Supplementary Information

In situ TEM ion irradiation and implantation effects on Au nanoparticle morphologies

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Experimental

The *in situ* ion irradiation TEM (I^3TEM) facility consists of a JEOL (Tokyo, Japan) JEM-2100 TEM connected to both an EN Tandem (0.8 - 6 MV, National Electrostatics Corporation, Middleton, WI, USA) and a Colutron accelerator (0.5 - 10 kV, Colutron Research Corporation, Boulder, CO, USA). There are only ~10 such active facilities in the world.[1] These various facilities were purpose-built to examine different ion beam effects, and thus employ a variety of different microscopes, ion sources, energies, and beam geometries to meet those specific goals. The I^3TEM is unique in that it allows for concurrent high- and low-energy ion beams of a broad range of species through the same port, minimising potential directional effects like shadowing. This facility allows the collection of in-depth information about radiation effects on the nano- or microstructure of materials as a function of ion species, dose rate, total dose, and irradiation environment.

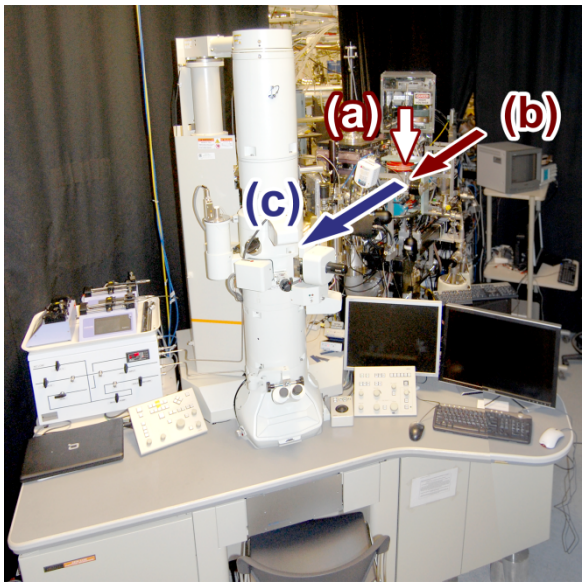

Fig. S1. The I^3TEM and associated hardware: (a) Colutron beam line, (b) Tandem beam line, and (c) combined beam line connected to the TEM.

Supplementary Information

The NPs used in the 3 MeV Cu^{3+} irradiation experiments were purchased from Sigma Aldrich (St Louis, MO, USA). These NPs were citrate-stabilised and 20 nm in diameter. Au NPs were drop-cast deposited onto holey carbon type-B, 300 mesh, copper TEM grids from Ted Pella, Incorporated (Redding, CA, USA). The NPs thus sat on the carbon support film surface, i.e. they were not embedded in a matrix, and more closely approximated freestanding nanoparticles. One grid per experiment was loaded into the I^3TEM using either a JEOL single- or double-tilt TEM stage. At the time these experiments were performed, Cu was the heaviest element that could reliably produce a stable beam with good current within the TEM. The system has since been refined, and elements as heavy as Au are now usable.

The Au NP samples used for the 10 keV He^+ implantation experiments were synthesised according to Frens,[2] with some minor adaptions. Auric acid ($HAuCl_4$) and trisodium citrate dihydrate (Na_3-cit) were used as received from Aldrich. A 0.04 M Na_3-Cit (0.30 g, 1.0 mmol ~26 mL water) solution and a 0.001 M $HAuCl_4$ (0.14 g, 0.41 mmol in ~400 mL water) solution were synthesised. To a stirring auric acid solution, 6.0 mL of a Na_3-Cit was rapidly added, which immediately turned blue, and then after about 1 minute, a red solution persisted. The reaction mixture was immediately quenched in an ice bath. This solution was similarly drop-cast deposited onto carbon film TEM grids. Particles were ~60 nm in diameter.

Ion irradiation with 3 MeV Cu^{3+} ions was performed using a Tandem accelerator with a dose rate of ~5-11 $\times$ 10^{11} $Cu^{3+}/cm^2/s$. During Cu^{3+} ion irradiation, the ion beam spot size was determined by performing beam burns using tape adhered to a custom single tilt holder. The Cu^{3+} beams from the Tandem typically had a minimum uniform area at least as large as the 3 mm diameter TEM grid.

