

In-situ Transmission Electron Microscopy to Probe the Electrochemical Deposition of Nanostructured Materials

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Nanomaterials and nanostructured materials have been used extensively in biosensing platforms, and their morphology strongly influences the detection limit and dynamic range of these sensing systems [1]. This makes it very important to precisely tune the biosensing substrate at the biomolecular scale or the nanoscale. To develop nanostructures with desired morphology, a detailed understanding of the growth mechanism is very essential. Considerable effort has been devoted to investigate the mechanisms involved in electrochemical deposition, but controversy regarding the growth modes still remains due to the lack of direct experimental proof of the nucleation and growth kinetics [2]. Real-time observation of the growth process through high resolution in-situ microscopy allows direct and precise study of the structural evolution; however, some difficulties in real-time imaging in liquid environments remain [3].

Here we have used an electrochemically-biased liquid cell inside a transmission electron microscope (TEM) to investigate the growth of Au nanoparticles on carbon microelectrodes. The liquid cell has built-in electrical and fluidic circuitry, which enables us to simultaneously collect electrical signals and electron micrographs during the whole process [4]. We evaluated this system by applying cyclic voltammetry to carbon electrodes modified with platinum nanoparticles in sulfuric acid solutions. In addition, we studied the effect of electron beam dose on the thickness of the liquid layer using Electron Energy Loss Spectroscopy (EELS) and TEM imaging. With this approach, we captured the electrochemical growth process of Au nanoparticles in chloroauric acid solutions under a fixed potential.

The cyclic voltammograms obtained using the liquid cell are comparable to those obtained using standard electrochemistry cells, indicating the system's capability to study in-situ electrochemical processes. Bubbles can be generated in two ways: for large area and using a high electron beam current density (in the order of 0.63 pA/nm²) or applying a negative enough bias voltage. Bubbles grow under a beam current density of 0.026 pA/nm² or higher and shrink under 0.0061 pA/nm² or lower (Figure 1). The electron beam also induces homogenous nucleation and growth of Au nanoparticles in solutions of chloroauric acid, while dissolves the grown particles if the beam current density is tuned high enough. Therefore suitable conditions are identified to conduct the in-situ electrochemical studies, under which high resolution imaging is possible inside bubbles having a thin electrolyte layer. This enables the initial stages of electrochemical deposition to be captured (Figure 2). Quantitative analysis of the electrochemical current versus time curves (Figure 3a) and images (Figure 3b, c, d, e) was done to study the nucleation/growth mechanism. The growth of Au exhibits a progressive nucleation and growth.

In conclusion, we have applied an effective in-situ microscopy system to investigate electrochemical process under different solution, electron beam, and potential conditions. We also evaluated the electron beam effects and demonstrated how to control electrolyte thickness for high resolution imaging [5].

References:

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 [5] The authors acknowledge funding from NSERC under the Discovery Program. Dr. G. Silveira and A. Duft is thanked for their helpful contributions to this work.

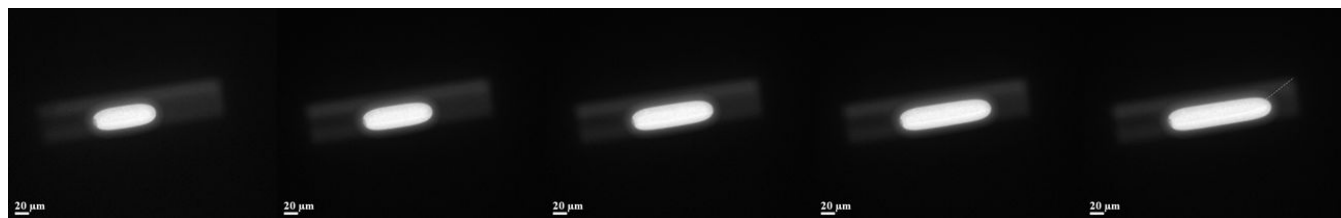


Figure 1. Evolution of a bubble in water under beam current density of 0.026 pA/nm^2 ; Images a, b, c, d, e were acquired at 15 s intervals under TEM mode.

