

***Operando* Quantitative Electrochemical STEM Studies of Cu Underpotential Deposition on Nanocrystal Surfaces**

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Underpotential deposition (UPD) enables the formation of monolayer metal adsorbates whose electronic properties can be significantly different from those of the bulk material [1]. While studied extensively for bulk polycrystalline and single-crystal electrodes by conventional electrochemical, X-ray and TEM methods [2–4], UPD kinetics for individual nanoparticles can deviate from their bulk counterparts due to the distinct differences in the distribution of local electric fields and transport. UPD at practical nanocrystal surfaces remains elusive due to the lack of spatially and temporally resolved *operando/in situ* techniques that can provide nm-scale structural information at interfaces [5].

Here, we present the UPD of monolayer Cu at single-crystal Au nanocube electrode surfaces, based on a quantitative, correlative analysis of electrochemical results and *operando* electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM). *Ex situ* STEM-EELS mapping shows a Cu UPD apparent thickness on Au cubes of ~ 5 Å (Fig. 1b, inset), which is an upper limit to the actual thickness of the Cu monolayer due to sample mistilts and beam spreading as the sample thickness is $\sim 10\times$ the depth of field. *Operando* EC-STEM uses a three-electrode cell with Pt working, counter and reference electrodes (Fig. 1a). Cyclic voltammetry (CV) profiles of Cu electrodeposition show the broad Cu deposition and sharp Cu stripping peaks at ~ 0.3 V vs. standard hydrogen electrode (SHE) (Fig. 1b), which matches the corresponding peaks obtained from a standard electrochemical cell.² Quantitative analysis of the Cu stripping peak currents gives a current vs scan rate scaling of $I_p \propto v^{0.43}$ (Fig. 1c), which suggests a diffusion-controlled redox process ($I_p \propto v^{0.5}$), similar to Cu deposition from Cu^{2+} . However, it is different from results from a conventional electrochemical cell where a surface-controlled stripping process predicts a correlation of $I_p \propto v$ [6]. The difference is mainly due to the diffusion of anions to counterbalance the Cu^{2+} generated from Cu stripping.

Operando EC-STEM directly visualizes the potential- and spatially-resolved Cu electrodeposition kinetics on Au nanocubes at Pt substrates without beam-induced damage at a very low dose of 2 e/nm^2 (Fig. 2a). Cu electrodeposition forms a planar coating at a mild potential of -0.1 V (Figs. 2d–e); island-shaped grains at an intermediate potential of -0.2 V (Figs. 2f–g); and nanodendrites at an aggressive potential of -0.3 V (Figs. 2h–k). At -0.3 V, Cu particles (**b**), marked by the white box, preferentially grew on the Au nanocube and formed well-defined dendrites. The Cu particle (**c**), marked by the red box, initially remained isolated from the Pt WE and thus electrochemically inactive. At 240 s, this particle came into contact with the continuously growing Cu dendrites underneath and was “electrified”, which initiated further Cu electrodeposition on this particle. Quantitative STEM imaging analysis of those two particles shows a first derivative of $\frac{\Delta A}{\Delta t}$ (i.e. the growth rate) with an exponent of ~ 0.5 , indicating a diffusion-controlled process (Figs. 2b–c). *Ex-situ* 4D-STEM diffraction imaging, performed on the same locations as in EC-STEM, show that both Cu and Au exhibited diffraction patterns close to the [110] zone axis (Figs. 2i–m), indicating that Cu electrodeposition was guided by the crystallographic orientation of the Au nanocube substrates. A false-color dark-field 4D-STEM map based on Au/Cu(115) clearly shows the ~ 10 nm Cu nanodomains on Au (Fig. 2n).

In summary, *operando* EC-STEM quantitatively resolved the potential-dependent kinetics of Cu UPD at nm-scale and revealed that the crystal orientation of the diffusion-controlled Cu electrodeposition was guided by the Au nanocube substrates [7].

