the laser polarization. Here, the angles θ of the dual-cores are determined with respect to the horizontal, as shown in Fig. 2c. We find that with increasing fluence, the angular spread of the dual-cores (as measured by the standard deviation of the angle θ) decreases (Fig. 2d). At the same time, the yield of the dual-cores increases with laser fluence, reaching about 30% at the highest fluence employed here (Fig. 2e). The lines in Fig. 2d and 2e represent linear fits of the data that serve to guide the eye.

Figure 3a reveals that it is the linear polarization of the ultrafast laser pulses that determines the alignment of the dual-cores. When we use a half-wave plate in the laser beam path to rotate the polarization by 90°, the angular distribution of the dual-cores (irradiated with $6 \cdot 10^6$ pulses at 30 mJ/cm^2) shifts by the same angle within experimental accuracy (Fig. 3a, green and blue histograms, the lines indicate Gaussian fits with a constant offset). In contrast, irradiation of the core-shell particles with circularly polarized light under otherwise identical conditions produces a broad angular distribution (orange histogram in Fig. 3b). Furthermore, we find that the pulse duration plays a crucial role in the formation of the dual-core particles.

Whereas both femtosecond and picosecond pulses (≲3 ps, obtained by stretching the output of the femtosecond laser) can be employed to form the dual-core particles, nanosecond pulses of similar fluence leave the gold cores largely unchanged. When we increase the fluence of the nanosecond pulses further, the gold cores simply evaporate as evidenced by the micrograph in Fig. 3c ($6 \cdot 10^6$ pulses, 41 mJ/cm^2). In some instances, narrow channels in the silica shell can be observed that appear to be created as a result of the evaporation process. Evidently, ultrafast pulses are necessary to form the dual-core particles, which strongly suggests that ionization of the core plays a central role in the fragmentation mechanism. Ionization can only be achieved with ultrafast pulses and indeed has been observed in previous studies for similar laser pulse parameters.[20–23,29] As discussed above, on ultrafast timescales, the electrons do not have sufficient time to equilibrate with the lattice, so that multiphoton emission can be induced. In contrast, nanosecond laser pulses will simply heat the gold cores to high temperatures without causing significant ionization.[10,29]

In order to unravel the formation mechanism of the dual-cores, we carry out *in-situ* observations of individual particles under laser irradiation. Typical sequences of events are shown in Fig. 4 (see also Movies 1-3). They reveal that the mechanism involves the stepwise ejection of small gold fragments from the core. When the nanoparticle displayed in Fig. 4a is irradiated with femtosecond pulses (16 mJ/cm^2), its gold core ejects a small particle of about 2 nm diameter (Fig. 4b) along the direction of the laser polarization (double-headed arrow in (a)). Subsequently, further particles of 1-2 nm diameter (about 30-200 atoms) are emitted (Fig. 4c,d), which can then be seen to coalesce into a single mass (Fig. 4e). This secondary gold core continues to grow by absorbing further particles (Fig. 4f) until both cores eventually reach a similar size (Fig. 4g,h). We also observe that the shapes of the cores fluctuate under laser irradiation (Movies 1-3). This suggests that the cores melt after every laser pulse and then resolidify in varying configurations. Indeed, we estimate that after the laser pulse, the temperature of the cores initially exceeds the melting point of gold by hundreds of Kelvin, so that melting can be expected to occur rapidly, within tens of picoseconds.[36] We also frequently observe that the formation of a second gold core competes with the fusion of both cores, as illustrated by the sequence of micrographs in Fig. 4i-p. The core of the nanoparticle in Fig. 4i initially emits two small fragments (Fig. 4j). However, these particles are then reabsorbed by the core (Fig. 4k).

This process then repeats two more times (Fig. 4l-o), until two well-separated cores of similar diameter are finally formed (Fig. 4p).

In order to better characterize the emitted fragments, we stop the laser irradiation once a gold core has ejected just a small number of fragments, and image them at high magnification (Fig. S1). We find that their diameters range from 0.7 to 2.5 nm (about 10 to 500 atoms). These fragments have likely been created in a single emission event, since particle ejection occurs with a considerable angular spread. As further fragments are emitted from the core, some of them will coalesce with other particles already implanted in the silica shell. We note that we cannot exclude that even smaller fragments or individual atoms are also emitted from the core, since they may not offer sufficient contrast against the background of the thick silica shell.