Light ion irradiation with 10 keV He^+ ions was performed with a Colutron Model G-1 ion gun at a dose rate of ~1 $\times$ 10^{15} $He^+/cm^2/s$. Due to the substantial difference between the

two beam energies and ion masses, it is possible to steer the two beams by means of a bending magnet into the TEM along the same path, eliminating potential shadowing effects from having two beams incident from different directions. To estimate beam sizes during He^+ implantation, a quartz covered TEM holder tip (which acted as a scintillator) was inserted into the microscope, and a video camera system was used to view the size of the resulting fluorescent spot. These scintillator tips also allowed for straightforward alignment of the ion beam to the sample position. In contrast to the Cu^{3+} ion Tandem beams, the less energetic and lighter He^+ ion Colutron beam spot sizes were ~3 mm in diameter and somewhat oblong (due to bending from the TEM pole piece). Ion currents from the Tandem accelerator were measured by means of a Faraday cup mounted ~30 cm before the specimen. Colutron beam currents were measured by means of a specialised TEM holder consisting of a miniaturised unsuppressed Faraday cup.

The I^3TEM was operated at 200 kV and 100 pA/nm^2. A sample tilt of +30° was used to eliminate shadowing of either the electron or ion beam during the experiment. TEM micrographs were recorded using Tietz Video and Image Processing Systems (TVIPS) cameras. A TemCam-F416 (4096x4096) camera was used to collect still micrographs (including those for tomograms), and a FastScan-F114TR (1024x1024) camera was used in frame transfer mode to record video at 12 frames per second.

Sputtered particle distributions were determined by measuring particle area with ImageJ (National Institutes of Health, Bethesda, MD, USA). Given that most particles appeared to be roughly spherical, particle radius was estimated by taking $r = \sqrt{A/\pi}$. Particle volume was then determined from this radius.

