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Evolution of Gold Nanoparticles in Radiation Environments

Samuel A. Briggs and Khalid Hattar

Abstract

Gold nanoparticles are being explored for several applications in radiation environments, including uses in cancer radiotherapy treatments and advanced satellite or detector applications. In these applications, nanoparticle interactions with energetic neutrons, photons, and charged particles can cause structural damage ranging from single atom displacement events to bulk morphological changes. Due to the diminutive length scales and prodigious surface-to-volume ratios of gold nanoparticles, radiation damage effects are typically dominated by sputtering and surface interactions and can vary drastically from bulk behavior and classical models. Here, we report on contemporary experimental and computational modeling efforts that have contributed to the current understanding of how ionizing radiation environments affect the structure and properties of gold nanoparticles. The future potential for elucidating the active mechanisms in gold nanoparticles exposed to ionizing radiation and the subsequent ability to predictively model the radiation stability and ion beam modification parameters will be discussed.

Keywords: radiation damage, gold nanoparticles, sputtering, radiation therapy, ion beam modification

1. Introduction

Ionizing radiation is known to have the ability to drastically alter material microstructure and performance primarily through the displacement of constituent atoms from their lattice sites, resulting in the generation of damage and point defects [1, 2]. These point defects tend to diffuse and coalesce into larger, ordered defect structures such as dislocation loops, cavities, and stacking faults, typically resulting in deleterious effects in structural materials such as radiation-induced hardening and embrittlement or void swelling [1, 2]. Irradiation can also cause solute redistribution in alloys and composite materials, encouraging the precipitation of secondary phases or promoting localized corrosion, which has been utilized in metal, ceramics, and polymers to provide added functionality not previously possible [3–8]. The fundamental mechanisms of radiation damage and the subsequent effects on materials properties and performance have been and continue to be heavily studied in commonly used and candidate materials for nuclear reactor and extraterrestrial applications.

While the potential effects of ionizing radiation environments are not commonly considered when discussing nanoparticle performance, there are a subset of both current and potential future applications for gold nanoparticles that

necessitate investigation and understanding of how their structure and properties change when exposed to energetic photons and particles. Radiation therapy is likely one of the most notable examples, in which gold nanoparticle injections in the vicinity of a tumor or conjugation to antibodies such that they preferentially bind to cancer cells have been shown to increase local radiation dose during X-ray irradiation through secondary photon interactions, thus lessening the absorbed dose in surrounding healthy tissue [9–13]. A similar local dose enhancement effect has been shown for proton and heavy ion irradiation therapies, which are being pursued to further reduce dose to healthy tissue as a consequence of how energetic charged particles deposit a majority of their energy at the end of their range [14–16]. Furthermore, potential applications in satellites or space electronics would involve bombardment with high-energy cosmic radiation [17, 18].

The mechanism of radiation damage in materials with limited dimensions has been shown to be significantly different from bulk material behavior [19–23]. Due to the prodigious surface-to-volume ratio of nanoparticles compared to even thin films, they have emerged as an attractive material choice for many applications. However, this same surface-to-volume ratio results in sputtering and free surface effects ultimately dominating the radiation response [20, 21]. Put simply, instead of diffusing into organized defect structures, the generated point defects tend to annihilate at the particle surface, or material is ejected from the particle volume, as a result of the energetic collision [24, 25]. This can drastically alter the shape of individual particles and cause agglomeration of closely spaced particle groupings [26–28]. Such morphological changes have the potential to adversely affect their efficacy in applications where the high surface-to-volume ratio and local structure are essential for performance.

This chapter attempts to summarize the current body of work relating to interactions of ionizing radiation with gold nanoparticles. Broader reviews of the interaction of nanostructured materials can be found in the detailed reviews by A.V. Krasheninnikov and K. Nordlund titled “Ion and electron irradiation-induced effects in nanostructured materials” [21] and the more recent review by X. Zhang et al. titled “Radiation damage in nanostructured materials” [29]. As one might expect, the interactions of radiation with elemental gold is highly dependent on the species of the incident radiation. Both the length scales of interaction and energy transferred per interaction event can vary widely due to the energy, mass, and charge of incident radiation, as highlighted in **Figures 1** and **2**. As such, this chapter

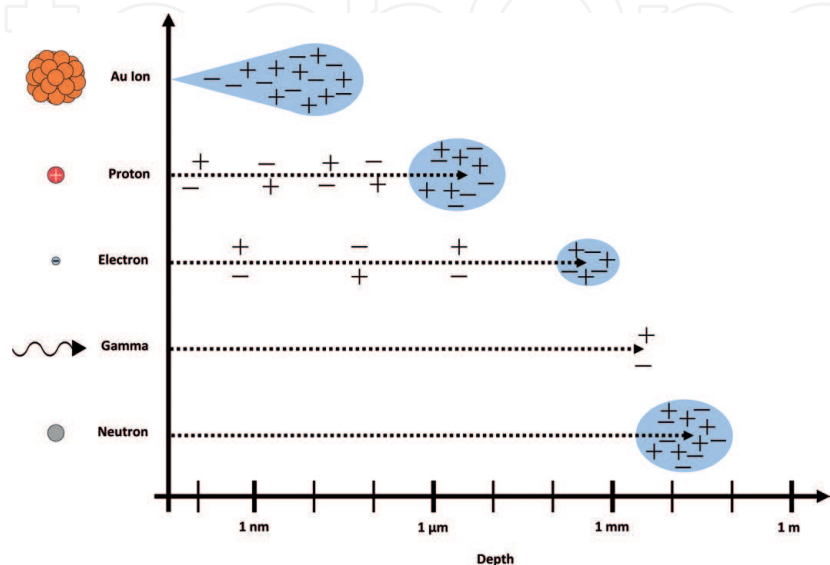


Figure 1. Illustration of the relative average interaction length scales for various types of radiation at an energy of 1 MeV incident on gold. Dotted lines indicate the mean free path of the incident particles. Positive and negative signs indicate ionization events, while blue highlighted areas denote displacement damage cascades.

