Supplementary Materials for

Radiolytic redox interplay defines nanomaterial synthesis in liquids

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Experimental Preparation

Solution for experiments was prepared using Silver Nitrate (Sigma Aldrich, ReagentPlus ≥ 99.0% titration) and water (Fischer Chemical, HPLC grade). For a water-ammonia solvent, ammonium hydroxide solution (Sigma Aldrich, 25-30% NH₃) was used. Solutions were placed in QuantamiX WETSEM QX-102 capsules and irradiated with electron beams of different energies in an FEI Quanta 250 FEG scanning electron microscope. All imaging was performed in high vacuum mode with an Everhart-Thornley secondary electron (SE) detector.

Simulation Details

The kinetic model from (8) has been used to simulate the problem. The reaction-diffusion equation can be given by

\[
\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + \sum_{j,k \neq i} k_{ij} C_j C_k - \sum_j k_{ij} C_i C_j + R_i
\]  

(S-1)

where \( C_i \) is the concentration of \( i \)th species, \( k_{ij} \) is reaction rate and \( R_i \) is the source term for creation of radiolysis species. We assume the medium remains stationary throughout the experiments and that temperature variations in the medium are small, so thermophysical properties of the domain will be uniform and constant.

The introduction of large numbers of charged particles (electrons and radiolysis products) raises the question of whether the motion of these particles will be influenced by electric fields. The estimated thickness of the Debye layer \( \kappa^{-1} = (\varepsilon \varepsilon_0 k_e T / 2 \rho \sigma^2)^{1/2} \) in a 1 mM aqueous solution of AgNO₃ is 10 nm, and the bulk solution outside of the Debye layer can be considered electrically neutral (24). The ion migration time \( t_{mig} = (\rho / \kappa^2 n_e k_e T)^{1/2} \) governs the time scale over which the Debye layer is established, and for our conditions this time is 190 ns. Since these length and time scales are much shorter than the length and time scales over which species diffusion and deposition occur, electric fields are negligible and no significant electroosmotic flow is expected in the fluid bulk. We do not consider the effects of electroosmotic flow at the fluid-membrane interface. This allows us to use the simple reaction-diffusion equation to model the system behavior.

The problem was simulated in COMSOL using a transport of diffuse species module. The dose rate source term was calculated via a Monte Carlo simulation using CASINO. This implementation uses the Joy and Luo (25) model for electron stopping power. The software calculates the total energy lost from all electrons passing through each cell of its mesh. We convert these values to a volumetric dose rate distribution and interpolate them onto the COMSOL mesh.
Figure S1. COMSOL simulation details. (A) Mesh on an axisymmetric domain in COMSOL. Electron beam is focused at $r = 0, z = 0$. (B) Dose rate extracted from CASINO for interpolation onto COMSOL mesh for a 30 keV electron beam.

The number of electrons simulated was 45 million and distribution of energy was plotted. The chemical equations, reaction rates, diffusivities, and G-values for radiolysis of DI water were taken from (8). Reduction mechanisms for Ag$^+$ used are shown below. For all the following reactions the rate constants were obtained from the NIST Chemical Kinetics Database (19), except when specified.

| Reducing species | Rate Constant |
|------------------|---------------|
| $e_{\text{sol}}^-$ | $4 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$ |
| $\text{H}^*$      | $1.2 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$ |

The mechanisms considered for reduction of Ag($\text{NH}_3$)$_2^+$ are

| Reducing species | Rate Constant $\text{M}^{-1}\text{s}^{-1}$ |
|------------------|---------------------------------|
| $e_{\text{sol}}^-$ | $3.2 \times 10^{10}$ |
| $\text{H}_2\text{O}_2$ | $1 \times 10^9$ |

The oxidation mechanisms considered for Ag as

| Oxidizing Agent | Rate Constant $\text{M}^{-1}\text{s}^{-1}$ |
|-----------------|---------------------------------|
| $\text{O}_2$    | $5 \times 10^9$ |
| $\text{OH}^*$   | $5 \times 10^9$ * |
| $\text{H}_2\text{O}_2$ | $3.5 \times 10^9$ |

*Rate constant unavailable, value consistent with order of similar reactions used.

Following additional pathways for water-ammonia system radiolysis were added.
| Reaction | Rate Constant |
|----------|---------------|
| $\text{Ag}^{+} + 2\text{NH}_3(\text{aq}) \rightarrow \text{Ag(NH}_3)_2^{+}$ | $K_{eq} = 1.6 \times 10^7$ |
| $\text{NH}_3(\text{aq}) + \text{OH}^* \rightarrow \text{NH}_2^* + \text{H}_2\text{O}$ | $9.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ |
| $\text{NH}_2^* + \text{OH}^* \rightarrow \text{NH}_2\text{OH}$ | $9.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ |
| $\text{NH}_2^* + \text{H}_2\text{O}_2 \rightarrow \text{NHOH} + \text{H}_2\text{O}$ | $9 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ |
| $\text{NH}_2^* + \text{O}_2(\text{aq}) \rightarrow \text{NH}_2\text{O}_2$ | $9.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ |
| $2\text{NH}_2^* \rightarrow \text{N}_2\text{H}_4$ | $2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ |
| $\text{OH}^* + \text{N}_2\text{H}_4 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{H}_3$ | $1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ |

The G-values used for radiolysis species of aqueous-ammonia system were weight averaged with respect to the weight percentage of NH$_3$ in aqueous ammonia from G-values of pure water system.