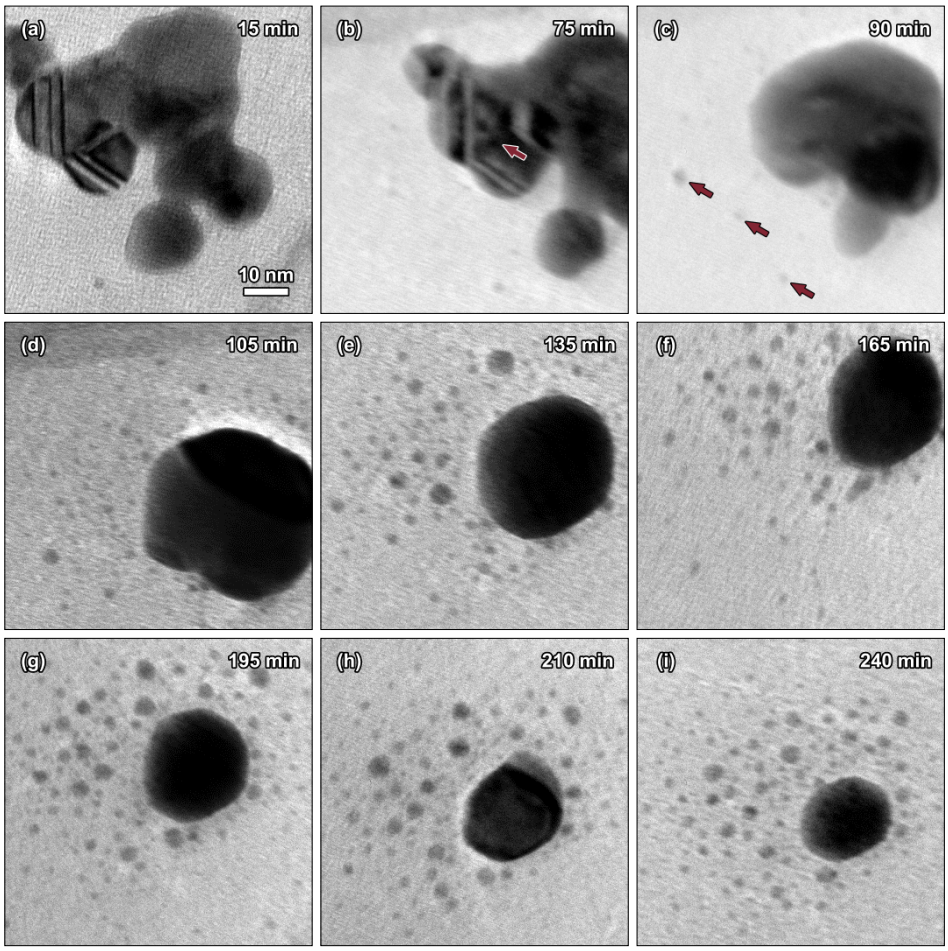

Fig. S2. Micrographs showing Au NPs during *in situ* ion irradiation with 3 MeV Cu^{3+} after [min (exposure x 10^{15} Cu^{3+}/cm^2)]: (a) 15 (~0.75), (b) 75 (~3.4), (c) 90 (~4.1), (d) 135 (~6.1), (e) 195 (~8.8), (f) 240 (~11). Scale bar is the same for all micrographs. Red arrows in (b) and (c) indicate an annihilated twin and sputtered particles, respectively.

Note that the halos in Fig. S2d-f were asymmetric about the large NP cluster, a possible indication of a directional effect. The most notable changes up to 75 min (~3.4 × 10^{15} Cu^{3+}/cm^2) consisted of neck growth between particles, and the loss of one twin boundary (Fig. S2a-b). Significant morphological changes occurred by 90 min (~4.1 × 10^{15} Cu^{3+}/cm^2); the NPs had coalesced into a single mass, twin and grain boundaries were not distinguishable, and a surrounding halo of ejected material had formed (Fig. S2c).

In TEM micrographs, a 2-D projection of a 3-D object is recorded. While useful information can be obtained from the images during ion irradiation, more information regarding structural damage caused by ion irradiation was desired. To obtain this, an electron tomography data collection technique was employed that, after processing, generates a 3-D

model of the irradiated sample. Electron tomography involves recording images about a tilt axis every few degrees over the desired tilt range, then processing the images together to form a 3D reconstruction.[3] Here, tilt series were collected by taking an image every 2° of tilt on the x-axis from -42° to +42°. An initial tilt series was collected at the region of interest (ROI) prior to irradiation. Subsequently, the ROI was tracked manually during irradiation for a prescribed time interval. Then, the ion beam was blocked by means of a Faraday cup, and the sample was allowed to cool to eliminate drift before acquiring the next tilt series. Collecting such sets of tomography data after short periods of irradiation allowed for a sequence of 3D reconstructions representing structural damage to the Au NP over time, or as a function of dose rate. The conventional 2D micrographs and 3D tomography reconstructions, when examined together, give a comprehensive view of the radiation damage caused to the NPs by heavy ion irradiation. Please see the attached tomogram movies from which the panels of Fig. 2 were selected.

The electron beam induced some sintering, even under typical imaging conditions, as seen in Fig. S3. To minimise these effects, Cu^{3+} and He^{+} irradiation were performed in intervals while observing a nearby area or with the electron beam blanked, respectively. Images were collected between the irradiation intervals as quickly as possible, while using the lowest intensity possible. The NPs in the tomography tilt series were under constant observation, and there was likely some influence from the electron beam. However, the behaviour of those NP clusters was similar to the NP clusters irradiated by Cu^{3+} without the electron beam, i.e. the ion beam effects were far more prominent than the sintering induced by the electron beam.

