On the Unusual Electrochemical Stability of Nanofabricated Copper Clusters**

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Small metal clusters are known to have electronic and structural properties that often differ vastly from those of the respective bulk material. Particularly in the 1 – 10 nanometer range (i.e. several tens to a few hundred atoms), where the metal clusters are too large for a molecular description, yet too small for ignoring the reduced dimensionality, quantum confinement effects are expected to play a dominant role. While studies of the latter effects are frequent for thin metal layers on, for example, semiconductor substrates,[1] fewer studies have been made for small metal particles.

Small clusters of copper can be arranged on gold surfaces by the tip of a scanning tunneling microscope (STM).[2–4] Copper is first electrodeposited from solution onto the STM tip and then transferred from the tip to the substrate by an appropriate tip approach, during which a so-called "jump-to-contact"[5] occurs. The resulting metal bridge between the tip and sample breaks upon retraction of the tip, leaving a copper cluster on the surface. Tip approach, as well as tip position, are externally controlled by a microprocessor. The height of the copper clusters can be controlled between two and approximately five atomic layers (i.e. 0.4 to 1.0 nm) by varying the tip approach.[2, 3] The apparent width of the clusters is about 3.5 nm (measured as the full width at half maximum cluster height, FWHM) and since this measurement is subject to the limits of lateral resolution of the STM, the actual cluster width is obviously somewhat less. Under such premises one cluster should contain roughly 100 copper atoms. These nanofabricated particles revealed a surprisingly high stability against anodic dissolution.[3, 4, 6] This unusual behavior prompted a more systematic investigation, as stable clusters are sought after as electrocatalysts.

In Figure 1, an STM image of an array of 25 tip-induced copper clusters on a gold(111) surface is shown. At $E_{\text{sample}} = +10$ mV versus Cu/Cu^{2+} the surface is covered with a monolayer of copper due to underpotential deposition (UPD);[7] hence the copper clusters are sitting on this monolayer. The clusters have an average height of 0.6 nm and a width (FWHM) of 3.2 nm.

In order to avoid bulk copper deposition from solution onto the gold substrate, the electrode potential was usually set to +10 mV versus Cu/Cu^{2+}, that is, positive of the Nernst potential, where bulk copper deposition from solution is thermodynamically impossible. On the other hand, bulk copper is unstable positive of the Nernst potential and copper clusters should be readily dissolved at +10 mV. Tip-induced copper clusters withstand anodic dissolution at +10 mV for a surprisingly long period: In Figure 2 the height of tip-induced copper clusters on the gold substrate is shown as a function of time for three different electrode potentials. At +10 mV versus Cu/Cu^{2+} the cluster retains its height for more than 50 min, whereas at +200 mV versus Cu/Cu^{2+} the cluster disappears rapidly (except for a second layer on top of the UPD layer). At +100 mV versus Cu/Cu^{2+} the copper cluster dissolves layer-by-layer and the remainder becomes more stable with each dissolved layer.

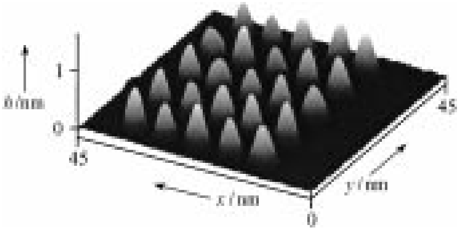

Figure 1. In situ STM image of an array of 25 tip-induced Cu clusters on Au(111) in 0.05 M H_2SO_4 + 0.05 mM $CuSO_4$. $E_{\text{sample}} = +10$ mV, $E_{\text{Tip}} = -50$ mV vs. Cu/Cu^{2+}; $I_{\text{Tunnel}} = 2$ nA.

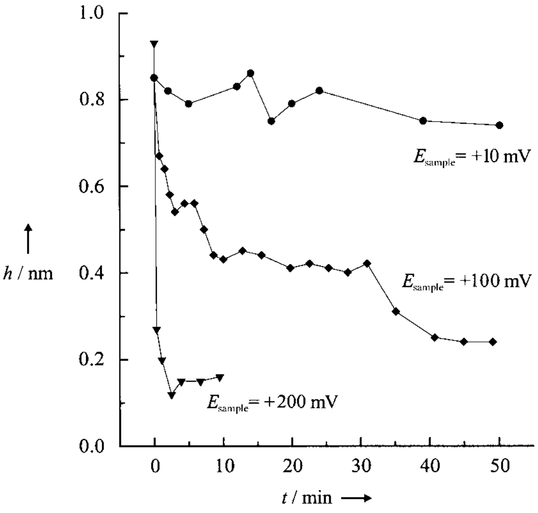

Figure 2. Heights (h) of three tip-induced Cu clusters on Au(111) in 0.05 M H_2SO_4 + 0.1 mM $CuSO_4$ as a function of time for three different sample potentials.