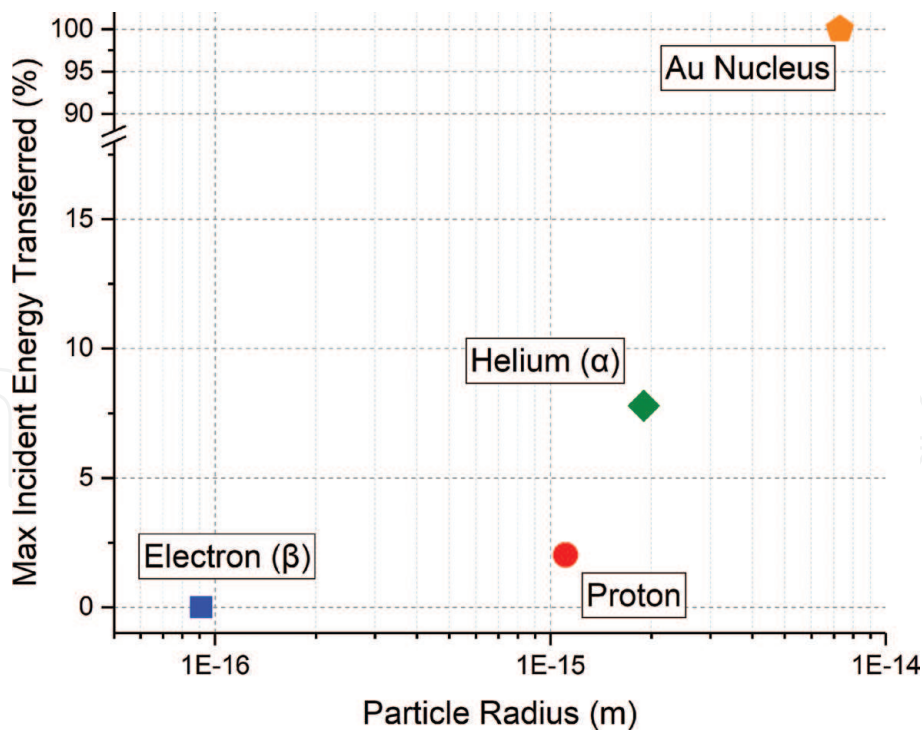


Figure 2.
Plot showing the theoretical maximum fraction of incident particle energy transferred via a ballistic collision of various particle types with a gold atom.

is organized according to the type of radiation environment a gold nanoparticle might encounter, and the subsequent sections highlight experimental studies of how the structure and properties of gold nanoparticles are altered by bombardment with specific types of energetic radiation. Section 2 discusses ionizing photon interactions, while Section 3 considers neutron environments. Sections 4–6 focus on different types of charged particle irradiation: beta particles (electrons/positrons), light ions (protons through alpha particles), and heavy ions. Section 6 also explores potential applications of ion beam modification in both freestanding and embedded gold nanoparticles from heavy ion bombardment. Finally, Section 7 discusses future experimental and modeling work needed to enhance our understanding of radiation effects in gold nanoparticles and speculates as to potential future applications combining gold nanoparticles with radiation environments.

2. Ionizing photon interaction with gold nanoparticles

The three primary interactions of photons with matter include the photoelectric effect, Compton scattering, and pair production [30]. In a photoelectric event, a photon completely transfers its energy to an orbital electron, ejecting it from its shell and ionizing the atom. This is the dominant interaction mechanism for low-energy ($E < \approx 0.5$ MeV) photons. In Compton scattering, an incident photon transfers a portion of its energy to an orbital electron, and both the electron and photon continue on, typically with different trajectories when compared to the incoming photon. This will be the dominant interaction mechanism for incident photons of intermediate energies (≈ 0.5 MeV $< E < \approx 2$ MeV). Finally, pair production dominates for high-energy photons and can only occur for incident photons greater than 1.022 MeV. In pair production, a photon interacts with the electromagnetic field surrounding the atomic nucleus and is converted into an electron and a positron, with the total photon energy less the rest energy of the two particles (0.511 MeV each) being shared between them. It should be noted that for high photon energies

(> \approx 8 MeV), photodisintegration can also occur, in which the incident photon causes the atom to emit one or more neutrons, potentially resulting in a radioactive isotope of gold [31].

Since incident photons interact primarily with the orbital electrons, the high atomic number (79) and density (19.32 g/cc) of gold significantly increase the likelihood of interaction compared to most other materials. The creation of secondary ionizing radiation through these photon interactions is the primary reason for the attractiveness of gold nanoparticles in radiation therapy applications [10]. Electrons and positrons resulting from the described interactions will lose their energy as Bremsstrahlung radiation (also known as braking radiation) as they slow down, and X-rays and Auger electrons will be produced as electrons shift from higher-energy orbitals to replace those ionized from lower-energy orbital positions. Furthermore, positrons generated from pair production will eventually annihilate with another electron, resulting in the generation of two 0.511 MeV photons. An illustration of these potential interaction mechanisms and resulting secondary radiation effects is shown in **Figure 3** [10]. This secondary radiation will typically deposit its energy in the vicinity of the gold particles, which can be taken advantage of to increase dose to cancerous cells [10, 11].

Photon irradiation experiments involving gold nanoparticles are prevalent, as X-ray therapies for cancer treatment are a fairly common practice [32–34]. While these studies are predominantly focused on the biological effects in the vicinity of cancerous tissue, they highlight how photons interact with these high atomic number (high-Z) nanoparticles to deposit their energy locally. High-energy photons are also expected to cause Frenkel pair displacement damage (i.e., vacancy and interstitial defect pairs), primarily through the energetic electrons that they tend to generate. However, the effects of these displacement effects on the long-term stability of nanoparticle structures, if any, have not been studied to our knowledge.

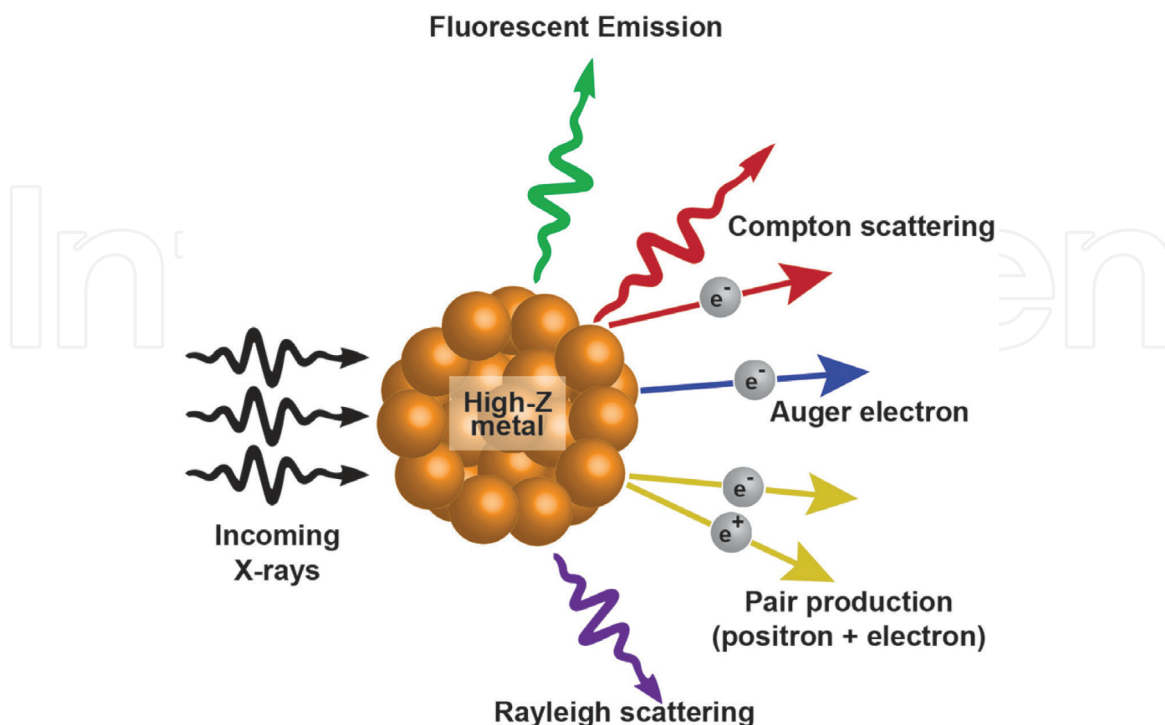


Figure 3.

