Electronic Supplementary Material (ESI) for RSC Advances.

SUPPEMENTARY INFORMATION

In situ liquid-cell transmission electron microscopy for direct observation of concentration-dependent growth and dissolution of silver nanoparticles

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Diffusion distance of the hydrated electron in aqueous solvent

The hydrated electron (e^-_{aq}) had the lowest reduction potential (a standard reduction potential of –2.9 V) among the reducing agents[1] generated by the ionizing radiation. In other words, hydrated electrons were dissipated via reactions with other oxidizing agents due to the high reactivity.[2] In the steady state, the concentration gradient of hydrated electrons is known to be given by the diffusion equation with spherical symmetry;[2,3] i.e.:

$$\frac{\partial[e^-_{aq}]}{\partial t} = D\nabla^2\left[e^-_{aq}\right] = \mathrm{D}\frac{\partial}{\partial R}\left(R^2\frac{\partial[e^-_{aq}]}{\partial R}\right) = 0, \qquad (1)$$

so that we have:

$$\left[e^-_{aq}\right](R) = \frac{a}{R} + b, \qquad (2)$$

where a and b are constants and R is the diffusion length.

In our steady-state experimental conditions, hydrated electrons could diffuse from the periphery of the illumination area (which has a higher dose than the central region) to the visible area.

The area illuminated by the electron beam was clearly distinguishable from the non-illuminated area because chemical reactions were induced only by the electron beam. Figure S1 shows a low-magnification TEM image of the region where the in-situ experiments were carried out. A circular trace can be seen following the experiment, which was caused by the local high electron density at the edge of the illuminated electron beam.

The maximum diffusion length was obtained by measuring the radius of the trace, which was obtained from the length of line AB, and was found to be as approximately 800 nm. Note that the measured trace of the electron-beam-induced reactions was larger than illuminated area. This is attributed to diffusion of hydrated electrons from the edge of the illuminated area, and hence the maximum diffusion length from the illumination edge to center of the visible area should be less than 800 nm. The diffusion length of hydrated electrons is reportedly approximately 1.25 μm from a point source,[3] which is similar to the measured value reported here.

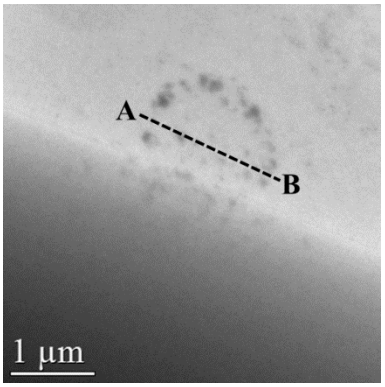

Fig S1. Low-magnification image of the illumination area following the in-situ experiment.

Considerations of the volume effect

Variations in the volume of liquid cell reportedly occur due to window bowing, which is induced by the pressure difference between the liquid and the TEM column, and by the presence of air pockets.[4,5,6] Inhomogeneous growth may result if the total number of silver ion precursors is inhomogeneous due to a volume difference.

With conventional TEM, the spatial resolution is a function of the thickness of the liquid;[7] i.e.:

$$d_{TEM} = 6 \times 10^{12} \frac{\alpha C_c T}{E^2}, \quad (3)$$

where α is the objective semi-angle, C_c is the chromatic aberration coefficient, E is the beam energy, and T is the thickness of the liquid. It follows that d_{TEM} is proportional to the thickness of the liquid; therefore, if the local volume in the visible area varies, and then the resolution would also vary. Furthermore, it has been reported that significant differences in the image may occur even with a difference in thickness of only a few nanometers.[8]

Figure S2 shows a snapshot from the movie, together with the corresponding intensity profile along the line CD. No clear differences in the resolution were visible. Furthermore, the number of background electrons along line CD did not vary significantly. Thus, the volume difference does not appear to be a significant contributing factor in the inhomogeneous growth of the silver nanoparticles.

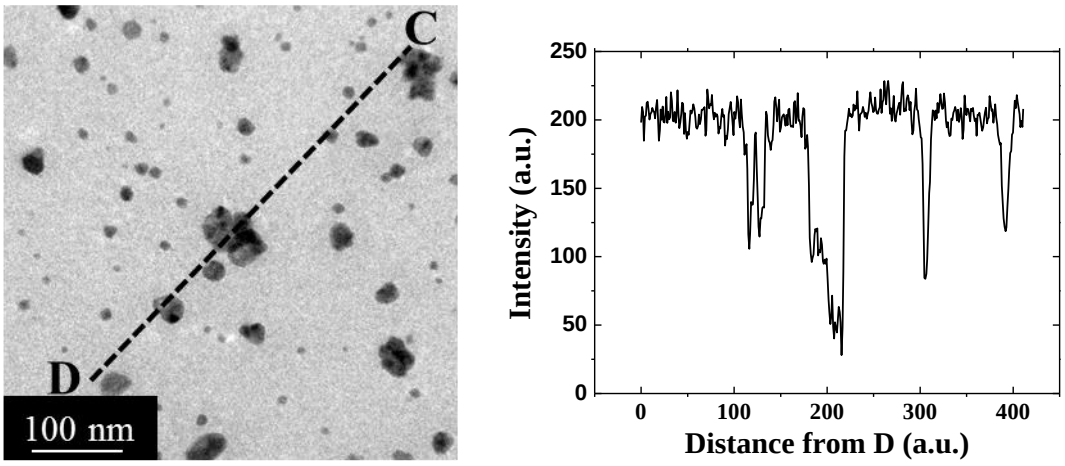

Fig S2. A snapshot from the movie, together with the intensity profile along the line CD.

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