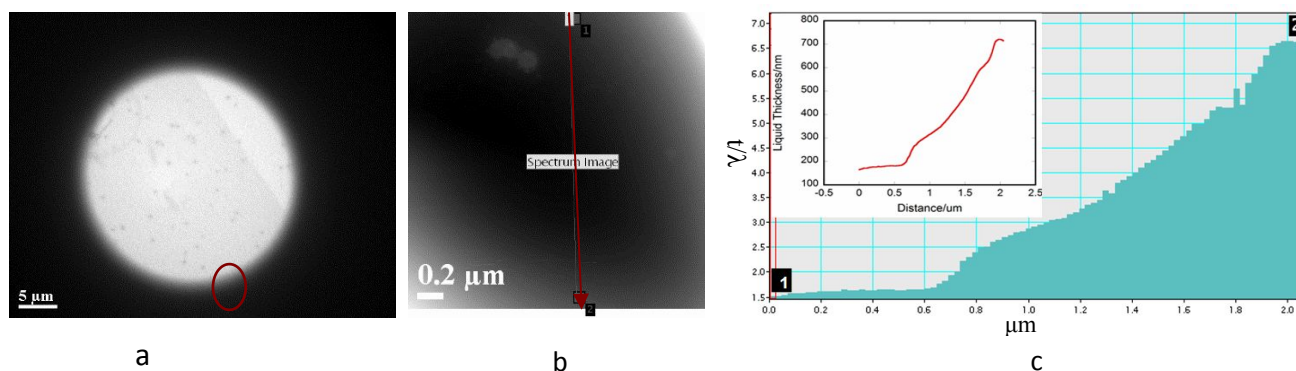


Figure 2. Thickness distribution of liquid-bubble interface measured by EELS: a. TEM image showing the bubble generated in water; b. Zoomed-in HAADF image of the interface indicated by the red circle in a, and EELS was conducted through a line shown by the red arrow; c. Measured relative thickness (t/λ) of the liquid along the line in b and inserted plot shows the calculated absolute liquid thickness.

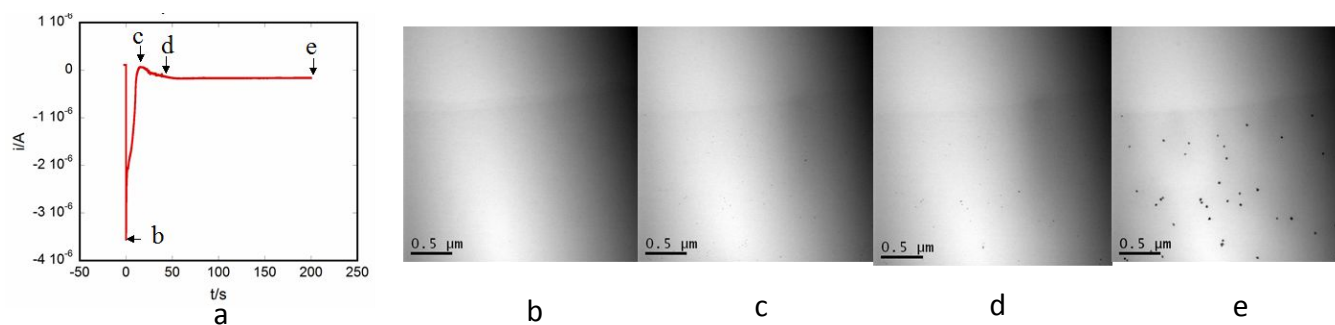


Figure 3. Current transient curve and corresponding images showing the in-situ deposition of Au on carbon from 180 nm-thick chloroauric acid under a fixed potential of -0.6 V for 200s. Bright field STEM images b, c, d, e are related to the time points indicated by the arrows in the current vs. time curve in a).