Schematic illustrating potential interactions of incident photons with a gold atom or other high-Z materials [10]. Source: <http://tcr.amegroups.com/article/view/1550/html>. AME Publishing Company. Republished with permission of Pioneer Bioscience Publishing Company, from D. Kwatra et al., *Translational Cancer Research*, 2(4), pp. 332, 2013; permission conveyed through Copyright Clearance Center, Inc.

In addition to understanding the role of radiation on the nanoparticle and the surrounding material, a few research groups have shown that gamma and other forms of ionizing photons can even be used to induce nucleation and growth of nanoparticles out of solution including far-from-equilibrium structures that might be difficult to obtain through other more classical chemical synthesis routes [35, 36]. Most studies and reviews of the response of gold nanoparticles to various stimuli limit themselves to ionizing radiation produced by photons [37]. To expand these previous reviews and studies, the remainder of this chapter will focus on neutron, beta, alpha, and heavier charged particle irradiation effects on gold nanoparticles.

3. Neutron interaction with gold nanoparticles

To understand the interactions that can possibly occur between an energetic neutron and a gold nanoparticle, one must first understand the well-studied interaction of a neutron and a gold atom. As gold is monoisotopic, Au-197 is assumed as a target for the purposes of gauging probable interactions. Thus, neutron interactions with gold atoms are dominated either by radiative capture (n,γ) reactions or by scattering. Capture reactions are most prevalent for thermal neutron spectra ($E < 1$ eV), though there is a notable resonance absorption peak for energies near 4.9 eV and several other resonances between 60 eV and 2 keV [38]. This absorption reaction coincides with emission of a gamma ray with an energy between 4.78 and 6.52 MeV [39] and results in an Au-198 nucleus that subsequently decays to stable Hg-198 via beta particle emission with an energy release of 1.37 MeV and a half-life of 2.7 days. The reaction can also potentially result in two metastable states of Au-198 that emit 312 and 811 keV gamma rays with half-lives of 124 ns and 2.3 days, respectively.

Scattering interactions are more common for higher energy neutron spectra. Due to the large difference in mass between neutrons and gold nuclei, neutrons undergoing elastic scattering interactions (i.e., ballistic collisions) only transfer approximately 1% of their energy to the nucleus [1]. Inelastic scattering interactions, though less common, can transfer significantly more energy, leaving the nucleus in an excited state that results in gamma ray production. With sufficiently energetic incident neutrons, both scattering mechanisms are capable of generating gold primary knock-on atoms (PKAs) and generating displacement damage in the material microstructure.

No evidence of experimental work investigating neutron effects on individual particle structure or morphology was found, likely due to the challenges associated with working with neutron beams or research reactors and the high fluences required to induce appreciable damage. The mean free path (average distance traveled before interaction) of a neutron is much higher than that of a charged particle due to the lack of Coulombic interaction (see **Figure 2**), such that a vast majority of neutrons incident on a gold nanoparticle are not expected to result in a damage event. However, local injection of gold nanoparticles has recently been shown to enhance the effectiveness of neutron radiation therapies [40].

4. Beta particle interaction with gold nanoparticles

Charged particles are common by-products of radioactive decay and nuclear reactions and are a primary component of cosmic radiation. Accelerators and ion beams are also common ion sources used in both research and industry. For example, ions are frequently used in radiation damage experiments to simulate material microstructures resulting from neutron radiation exposure in nuclear

reactor environments primarily because it is much less costly and can achieve similar damaged microstructures in a fraction of the time [41]. Accelerators also have a slew of other potential applications ranging from materials analysis (e.g., electron microscopes, Rutherford backscattering) to ion beam modification.

Beta (electron or positron) radiation either incident on or produced in gold will primarily lose its energy via ionization and Bremsstrahlung radiation. As mentioned in the introduction, Bremsstrahlung radiation occurs due to electron acceleration from interaction with an atomic nucleus and results in the production of a photon of energy equal to the energy lost by the electron. This interaction is again Z-dependent and is quite common for high-Z materials like gold [42]. While displacement or knock-on damage resulting from electrons is commonly observed in transmission electron microscopy experiments [43], the significant difference in the masses of an electron and a gold nucleus requires electron energies in excess of 1.35 MeV to create a single Frenkel pair [44]. In many cases the role of the electron beam in altering the nanoparticle stability during these studies is not a result of interaction with the gold atoms itself, but with the organic capping ligands, as a result the stability of the gold nanoparticles to beta radiation is often dictated by the organic capping agent chosen [45]. One of the many examples of gold nanoparticle sintering due solely to electron beam effects can be seen in **Figure 4** [68]. The details of the particle orientation, organic capping, support film, and electron beam condition will alter the sintering rate, particle reorientation, and possible grain boundary character formed during the sintering process. This area is well studied in the electron microscopy community and is not reviewed further in this chapter. Interested readers are referred to the newest edition of the classic Williams and Carter textbook, which contains significant additions discussing a range of electron beam effects [43].