**Imaging-Induced Ag Growth**

It is known that imaging with the electron beam in scanning mode is capable of growing solid Ag deposits. However, growth caused by scanning mode imaging is uniformly distributed throughout the area impacted by the electron beam, so it cannot be responsible for producing either the pillar or ring deposits seen in our results. In Fig. S2, we present images of deposits imaged immediately after deposition and after up to 60 s of continuous imaging under a 30 keV, 2 nA scanning electron beam. We see that deposition caused by imaging has little impact on the resultant images for our conditions.

![Figure S2. Evaluation of imaging effects.](image_url)

Comparison of deposits after (A) 5 s, (B) 23 s, (C) 38 s, and (D) 60 s of imaging exposure using a 30 keV, 2 nA scanning electron beam after deposition. Focused electron beam irradiation is 30 keV for 30 s in all cases. 1 mM Ag(NH$_3$)$_2^+$ in 30% NH$_3$. Scale bar is 30 µm. Note that there is no noticeable difference in the deposits due to the imaging.
Time-Resolved Development of Ring Deposit

Figure S3. Deposit formation over time. Comparison of deposits formed with (A) 1 s, (B) 5 s, (C) 10 s, (D) 20 s, and (E) 30 s of irradiation. A central deposit is already recognizable at 1 s. The ring is faintly visible by 10 s and more prominent at 20 s and 30 s. This confirms our simulated results that ring formation occurs over time scales much longer than the central deposit.

Ag Creation Rates over Time

While points near the central deposit do see very large reaction/net creation (reduction minus oxidation) rates in the water-ammonia simulations, these persist for only very short times. Although the net Ag creation rate at larger radial positions never reaches values as high as those closer to the center, they remain appreciable for much longer. The total amount of deposition at a point is the integral of the net creation rate at that point over the entire exposure time, and our simulation shows that total deposition values in the ring region are two orders of magnitude higher than in the intermediate region (between the pillar and ring) after 30 s of irradiation. This is immediately clear in examining Fig. S4, which compares the net creation rates over time for two radial positions in the 30 keV beam simulation. Almost instantaneously, the net creation rate reaches its maximum at both positions and begins to decay. The rate at the 7 μm radial position is initially higher but falls below that of the 14 μm position in less than 1 ms. At 7 μm, the rate remains negligible for nearly the entirety of the 30 s irradiation time, while at 14 μm, the rate
reaches 10 mol/m$^3$·s within about 1 s and gradually decays to near zero over tens of seconds. It is the slower creation of solid Ag over this time scale that is responsible for the creation of the ring.

Figure S4. Spatial comparison of net Ag creation rates. At radial positions $r = 7 \, \mu$m, in the intermediate region between the central pillar and the ring, and $r = 14 \, \mu$m, at the ring location, in a 30 keV beam simulation in water-ammonia. Note that the rate at 7 μm falls off to near zero within milliseconds, while at 14 μm it is appreciable for much longer times.

Consideration of Thermal Effects

We do not model nonuniformities in the properties of the solution in our simulation. However, we have investigated the potential effects of heating by the electron beam. As a limiting case, we consider the scenario in which all the beam energy is converted into thermal energy in the solution, using the calculated dose rate distribution as a volumetric heat generation term. We calculate a maximum temperature rise of 13° C above far field values at the hottest point after 30 s of irradiation. The simulated temperature profile in the domain after 30 s of irradiation with a 30 keV electron beam is shown in Fig. S5.

There are two main pathways by which temperature changes can affect the system—changes in thermophysical properties of the solution and buoyancy-driven flows in the domain. Diffusion coefficients in liquids are linearly proportional to absolute temperature. We performed a simulation with the diffusion coefficients of all species increased based on the maximum predicted temperature rise and found no discernible difference in the predicted ring positions.
For convective effects, we use scaling analysis and thermal simulations to determine whether thermally induced flows may have an effect on species distributions. Thermally induced flows in this configuration would move upward along the axis of the electron beam towards the membrane and then radially outward from the beam impingement point near the membrane surface. Scaling arguments \((2I)\) indicate the scale of the maximum expected velocities, \(u_s\), will be \(u_s \cong (\alpha / L_s)Ra^{1/2}\), where \(\alpha\) is the thermal diffusivity of the liquid and \(Ra\) is the Rayleigh number. The Rayleigh number is defined as \(Ra = g \beta \Delta T L_s^3 / \nu \alpha\), where \(g\) is gravitational acceleration, \(\beta\) is the coefficient of thermal expansion, \(\Delta T\) is the driving temperature difference, \(L_s\) is the length scale across which the temperature difference acts, and \(\nu\) is the kinematic viscosity of the fluid. Using the velocity scale, we can determine the mass diffusion Peclet number, \(Pe = u_s L_s / \nu\). For our conditions with a 30 keV beam and taking a characteristic length scale of 10 μm, we find \(u_s \cong 2E - 4 \text{ m/s}\) (this is confirmed by simple COMSOL simulations) which suggests \(Pe\) is \(O(1)\). This means advective effects are at most of similar magnitude to diffusive effects. Therefore, moderate advection of species outward from the beam impingement point may contribute to the discrepancy we see between predicted and observed results at higher beam energies.

**Figure S5. Thermal effects in aqueous environment.** Heating for 30 s with a 30 keV, 2 nA electron beam. All electron beam energy is assumed to be converted into thermal energy, using a volumetric heat generation rate equal to the spatial dose rate of electron energy loss shown in Fig. S1B.
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