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Radiolysis during Liquid Cell Electron Microscopy

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Recent advances in liquid cell electron microscopy [1, 2] have enabled real time imaging of objects suspended in liquids and processes taking place in liquids with the nanometer resolution of the electron microscope. As ionizing radiation passes through the suspending medium, energy is transferred from the fast-moving electrons to the irradiated medium. This energy excites and dislodges orbital electrons, which results in the generation of radical and molecular species such as H_2, O_2, H_2O_2, and hydrated electrons [3-5]. The hydrated electrons, oxidizing agents, and gaseous species can cause, respectively, reduction and precipitation of cations from solution, dissolution of metals, and nucleation and growth of bubbles [6-10]. A quantitative understanding of electron beam-induced effects is critical to assess whether the electron beam significantly affects the imaged phenomenon, to correctly interpret experiments carried out with liquid cells, mitigate unwanted effects, and take advantage of beam effects.

We have used a mathematical model that includes the production of species by the electron beam, their destruction by reverse reactions, and their diffusion outside the irradiated region, to compute the concentrations of radiolysis products as functions of beam intensity, beam size, time, position relative to the beam's center, and solution composition (Figure 1). We will describe this model and show that the complex reactions between species can produce effects such as enhanced concentration of oxygen near the edge of the irradiated region (Figure 1a). We compare the model predictions with experiments carried out in a liquid cell, the *nanoaquarium* [11], at 300 kV in a Hitachi H9000 TEM and at 30 kV in an FEI Quanta FEG ESEM with a transmission detector, in each case images at 30 fps.

One key conclusion of the calculations is that the concentrations of radiolysis products do not increase unabated, but rapidly (within seconds) reach equilibrium levels. The existence of equilibrium is supported by experiments in which we monitored periodic bubble nucleation and growth [6]. A second conclusion is that the behavior expected in the liquid cell depends sensitively on the species initially present in the solution. Experiments in which we examined bubble formation as a function of initial H_2O_2 concentration showed trends that were in qualitative agreement with our theoretical predictions.

The electron beam is well known to be able to reduce metal ions in solution, forming metal nanoparticles [6-10], and to aggregate metal particles [12]. However, etching and dissolution of metallic nanoparticles is also possible (Figure 2). We correlated growth and etching of nanoparticles with irradiation dose rate and the ratio of the concentrations of reducing and oxidizing species. These results help understand the phenomena that are observed as a result of increasing or decreasing the spot size.

As well as studying liquid phase reactions, liquid cell microscopy provides a unique tool for studying radiolysis and for examining the behavior of materials subjected to radiation. We hope that the modeling tools described here will be useful for interpreting microscopy data obtained with liquid cells [13].

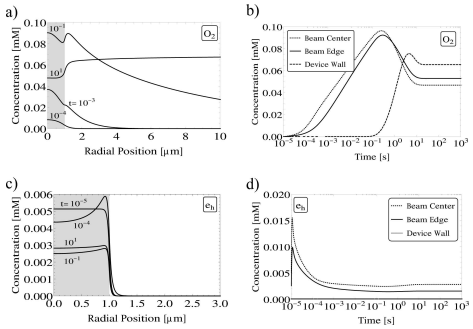

Figure 1: Heterogeneous model predictions of the spatial and temporal evolution of radiolysis products. The left column depicts the concentrations of two key species, oxygen and hydrated electrons, at various times as functions of the radial distance from the center of the irradiated region. The right column depicts the concentrations of the same products at the center and edge of the irradiated region and the outer impermeable surface of the liquid cell as functions of time. The beam and liquid cell radii are, respectively, 1 μm and 50 μm. The beam current is 1 nA and the dose rate is 7.5xl0^7 Gy/s.

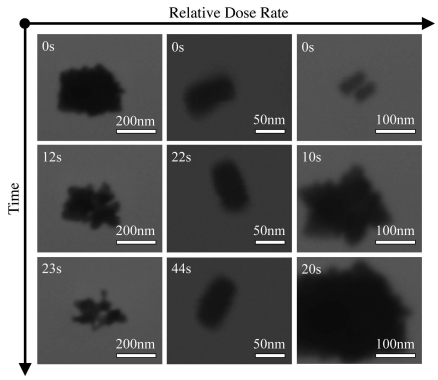

Figure 2: Growth and etching of Au nanoparticles as a function of dose rate (beam parameters). At low dose rate the particles show etching behavior (first column) while at higher dose rate growth occurs (third column). As the dose rate increases so does the ratio of the concentrations of reducing species and oxidizing species.

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