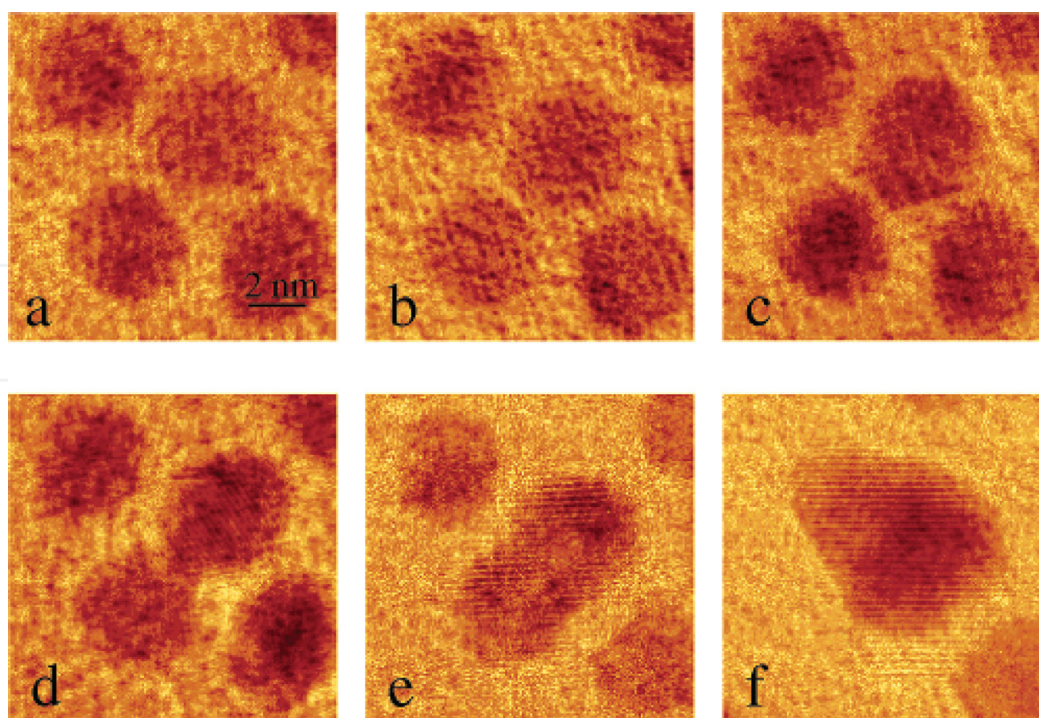


Figure 4. Bright-field TEM images of dodecanethiol-passivated gold nanoparticles with core diameter 4.8 nm (a) before and after focused 200 keV electron beam irradiation with a dose of (b) 7.1, (c) 16.4, (d) 33.7, (e) 73.7, and (f) 149.8 $\mu\text{C}/\mu\text{m}^2$ [68]. Source: <https://pubs.acs.org/doi/abs/10.1021/la0533157>. American Chemical Society. Reprinted with permission from Y. Chen et al., *Langmuir*, Vol. 22, pp. 2851, 2006. Copyright 2006 American Chemical Society.

5. Light ion interaction with gold nanoparticles

For the purpose of this chapter, light ions will be defined as energetic particles as light as proton or as heavy as helium ions (alpha particles). Alpha particles are common products of radioactive decay for actinides and other heavy radioactive isotopes, but, along with protons, deuterons, and tritons, they can also result from and induce a number of different nuclear reactions. For example, irradiation of Au-197 with protons with energies of 4.5 MeV or higher can cause a (p,n) reaction resulting in the production of metastable Hg-197m [46]. However, threshold energies of these reactions for gold are, in most cases, sufficiently high and reaction cross sections sufficiently low that these types of interactions rarely occur in practical applications. More often, light ions will interact via ionization and through Coulombic forces. Similar to the other types of interactions discussed, ionization has the potential to result in the emission of characteristic X-rays and other secondary radiations. Coulombic interactions with other atomic nuclei can tend to cause displacement damage, usually in the form of Frenkel pairs or small, isolated cascades.

Proton irradiation experiments have commonly been conducted in the context of increasing local dose for proton therapy-based applications [16, 47, 48]. Again, the primary mechanism for this dose enhancement comes from local energy deposition from ionization and secondary radiation that is produced. He irradiation experiments are not typically performed, but the effect can be assumed to be similar. Evidence of the effects of proton and He irradiation on individual gold nanoparticle structure is lacking in the literature.

6. Heavy ion interaction with gold nanoparticles

Energetic heavy ions, which will be defined as ions heavier than a helium atom, can result from recoil following a nuclear reaction, decay, or fission events, though sources relevant to gold nanoparticle applications will often likely come from particle accelerators. Initiation of nuclear reactions with heavy ion irradiation is improbable, and energy is typically deposited via ionization and Coulombic interaction similar to their less massive counterparts. The primary distinction is that, due to their size, heavy ions are capable of transferring much more energy to the gold atoms they interact with, resulting in large displacement damage cascades (see **Figures 1** and **2**). Cascade clustering, in which several point defects are formed as a result of a single interaction event and coalesce into larger and less mobile defect structures, results in a much more disordered microstructure and production of a smaller fraction of freely migrating defects. Complex interactions between these point- and multi-defect structures can significantly affect their stability and mobility [49]. As alluded to in the introduction, the effects of limited dimensions in the formation of surface cascades and sputtering in gold have been well known for over two decades [50]. At these limited dimensions, the effect of viscous flow during ballistic interactions is thought to have a significant role [50, 51]. These and many other size effects resulting from heavy ion irradiation in gold nanoparticles will be explored in greater detail in the following subsections.

6.1 Radiation stability of freestanding gold nanoparticles

In general, the response of nanostructured materials to radiation damage is still poorly understood [29]. Despite the limited understanding in the general field, freestanding gold nanoparticles (usually drop casted onto carbon or silicon nitride TEM

grids) have been used as the model system for testing and validation of TEM with in-situ ion irradiation capabilities [52–54]. Expanding on the known enhanced sputtering rates observed in gold thin foils exposed to a range of noble gas ions [55], it was later shown by Ilinov et al. that gold nanorods irradiated with 80 keV Xe demonstrated sputtering rates with three orders of magnitude higher than predicted by classical sputtering simulations [27]. These results have been verified multiple times in various facilities around the world. A detailed qualitative example can be seen in **Figure 5** [56]. By performing in-situ TEM experiments, individual nanoparticles, as well as the individual number of ion strikes on that particle, can be tracked for the duration of the experiment. This surprising set of results means that classical models and expectations no longer hold true when predicting the radiation response of gold nanoparticles.

These experimental results contradict the classic Monte Carlo-based simulations of sputtering effects [57]. A more catastrophic image of radiation damage in various sizes and morphologies of gold nanoparticles is predicted by molecular dynamic simulations of heavy ion irradiation [20, 26, 27, 56, 58]. An example of these types of simulations comparing the expected sputtering from a flat surface versus significantly increased sputtering from a nanoparticle can be seen in **Figure 6** [58]. The recent work has correlated the in-situ TEM observation of nanorod evolution and sputtering with molecular dynamic simulations that provide greater insight into the role of local crystal orientation on the effects of individual ion strikes relative to the nanoparticle orientation [26, 56]. The sputtering of the nanoparticles has also been tied to sintering of clustered gold nanoparticles, which is not surprising due to the work imparted into such a small volume. This is best seen when the particles are examined via electron tomography, as can be seen in **Figure 7** [28]. Despite the higher number of studies into the radiation stability of gold nanoparticles, few studies explore the effects of gold particle size and morphology or the myriad of irradiation environmental variables. One of the few systematic studies looked at the response of gold nanoparticles during self-ion

