Electronic Supplementary Information (ESI)

Extracting Nano-gold from HAuCl$_4$ Solution Manipulated with Electrons

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S1. Calculated procedures

Calculation of the electric potential

High-quality deionized water is an excellent insulator, whose conductivity is only ~ 5.5×10^{-8} S·cm^{-1}.[1] Under the irradiation of electron beam, the emission of secondary or Auger electrons from the water can result in a positive charge potential within the irradiated volume.[2] The positive potential is expressed as,

$$V(r) = \frac{Q}{4\pi\varepsilon d}\left(1 - \frac{r^2}{a^2} + 2\ln\frac{r_0}{a}\right)\ldots\ldots\ldots(1)$$

where Q is the total charge trapped into the irradiated area in water. ε is the dielectric constant of the aqueous solution. a is the radius of electron beam (0.5 μm). r_0 is the distance (250 μm) between the centre of electron beam and the location with the potential at ~ 0 V. d is the thickness of water solution. Here we use the inner edge of silicon reservoir as the zero potential site. r is the distance away from the electron beam centre.[2]

$$Q = \frac{I_0(\delta^x + y^x)\varepsilon}{\gamma}\ldots\ldots\ldots(2)$$

$\delta^x + y^x$ is the integrated yields of secondary and Auger electrons, which is calculated to be ~ 0.065-0.120 for water solution by using CASINO software.[3] The electron beam current I_0 is 1.26 nA (dose rate I is ~100 e$^-$·Å^{-2}·s^{-1}) in the experiment. γ is the conductivity of aqueous solution in S·cm^{-1}. The theoretical conductivity of aqueous solution is correlated to its basic physical and chemical properties of ions[4]

$$\gamma(S \cdot cm^{-1}) = \sum_i C_{i+}\lambda_{i+} + \sum_j C_{j-}\lambda_{j-}\ldots(3)$$

C_{i+} and C_{j-} are the concentrations of i cation and j anion, respectively. λ_{i+} and λ_{j-} are the ion conductivities in aqueous solution, with 349.6 S·cm^2·mol^{-1} for H$^+$ and 199.1 S·cm^2·mol^{-1} for

OH⁻, respectively, and the conductivities for these two radicals (H^+ and OH^-) in water are dominatingly higher than the ones for other hydrated metal ions in aqueous solution.[5] Here we should point out that Si_3N_4 film has a much lower electric conductivity (of $\sim 10^{-6}$-10^{-15} S·cm^{-1}) comparing with water.[6,7] This fact may increase the maximum potential of charging effect in water solution under the irradiation of electron beam.
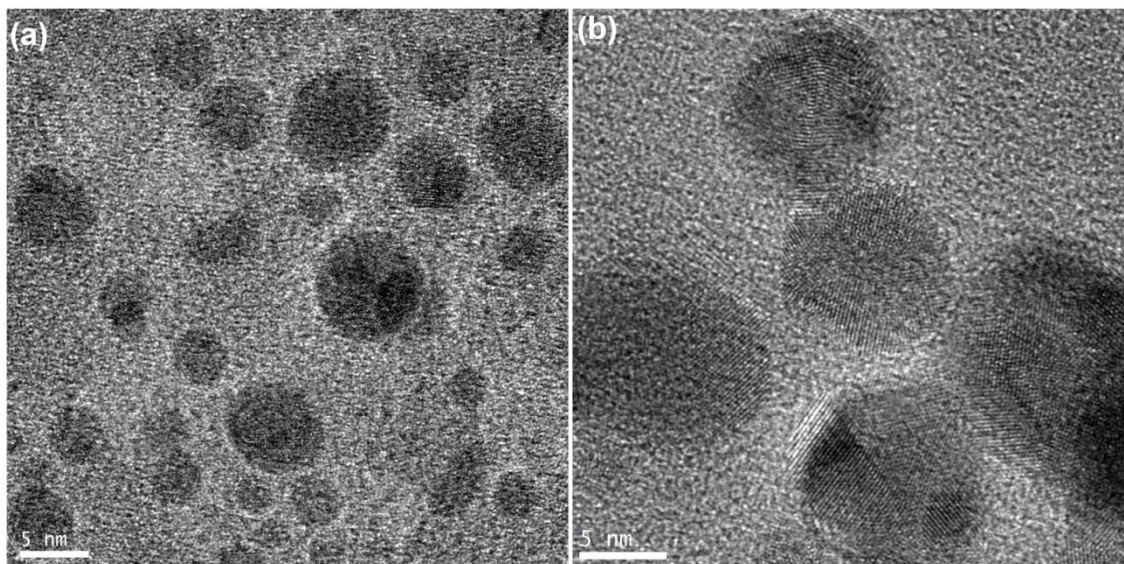