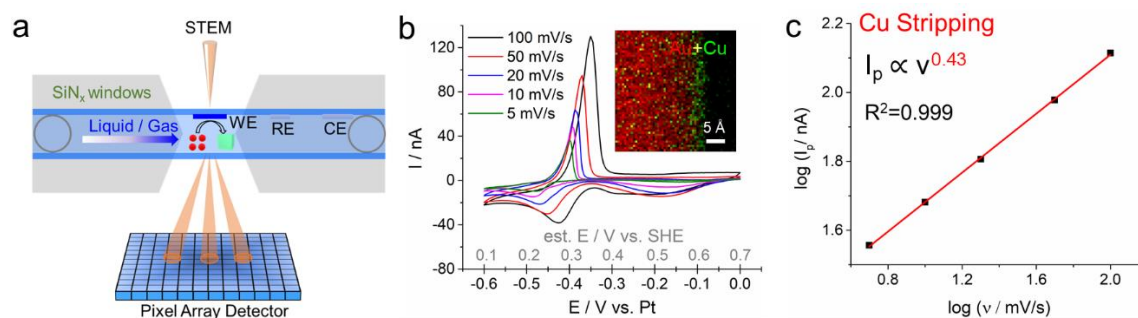


Figure 1. (a) Schematic of *operando* EC-STEM cell with the capability to enable quantitative electrochemistry and simultaneously track dynamic evolution under operating conditions. (b) CV profiles of Cu electrodeposition on Au nanocubes in Ar-sat. 1 mM CuSO₄ / 0.1 M NaClO₄ in the EC-STEM. Inset, *ex situ* STEM-EELS of monolayer Cu deposited on Au cube surface. (c-d) Quantitative analysis of Cu stripping peak currents in (b) vs. scan rate.

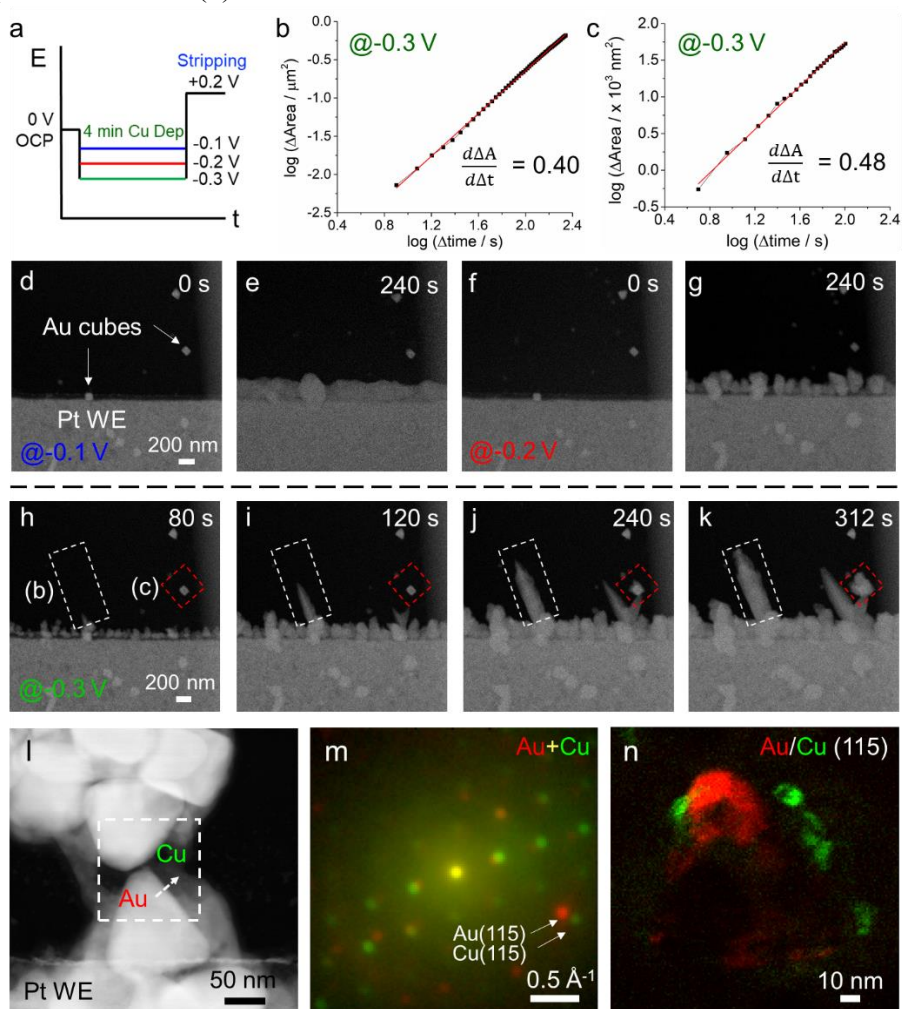


Figure 2. *Operando* EC-STEM during Cu electrodeposition under steady-state conditions. (a) Experimental procedures of Cu electrodeposition at -0.1, -0.2 and -0.3 V followed by stripping at +0.2 V vs. Pt. (b-c) Quantitative STEM imaging analysis of the area increase vs. time of two Cu particles in the white and red boxes labeled b, c, respectively, in Fig. 2h. (d-e, f-g and h-k) *Operando* EC-STEM movies of Cu electrodeposition at -0.1, -0.2 and -0.3 V, respectively, at the identical location. (l-n) *Ex situ* 4D-STEM of Cu electrodeposited on Au nanocubes: (l) HAADF-STEM image. (m) Overlay of diffraction patterns for Au (red) and Cu (green). (e) Dark-field 4D-STEM maps of Au and Cu domains extracted from the Cu(115) and Au(115).

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