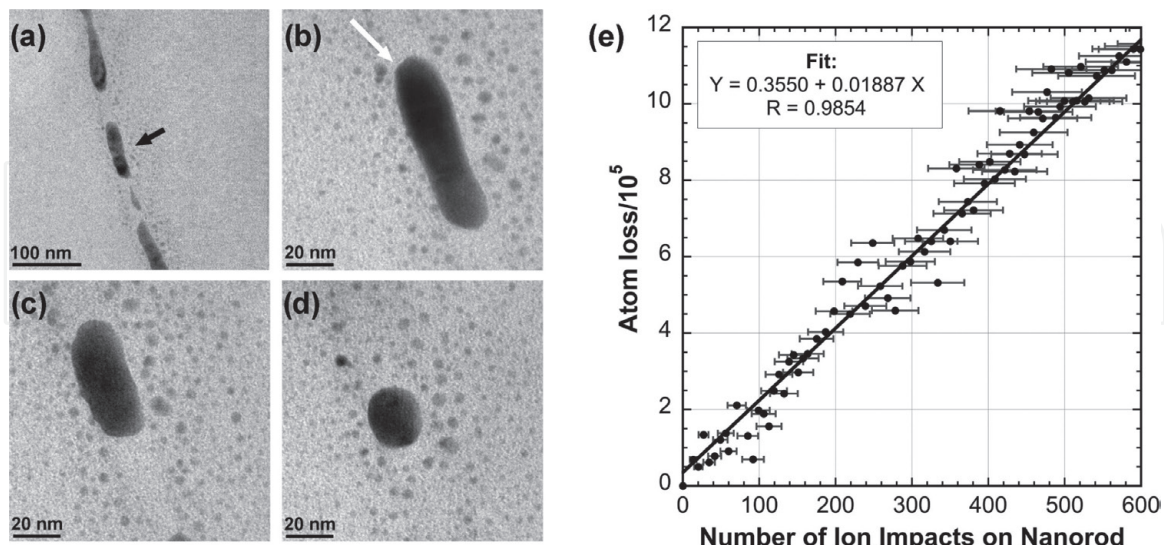


Figure 5.

*Changes to Au nanowire due to irradiation with 80 keV Xe ions. (a) Segmentation due to “necking” and breaking of nanowire at grain boundaries following irradiation to a fluence of $2.1 \times 10^{14} \text{ cm}^{-2}$, (b) nanorod at starting point for volume measurements—white arrow indicates projected direction of the ion beam which was incident at 60° to the specimen plane, (c) nanorod following irradiation to (additional) fluence of $1.6 \times 10^{13} \text{ cm}^{-2}$ (≈ 227 impacts on nanorod), (d) nanorod following irradiation to (additional) fluence of $5.5 \times 10^{13} \text{ cm}^{-2}$ (≈ 316 additional impacts on nanorod). All are bright-field TEM images and (e) plot of atom loss versus ion impacts for Au nanorod shown in panels (b)–(d) [56]. Source: <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.111.065504>. American Physical Society. Reprinted figure with permission from G. Greaves et al., *Physical Review Letters*, Vol. 111, pp. 065504-1, 2013. Copyright 2013 by the American Physical Society.*

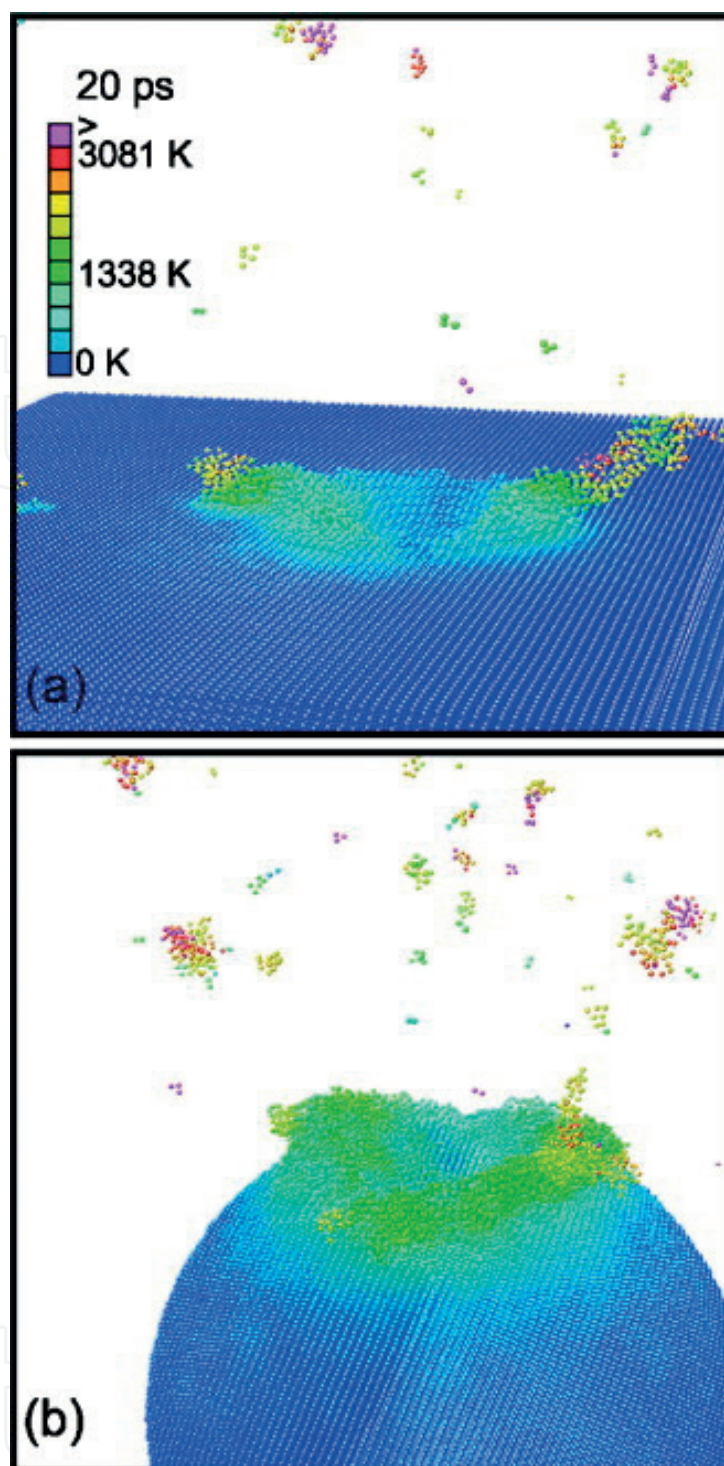


Figure 6. Perspective view of 16 keV Au impact on (a) plane surface and on (b) nanoparticle at time = 20 ps after impact. Color denotes the local temperature [58]. Source: <https://www.sciencedirect.com/science/article/pii/S1387380608000195>. Elsevier B.V. Reprinted from International Journal of Mass Spectrometry, Vol. 272, S. Zimmermann and H.M. Urbassek, “Sputtering of nanoparticles: Molecular dynamics study of Au impact on 20nm sized Au nanoparticles,” pp. 91-97, Copyright 2008, with permission from Elsevier.