Fig. S1 HRTEM images of the Au NP seeds in vacuum. (a) The Au NP seeds have a size range from 3 to 7 nm, the average size is 5 nm for the Au seeds. (b) HRTEM image shows that these Au NP seeds are multiplly twinned.
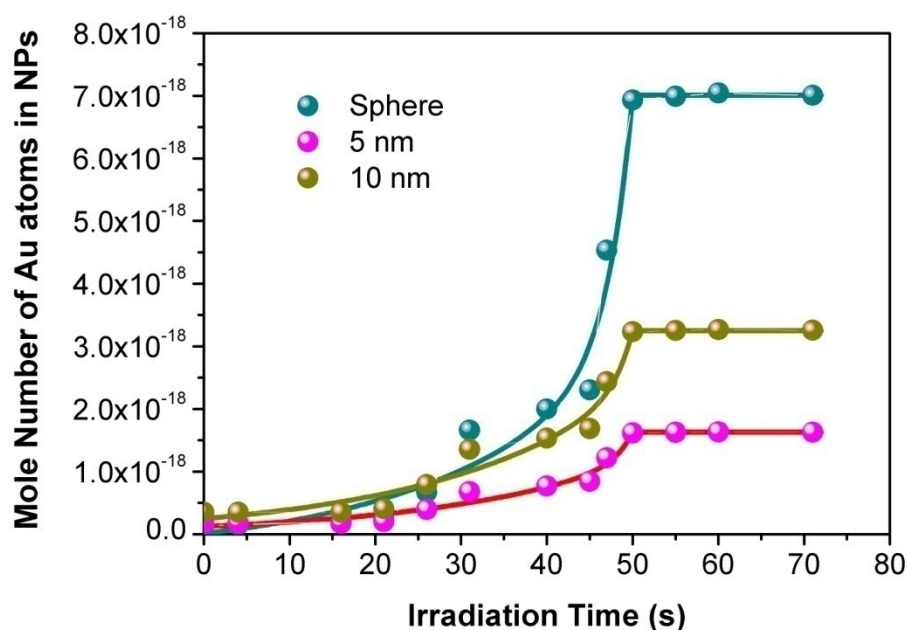
Fig. S2 Mole number of Au atoms in the Au nanoparticles in SEI: movie as a change of the electron beam irradiation time. Dots denote the experimental data and cures are the fitting results when we consider the Au nanoparticles with a thickness of 5 nm, 10 nm and sphere shape, respectively. As the pristine Au nanoparticles have a diameter of ~5 nm, we consider the growth of the Au nanoparticles following a lamellar structure with a thickness of 5 nm (orange line) or lamella structure with a thickness of 10 nm (yellow line). However, according to a previous liquid cell TEM report, the growth of Au nanoparticle adopts a ball structure when the thickness of water solutions between 200-400 nm.[8] In our experiment, the thickness of water solution is ~ 248±25 nm, so we also calculate the mole number of Au atoms in Au nanoparticles if considering the shape of NPs as a sphere.