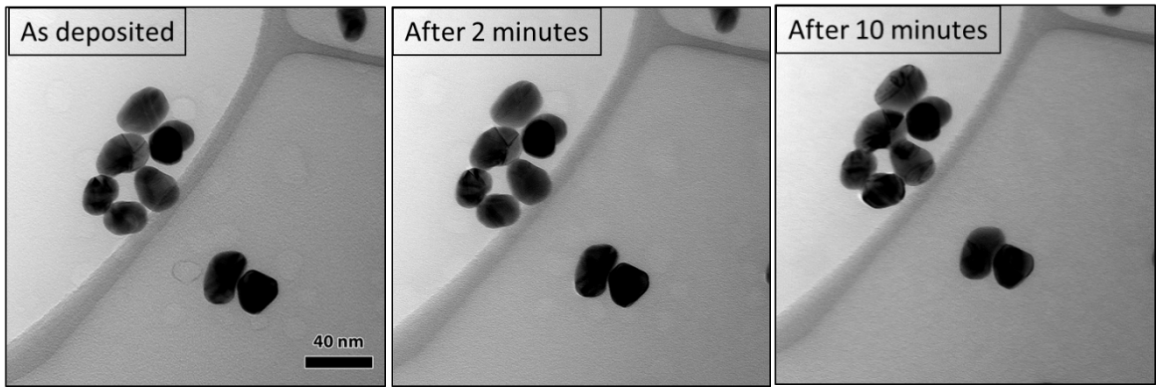

Fig. S3. Example of electron beam-induced sintering of Au NPs over a 10 minute time period. The beam was incident at typical imaging intensity (200 kV, ≤100 pa/cm^2), and no ion beam was present.

Upper-bound estimation of energy required to melt Au NPs

Property	Value	Unit
Melting point	1337.33	K
Heat capacity (at 25 ºC)	0.129	J/g/ºC
Latent heat of fusion	63	J/g
Density	1.932×10^7	g/m^3

Table S1. Relevant properties of Au

Given a spherical 20 nm diameter Au NP, the mass is 8.09×10^{-17} g. We make the simplifying assumptions of bulk melting temperature and unchanging heat capacity with temperature (Table S1). Heating the 20 nm NP particle from room temperature to its melting temperature (an increase of about 1000 ºC), and melting it thus requires approximately 192 J/g, which is ~1.55×10^{-14} J or ~97×10^3 eV. We note that this is an upper-bound estimation, as the bulk melting temperature is assumed, and small particle size is known to sometimes lead to a decrease in melting temperature.

SRIM/TRIM simulation details

Ion range simulations were performed using the Transport of Ions in Matter (TRIM) package within the Stopping Range of Ions in Matter (SRIM-2013) code.[4] Simulations were

performed with 5000 Cu^{3+} or He^{+} ions at normal incidence on a 20 nm layer of Au using the most detailed monolayer collision/surface sputtering methodology (Fig. S4). Outputs collected included backscattered, transmitted, and sputtered ions, as well as final ion position.

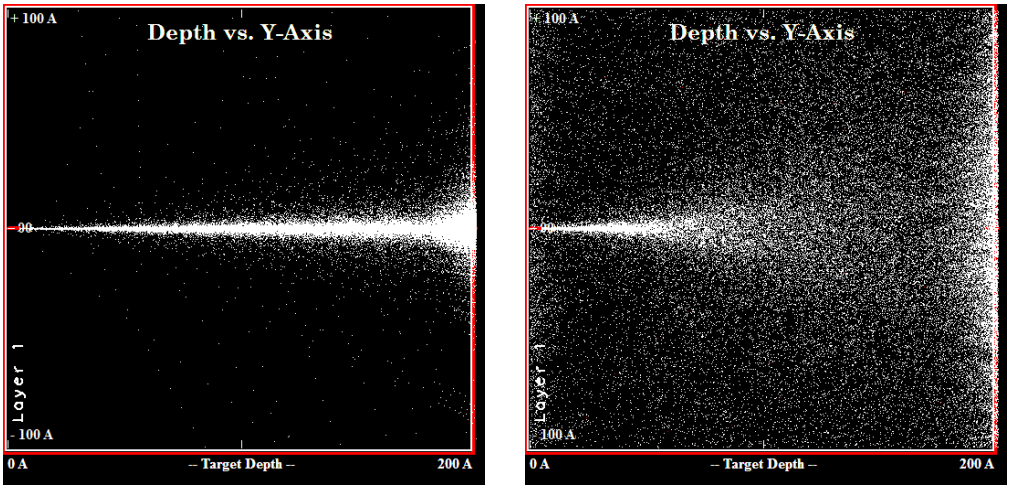

Figure S4. TRIM simulation output showing ion bombardment into a 20 nm Au layer. The white dots represent ion trajectories resulting from 5000 ions of (a) 3 MeV Cu^{3+} and (b) 10 keV He^{+}.