irradiation. This study explored particles with average diameters of 5, 20, and 60 nm and altered the gold ion energy between 46 keV, 2.8 MeV, and 10 MeV [59]. It is very clear from the results presented in **Figure 8** that the response and stability of nominally spherical gold nanoparticles are heavily dependent on the order of magnitude changes in particle diameter, as the diameter approaches that of the cascade volume. Another heavy ion irradiation effect that has been noted at an even higher energy regime (956 MeV Pb) is that the nanoparticles can be ejected or desorb from the surface as a result of ion irradiation [60]. The combination of the

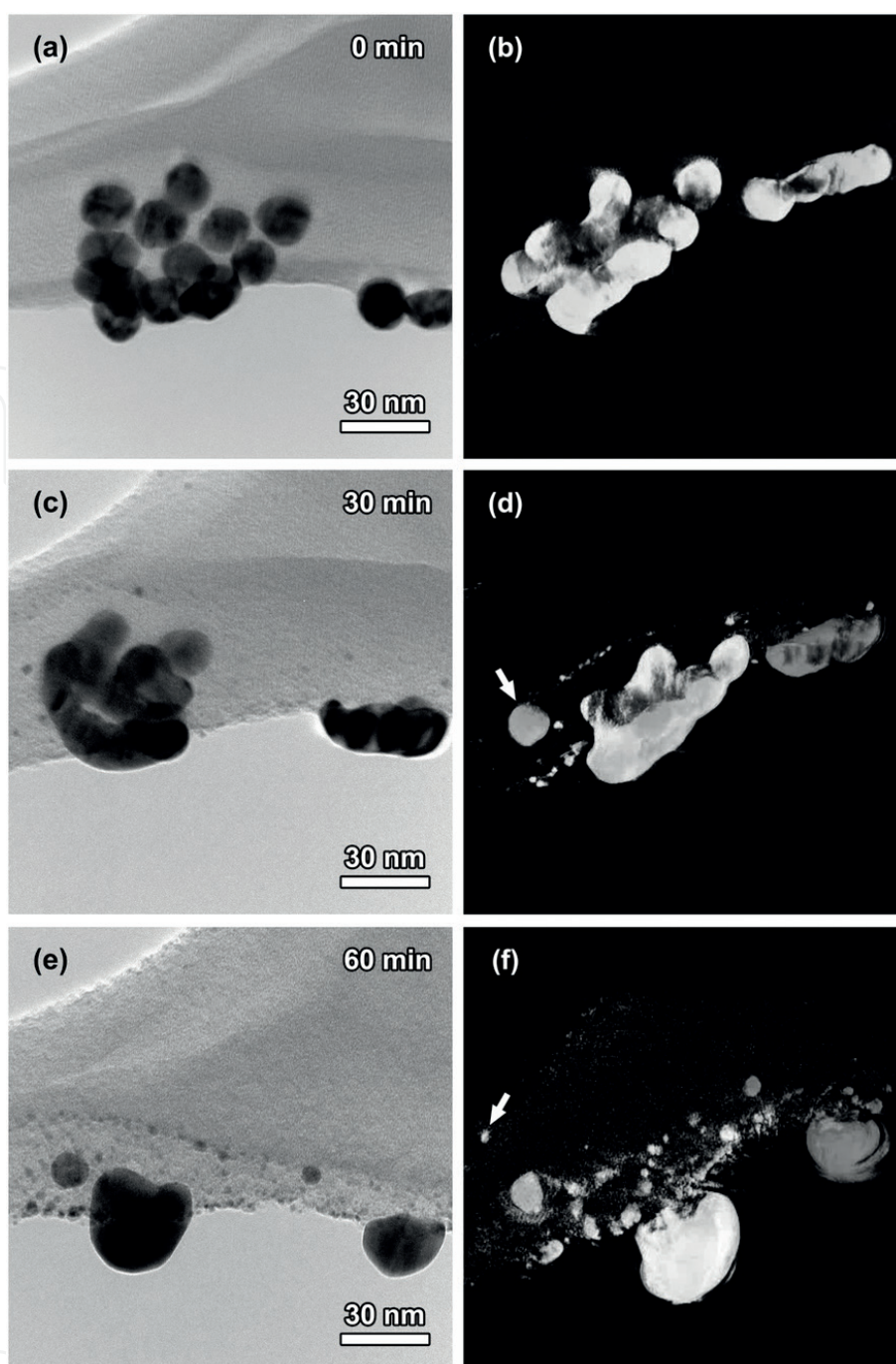


Figure 7.

Source electron micrographs and discrete 4D electron tomograms of Au nanoparticles irradiated with 3 MeV Cu^{3+} . (a, c, and e) Example micrographs from tilt series at increasing fluences up to $\sim 10^{15} \text{ cm}^{-2}$. (b, d, f) Corresponding 3-D tomogram reconstructions, rotated to a different angle from the source micrograph. Source: <http://pubs.rsc.org/en/content/articlelanding/2014/cc/c3cc49479a#!divAbstract>. The Royal Society of Chemistry. Reproduced from [28] with permission of The Royal Society of Chemistry.

increased sputtering, sintering, ballistic destruction, and possible ejection demonstrates that the response of gold nanoparticles to heavy ion irradiation is far from that expected by classical theories and models based on bulk sample geometries. As such, significant further investigation is needed before any commercialization in displacement damage environments is considered.

6.2 Radiation stability of embedded gold nanoparticles

In addition to the work done on freestanding gold nanoparticles, there have been several studies exploring the response of heavy ion irradiation to particles