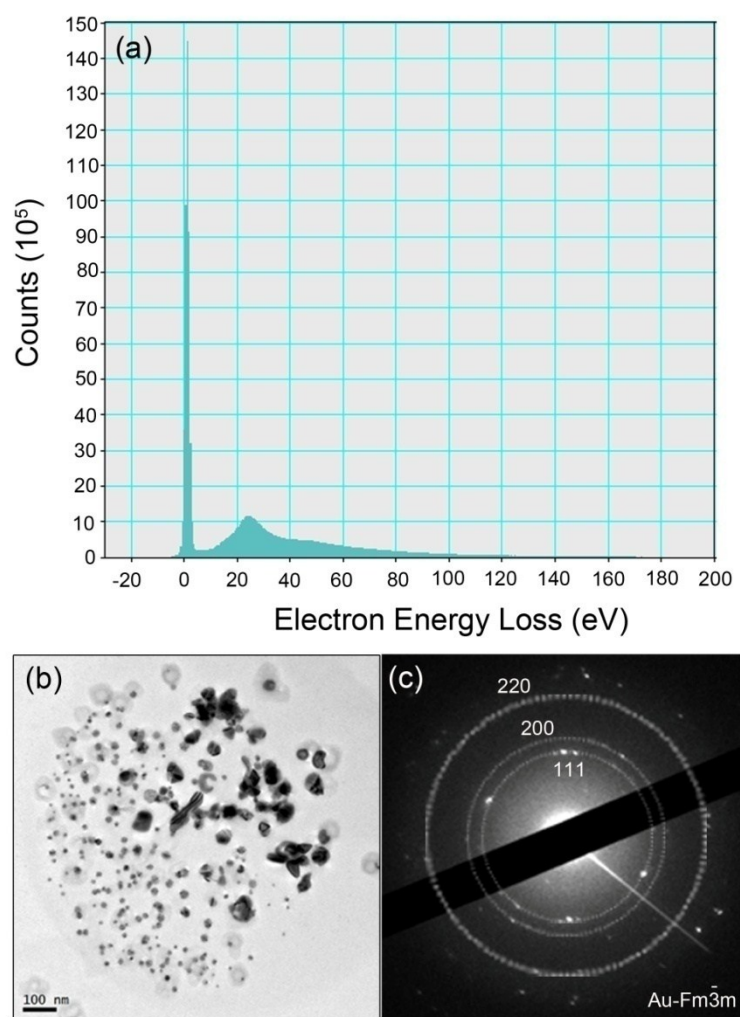Fig. S3 (a) EELS of the initial water. We can fit the thickness of water to be ~248±25 nm. (b) Au nanoparticles only precipitated from the water solution in the beam irradiated area. (c) Diffraction pattern (DP) shows that the nanoparticles have a crystal structure of Au- $\mathrm{Fm\bar{3}m}$.
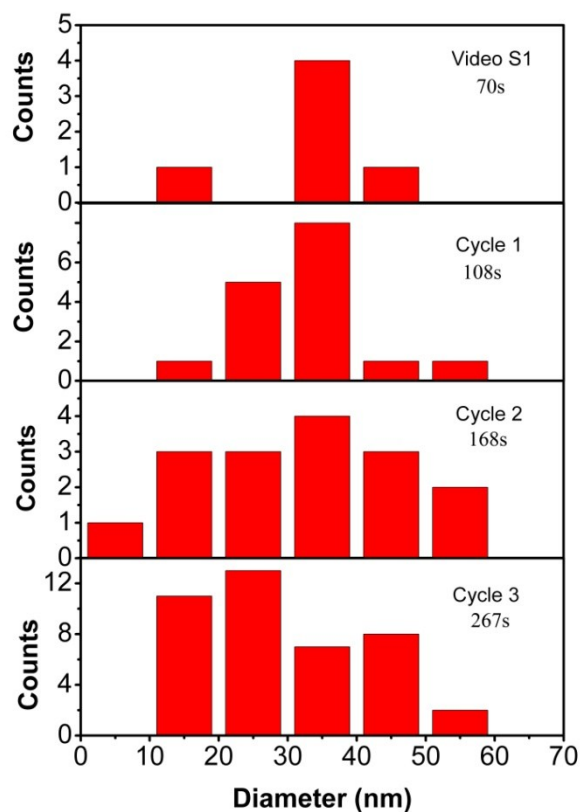
Fig. S4 Size distribution diagrams (particle diameter *vs*. counts of NPs) of the Au nanoparticles in ESI: Video S1 at 70s, cycle 1 at 108 s, cycle 2 at 168 s and cycle 3 at 267 s respectively (ESI: Video S2 and Fig. 7).

S2. Videos:

Here are two videos: Video S1 and Video S2. The videos show the growth of Au nanoparticles and the segragation of hydrated Au atoms in water solution under the irradiation of electron beam, as shown in ESI: Video S1 and Video S2. A steady-state of ~19 s recorded before Video S2 (Fig. 7).

References

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