For He ions, 2.4% stopped within the layer, 19.6% were backscattered, and the rest were transmitted. For Cu, no ions stopped within the layer; 99.92% were transmitted, and the remaining 0.08% were backscattered (Fig. S5). TRIM estimated sputter yields of 3.5 and 0.21 atoms/ion for 3 MeV Cu and 10 keV He, respectively. However, it is important to note that TRIM only considers sputtering from the flat surfaces.

The TRIM simulation output was also used to roughly estimate energy deposited by the bombardment. The program reports the final energy of each transmitted and backscattered ion, so the energy loss can be interpreted as energy deposited into the Au layer. Ions that stopped within the layer were treated as depositing all of their initial energy into the layer.

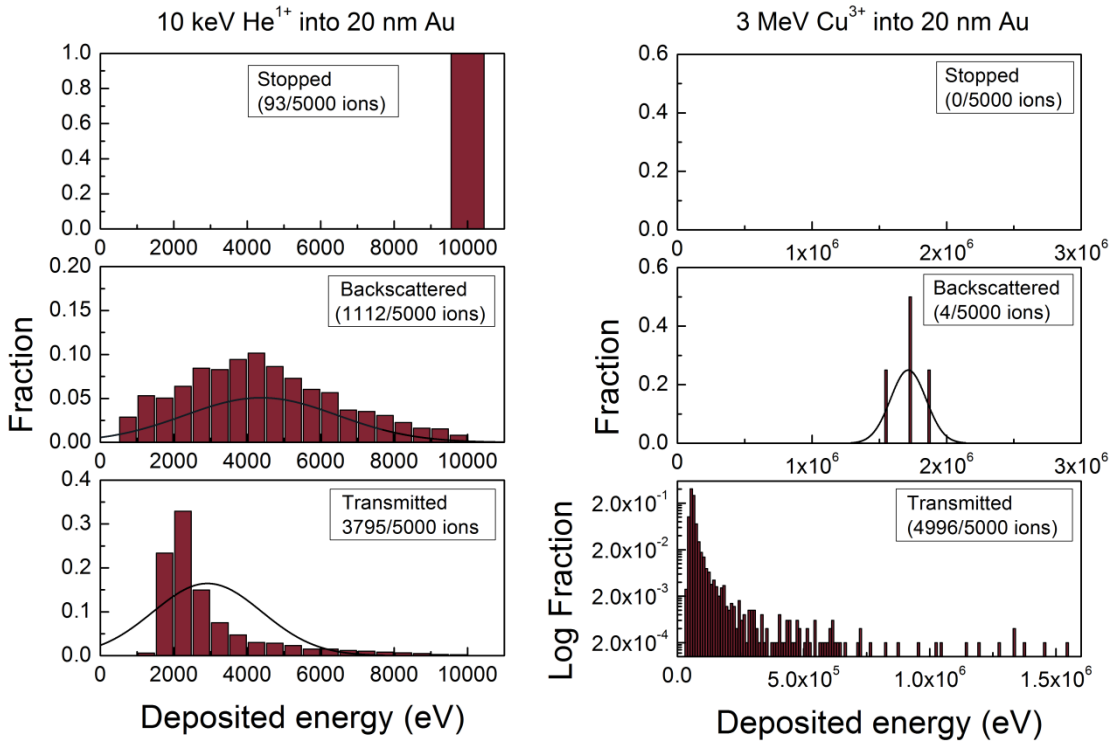

Fig. S5. Histograms showing the distribution of energies deposited into the Au layer during TRIM simulations of ion bombardment. The vertical axis "fraction" unit refers to the subset of ions in each panel, e.g. in the second panel the bars represent the fraction of the 1112 backscattered ions with given energies.

References

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2. G. Frens, *Nature-Phys Sci*, 1973, **241**: 20-22.
3. P. A. Midgley and R. E. Dunin-Borkowski, *Nat Mater*, 2009, **8**: 271-280.
4. J. F. Ziegler, M. D. Ziegler and J. P. Biersack, *Nucl Instrum Meth B*, 2010, **268**: 1818-1823.