The ejection of individual, small particles from the core strongly suggests that we are observing Coulomb fission of the ionized, liquid gold core. This interpretation is consistent with the fact that the process appears to be driven by the ionization of the cores, as discussed above, and that the cores melt under our experimental conditions. We note that our observations are in contrast to the mechanism previously proposed for the fragmentation of gold nanoparticles suspended in water that were irradiated with femtosecond pulses.[28,29] Based on transient absorption spectroscopy and *ex-situ* product analysis, it was concluded that the nanoparticles undergo Coulomb explosion, shattering into a large number of fragments after a single laser pulse. Clearly, this mechanism does not operate under our experimental conditions.

The micrographs in Fig. 4 suggest that the laser polarization determines the direction in which progeny droplets are ejected, thus controlling the alignment of the resulting dual-cores. This may appear counterintuitive, since Coulomb fission can only occur once the core has melted, which requires tens of picoseconds.[36] Furthermore, the process of Coulomb fission itself can be estimated to require another 100 ps for a liquid gold droplet of 20 nm diameter that is charged to the Rayleigh limit (see Methods for details).[26] At this point, however, the molten gold particle should have lost any memory of the polarization of the laser pulse.

In order to resolve this apparent contradiction, it is important to realize that under our experimental conditions, the photoemission of electrons from the core is highly directional and predominantly occurs along the laser polarization direction. At incident peak fields of 10^8-10^9 V/m, such as those in our experiments, the ionization process is dominated by multiphoton emission.[20–22] The local emission current from the particle is therefore roughly proportional to the 2nth power of the electric field at the particle surface, where n is the number of photons required to overcome the work function of the metal.[37] Here, about two photons (2.4 eV) are necessary to overcome the work function of gold (5.1 eV). Since the field at the particle surface resembles that of an electric dipole, the photoemission current should therefore follow a $\cos^4(\theta)$ dependence, as shown by the red line in Fig. 2b. In other words, near-field enhancement leads to a preferential emission of electrons along the laser polarization direction, as has been observed for multiphoton emission from a range of different nanoparticles.[20–22] Electrons injected into silicon dioxide thin films are known to populate trap states with lifetimes of seconds,[38,39] far exceeding the timescale of Coulomb fission. The directional emission of electrons should therefore create an anisotropic charge distribution in the silica shell that persists long enough to steer the emission of progeny droplets, thus resulting in the alignment of the dual-cores. We note that a related mechanism has been proposed to induce the elongation of silver nanoparticles in bulk glass under irradiation with femtosecond pulses.[40,41]

While many of the dual-core particles are aligned according to the laser polarization, a significant fraction is randomly oriented, as evidenced by the angular distributions in Fig. 3a. Occasionally, the emission of the first progeny droplet occurs in a random direction, which appears to determine the final alignment of the dual-cores. We speculate that in these instances, inhomogeneities in the silica matrix surrounding the gold core steer the emission of the first progeny droplet into a direction different from that of the laser polarization. This creates a void in the silica shell, which then drives the emission of subsequent progeny droplets in the same direction. Ultimately, a channel linking both cores is formed in the silica shell.

Figure 5 summarizes the multistep formation mechanism of the dual-core particles. An ultrafast laser pulse (240 fs) ionizes the gold core, with photoemission of electrons occurring predominantly along the polarization direction of the laser, so that an anisotropic distribution of negative charge is created in the silica shell (Fig. 5a). In a second step, the gold core melts and the ionized droplet undergoes Coulomb fission on a timescale of 100 ps (Fig. 5b). The highly charged progeny droplets are preferentially ejected towards the areas of concentrated negative charge in the silica shell and coalesce into a second core (Fig. 5c), a process that occurs in a matter of seconds. Lastly, the second core continues to grow through repeated absorption of progeny droplets, until both cores reach equal size (Fig. 5d). This process is complete after several minutes. We note that once the second core has formed, it can also be observed to undergo Coulomb fission. Progeny droplets are then continuously ejected from either core and absorbed by the other, a process during which the void in the silica shell connecting both cores becomes more pronounced. We infer that the final configuration of two equally-sized cores corresponds to a state of dynamic equilibrium.