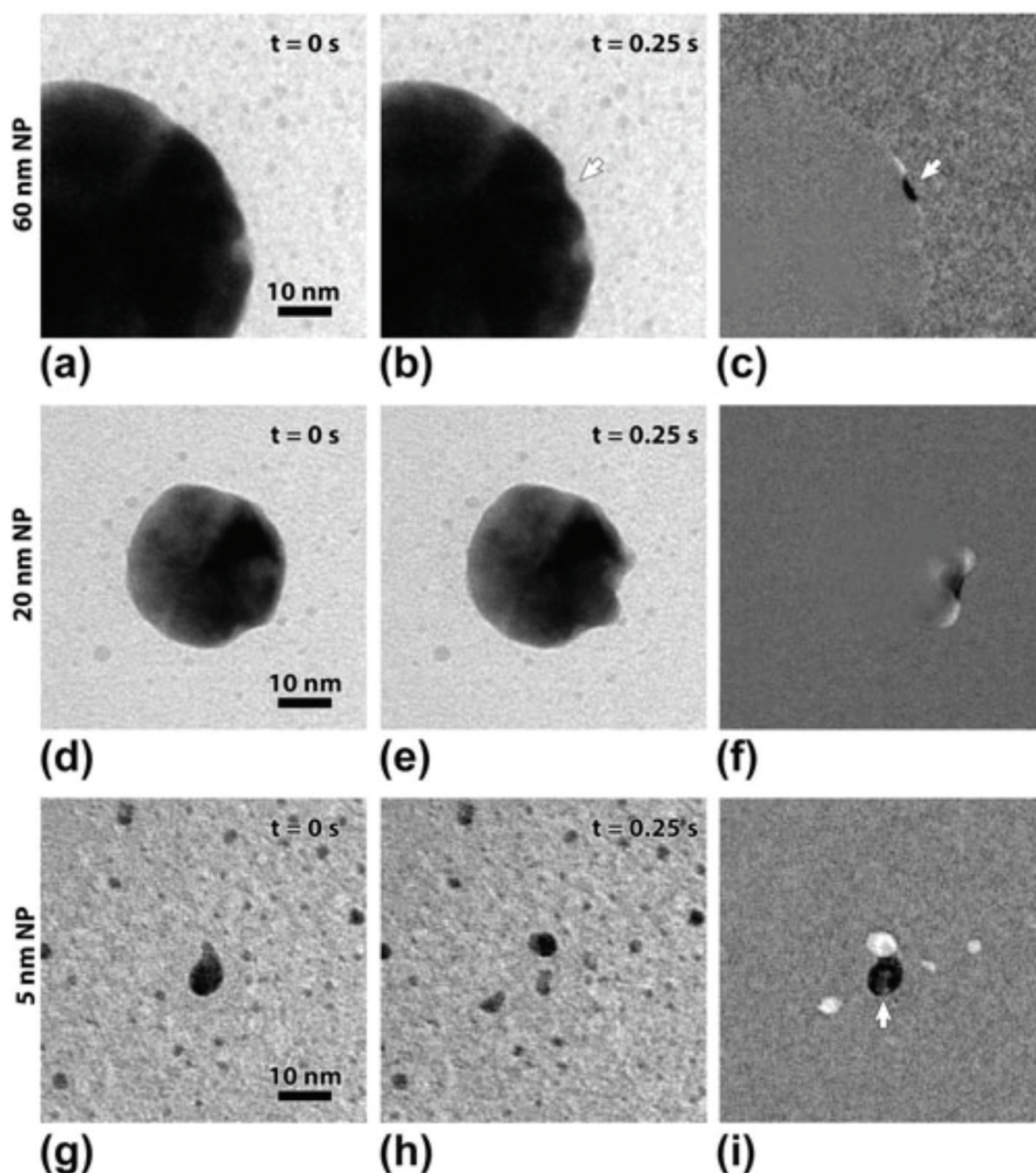


Figure 8.
 Effects of single 46 keV ions in gold nanoparticles of decreasing size. Note that the magnification is similar for all micrographs. Each pair of micrographs is separated by one frame, about 0.25 s here. (a–c) A single ion strike in a 60-nm nanoparticle created a surface crater, marked by the white arrow. (c) The difference image highlights the change between (a) and (b); features present only in (a) are dark, and newly formed features present only in (b) appear light. (d–f) A single ion creating a crater in a 20-nm nanoparticle. (f) The difference image and (g–i) ~5-nm teardrop-shaped nanoparticle was initially surrounded by a number of previously sputtered particles. (h) The nanoparticle exploded, leaving several particles nearby. (i) Difference image showing the locations of the old and new particles. The white arrow indicates a fragment from (h) that is difficult to see in (i) because it overlapped the original nanoparticle location. Source: <https://www.cambridge.org/core/journals/journal-of-materials-research/article/physical-response-of-gold-nanoparticles-to-single-self-ion-bombardment/F9933AF9ABAF6D1D3747AE1F8FFB5428>. Materials Research Society. Ref. [59], reproduced with permission.

embedded in a matrix. The most common matrix that has been used for these studies is amorphous SiO_x , as it provides a stark contrast in composition, density, and properties to that of the gold nanoparticles. Similar to the observations in the freestanding nanoparticles, Rizza et al. [61–63] have shown that sputtering plays an important role in the evolution of the embedded particles. In addition to watching the size of the particles decrease, the matrix provides a medium that serves to slow down the travel of the sputtered gold resulting in a satellite structure of smaller gold nanoparticles surrounding the original. The example micrographs and size

