

## Environmental Electron Microscopy: Electron Beam Effects in Electrochemistry

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Liquid containing environmental cell based TEM has, in recent years, become a powerful tool for studying dynamic systems at nanometer length scales.[1-7] Such cells typically confine several hundred nanometers of liquid between two electron transparent windows. These cells can be integrated with electrodes for electrochemical testing, and have been implemented to study processes including electro-deposition, electrolysis, and electrochemical batteries.[2-6] When performing in-situ electrochemical studies, particular caution is required to avoid spurious effects introduced by the electron beam. The electron beam is known to produce free radicals, induce reactions, generate bubbles, and affect the local potential.[3,8] Fortunately, many artifacts can be suppressed by reducing the electron beam flux and dose below certain threshold values.[8] To mitigate electron beam effects, in-situ studies are often performed under low dose conditions. A common method for validating the approach is to demonstrate that the system does not respond to the electron beam alone at doses and fluxes larger than those used for the experiment. However, such approaches can not negate the possibility of synergistic effects that may arise due to electrochemically imposed potential and concentration gradients.

Here we demonstrate that electron beam irradiation markedly affects the electro-deposition of gold despite the fact that the beam current density falls below a value determined to be suitable for imaging absent an applied field. The electrochemical cell utilized 25 nm thick gold as electrodes and 0.1 M  $K_2SO_4$  as electrolyte. The gold electrodes were fabricated using electron beam evaporation and photolithography. A mild beam intensity ( $10 \text{ A/m}^2$ ) was used for imaging. Figure 1a shows a gold electrode in the electrolyte solution. After 20 minutes of beam exposure, no detectable changes were induced at or around the electrode. A bias of -2.5 V was subsequently applied to the gold electrode to induce electro-deposition. After 50 s under applied bias, gold nanoparticles nucleate and grow in the solution far from the electrode (Figure 1b). No measurable deposition of gold occurred on the electrode. This result demonstrates a synergistic effect of electron beam irradiation and compositional gradients generated by the applied bias that results in a beam-induced reaction that would otherwise have not occurred. The lack of electro-deposition on the cathode suggests that the beam effectively removes the majority of gold ions from solution prior to their reaching the electrode. The results suggest the need for an improved quantitative and mechanistic understanding of electron beam effects, such that they may be understood in the context of more complicated physical environments.

### References

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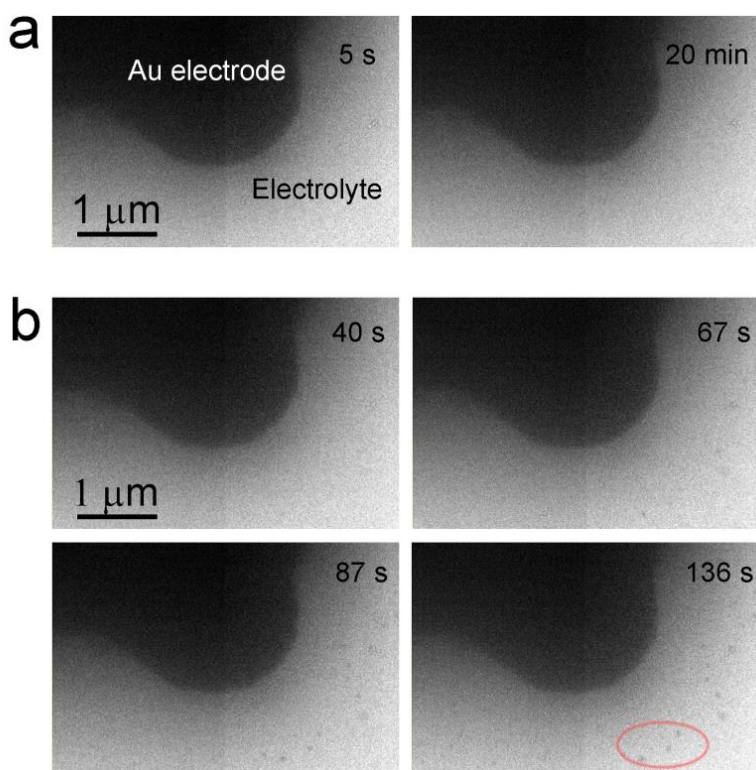


Figure 1. (a) TEM images showing a gold electrode in solution under electron beam radiation for 5 s and 20 mins. (b) Time-lapse TEM images depicting the nucleation and growth of gold nanoparticles around the electrode after electrical bias was applied for different times. Several nanoparticles are highlighted by a red ellipse.