For such a dynamic equilibrium to exist, the rate of mass ejection from a large droplet must exceed that of ejection from a small droplet. Although the kinetics of the system are complex, this is likely due to the fact that the volume of a progeny droplet is proportional to the volume of its parent droplet,[26] so that for every fission event, a larger droplet ejects more mass than a smaller droplet. Moreover, large gold particles are more easily ionized since the absorption cross section scales approximately with r^3 for gold particles of radii $r \leq 20$ nm.[33] Whereas larger droplets also require a higher critical charge in order to undergo fission, this critical charge only scales with $r^{3/2}$.[26]

Conclusion

In conclusion, we have presented an *in-situ* electron microscopy study of Coulomb fission in gold-core silica shell nanoparticles under femtosecond laser irradiation. Our experiments demonstrate the strength of *in-situ* observations on a single-particle level for elucidating complex mechanisms of laser reshaping of plasmonic nanoparticles that have only been incompletely understood and are difficult to study with other approaches. Our results also suggest a facile laser-mediated route for forming dual-core silica shell

nanoparticles, which otherwise require complex synthetic procedures.[42–45] Tuning the properties of the precursor particles should improve the yield as well as the degree of alignment of the dual-cores. This should, for example, make it possible to fabricate linearly dichroic surfaces of aligned dual-gold-core silica shell particles.

Methods

Estimate of the timescale for Coulomb fission. The timescale for Coulomb fission of the highly ionized liquid gold cores was estimated from the scaling behavior derived from numerical simulations.[26] The fission timescale, $t_{fission}$, is therefore given by

$$t_{fission} = \left(\frac{r^3 \rho}{\sigma}\right)^{\frac{1}{2}}$$

where r, ρ, and σ are the radius, density, and surface tension of the liquid gold core, respectively. Using $1.93 \cdot 10^4$ kg/m^3 and 1.15 J/m^2 for the density and surface tension,[46] respectively, a molten gold core of 20 nm diameter is expected to undergo fission on a timescale of 100 ps.

Figure 1. Formation of aligned dual-gold-core silica shell nanoparticles under femtosecond laser irradiation. (a,b) Micrographs of core-shell particles before and after femtosecond laser irradiation (22 mJ/cm^2, 10^6 pulses). The polarization is indicated with a double-headed arrow. Scale bar, 50 nm. (c) *In-situ* determination of the laser polarization (double-headed arrow) with photon-induced near-field electron microscopy. An energy gain-filtered image of a gold nanoparticle shows the dipolar near-fields during laser excitation. This experiment maps out a particular Fourier component of the z-component of the electric field, as encoded by the color scale. Scale bar, 100 nm. (d-f) At higher fluence (43 mJ/cm^2), the gold cores split into multiple particles. Scale bar, 15 nm. The double-headed arrow denotes the laser polarization.

Figure 2. Angular distribution and yield of the dual-cores as a function of laser fluence. (a,b) Angular distributions for two different laser fluences ($6 \cdot 10^6$ pulses). The red line in (b) represents an estimate of the relative photoemission current from the core. (c) Angles θ are measured as illustrated. The laser polarization is indicated with a double-headed arrow. (d) Angular spread (as measured by the standard deviation) as a function of laser fluence and linear fit (solid line). (e) Yield of dual-core particles as a function of laser fluence and linear fit (solid line).

Figure 3. Effects of laser polarization and pulse duration on the formation of dual-cores. (a) Angular distributions for orthogonal laser polarizations (-53° and +37°, indicated with double-headed arrows; $6 \cdot 10^6$ femtosecond pulses; 30 mJ/cm^2). The distributions peak at -49° and +36°, as determined from Gaussian fits with constant offsets. (b) Angular distributions after illumination with circular polarization ($6 \cdot 10^6$ femtosecond pulses, 30 mJ/cm^2). (c) After nanosecond laser irradiation ($6 \cdot 10^6$ pulses, 1 ns, 41 mJ/cm^2) the gold cores have evaporated. The polarization is indicated with a double-headed arrow. Scale bar, 50 nm.

Figure 4. *In-situ* observation of the formation of aligned dual-core particles. (a-h) Under femtosecond laser irradiation, the gold core ejects small droplets, which accumulate and fuse into a second core of equal size. (i-p) A core-shell particle undergoes repeated cycles in which a second core is formed and subsequently fuses again with the first. The laser polarization is indicated with a double-headed arrow in (a). Scale bar, 20 nm.

Figure 5. The formation mechanism of dual-core particles. (a) The femtosecond laser pulse ionizes the gold core. Electrons are preferentially ejected along the polarization direction. (b) The ionized gold core melts and undergoes Coulomb fission through emission of a highly charged progeny droplet. (c) Several progeny droplets accumulate and fuse into a second core. (d) A dynamic equilibrium is reached between both cores as they continue to fission.

Associated Content

The Supporting Information is available free of charge on the ACS Publications website at DOI: xzy.

Movies showing gold core fragmentation, captions for Movies, high magnification TEM images of small progeny particles.

The authors declare no competing financial interests.

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