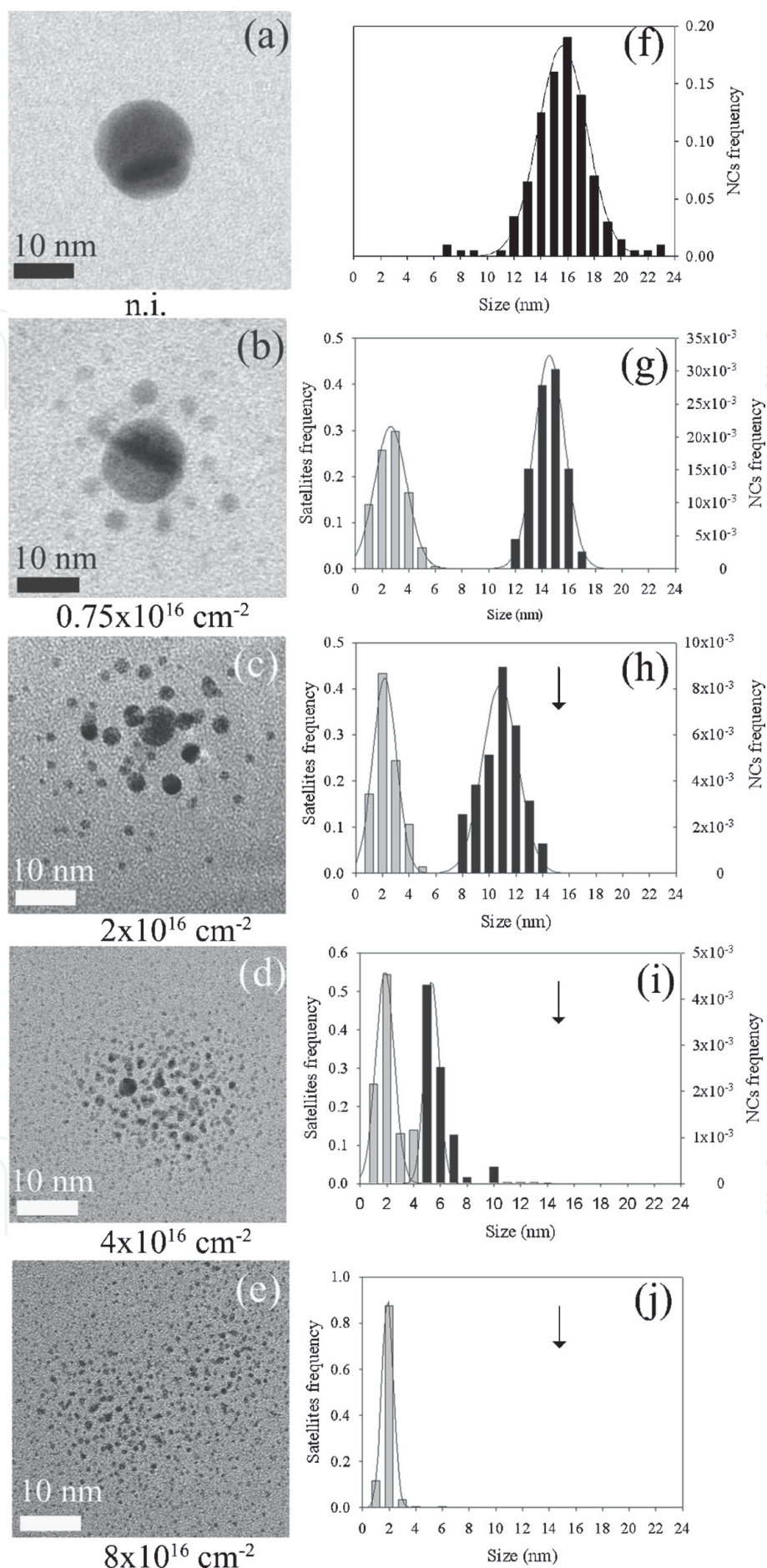


Figure 9. (a–e) Bright-field TEM micrographs of the time sequence of an embedded nanoparticle evolution under 4 MeV Au irradiation at 300 K at increasing fluences up to $8 \times 10^{16} \text{ cm}^{-2}$. (f–j) The corresponding size distributions of nanoparticle and resulting satellites [61]. Source: <https://aip.scitation.org/doi/abs/10.1063/1.2402351>. American Institute of Physics. Reprinted from G. Rizza et al., *Journal of Applied Physics*, Vol. 101, pp. 014321, with the permission of AIP Publishing.

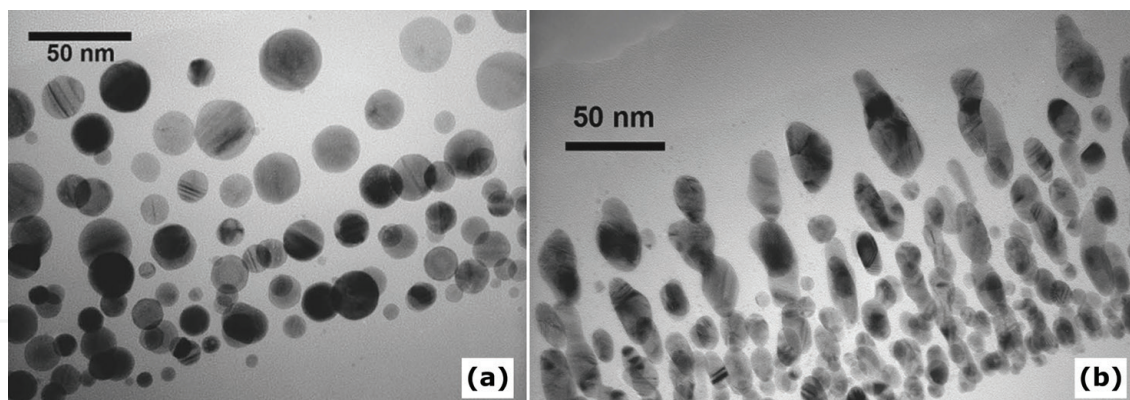


Figure 10.
 (a) Cross-sectional transmission electron microscopy image of pristine film and (b) cross-sectional transmission electron microscopy image of an irradiated film at 45° beam incident normal with 120 MeV Au [64]. Source: <https://aip.scitation.org/doi/10.1063/1.2764556>. American Institute of Physics. Reprinted from Y.K. Mishra et al., *Journal of Applied Physics*, Vol. 91, pp. 063103, with the permission of AIP Publishing.

distributions of this transition from the original embedded nanoparticle through this satellite structure to the final clusters of smaller particles can be seen in **Figure 9** [61]. The shape of the particles can also be altered depending on the irradiation condition. Mishra et al. showed that by irradiating gold nanoparticles embedded in SiO_x with 120 MeV Au to a fluence of 3×10^{13} ions cm^{-2} with the ion beam tilted 45° off normal, elongated embedded nanoparticles can be formed, as seen in **Figure 10** [64]. There are probably many more very unique far-from-equilibrium structures that can originate from embedded gold nanoparticles by varying environmental parameters during the ion irradiation. These structures can be further controlled by combining the radiation damage of the embedded particle with thermal diffusion to study classical Ostwald ripening and other diffusional steps [65, 66]. The evolution of these particles can be understood through a combination of rate theory and Monte Carlo modeling [63].

In addition to the embedding of gold nanoparticles in a ceramic matrix, an effort has also been made to explore the radiation response of polymer matrices embedded with gold and other heavy metal nanoparticles. It has been shown that such materials can serve as easily processible and portable radiation shields [67]. With further study developing on the concepts presented in these examples of ion irradiated embedded gold nanoparticles, a range of complex far-from-equilibrium structures can be envisioned with an even greater number of potential novel applications.

7. Future directions

Clearly, the response of both freestanding and embedded gold nanoparticles is drastically different than gold in bulk or thin-film morphologies and is highly dependent on the radiation environment, particle morphology, and surface conditions. Additional work is needed to elucidate the underlying physics governing the increased sputtering and other scaling effects observed in gold nanoparticles [26, 27, 56]. Without a detailed understanding of the mechanisms active when the displacement damage length scale of the radiation event approaches that of the size of the nanoparticle exposed, it will be challenging to employ gold nanoparticles in most radiation environments. If the significant enhancement of sputtering is inherent and cannot be overcome, then the application of gold nanoparticles subject to ionizing radiation may be limited to those environments that produce minimal dose or sputtering yields. Conversely, if properly understood and controlled, the enhanced sputtering yields may also open new fields of study and possible

applications utilizing the rapid degradation or the satellite morphology in the irradiated embedded nanoparticles seen in **Figure 8** [23, 61]. If not, the field may explore the response of other types of nanoparticles and nanostructured materials for inclusion in the next generation of devices that must withstand complex radiation environments. To be able to understand the effects of enhanced sputtering, systematic and thorough experimental and modeling efforts are needed along the lines of those presented in **Figure 6** [59].

8. Conclusion

Predicting the response of nanostructured materials for radiation environments is a new and rapidly developing field that is still poorly understood. The exposure to a range of ionizing photon irradiation has already found application in medical radiation therapies and will continue to gain traction in the coming years. In contrast, much less has been done to study neutron and charged particle irradiation effects on gold nanoparticles. The initial studies that have been done to study the radiation response of gold nanoparticles to charged particle irradiation indicate that a significant enhancement of sputtering yield is present. This enhanced sputtering leads to the rapid disintegration of the original nanoparticle and the formation of unique satellite nanoscale arrangements. Further modeling and experimental efforts are needed prior to the trusted incorporation of gold nanoparticles into other radiation environments (medical, space, or nuclear) being considered.

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Conflict of interest

The authors declare that they have no competing interests or conflicts.

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