In order to demonstrate the role of cluster size on the stability, considerably larger copper clusters were generated by normal copper deposition from solution. Such clusters were either obtained by nucleation and growth of copper at surface defects, such as monoatomic high steps,[7] or by using tip-induced clusters as nucleation centers[4] onto which copper was deposited from solution until the desired cluster size was reached. The stability of a 2.4 nm high copper cluster, grown by deposition from solution, against anodic dissolution at +10 mV versus Cu/Cu^{2+} is shown in Figure 3. The line scan across the cluster is shown as a function of time ($x-t$ scan). The mesalike cluster was deposited at −310 mV versus

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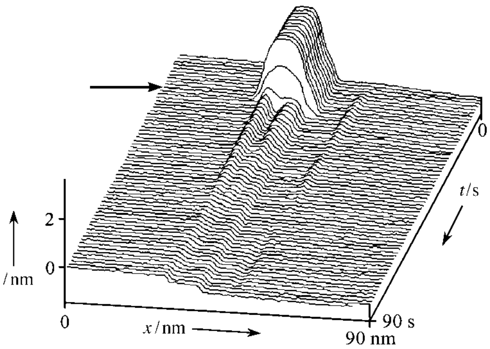

Figure 3. Scan ($x-t$) across an electrochemically grown Cu cluster on Au(111). The arrow at $t=15$ s indicates the sample potential jump from -310 mV to $+10$ mV vs. Cu/Cu^{2+}. Electrolyte: 0.05 M H_2SO_4 + 0.2 mM $CuSO_4$.

Cu/Cu^{2+} and its height remained constant during the first 15 s of imaging. At $t=15$ s a potential step to +10 mV was applied (arrow in Figure 3) and the cluster immediately disappeared as expected for normal, bulk copper. Equally noteworthy is that large copper clusters, grown electrochemically on top of the tip-induced clusters, readily dissolved at +10 mV versus Cu/Cu^{2+} except for a remnant almost identical in shape and height to the original tip-induced cluster.

In order to determine the dissolution potential of the small, tip-induced copper clusters, their heights were monitored as a function of potential. Two different experimental approaches were chosen to ensure exclusion of artifacts. In the first experiment set, a single tip-induced cluster was imaged in an $x-t$ scan, while the electrode potential was increased at a constant rate. Figure 4 shows an $x-t$ scan for a tip-induced cluster, where the potential scan was started at $t=7$ s at +10 mV increasing at 20 mVs^{-1} up to +250 mV. Therefore, the time axis also represents a potential axis. It is clearly seen that cluster dissolution starts at about $E_{\text{sample}} = +40$ mV versus Cu/Cu^{2+}. Further steps in the cluster height can be seen at around 80 mV and 170 mV. A small remnant, about one monolayer high, remains stable at 250 mV versus Cu/Cu^{2+} for another 12 s before the cluster is completely dissolved. Since height variations for a single cluster in $x-t$ scans can be influenced by thermal drift of the STM, a second experiment set was employed: We produced an array of 27 × 10 copper clusters and took an STM image at +10 mV versus Cu/Cu^{2+}. The whole array was again imaged while the potential was increased simultaneously from +10 mV up to +250 mV. This second image showed the decreasing cluster height with increasingly positive potential (Figure 5). Again we found the cluster height remains constant to about 50–60 mV before dissolution began. It thus appears that copper clusters, three to four layers high, are stable up to an electrode potential around 50 mV versus Cu/Cu^{2+}, smaller clusters are stable to around 180 mV, and the dissolution follows discrete steps. Figure 5, for comparison, shows also the stability range of large copper clusters, which presumably share properties of the bulk metal. The large clusters are almost nonexistent at the potential range used for small clusters.

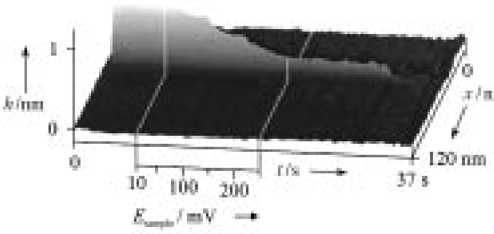

Figure 4. Scan ($x-t$) across a tip-induced Cu cluster on Au(111). The sample potential E_{sample} increased during imaging from +10 mV to +250 mV vs. Cu/Cu^{2+} at 20 mVs^{-1}. Electrolyte: 0.05 M H_2SO_4 + 1 mM $CuSO_4$.

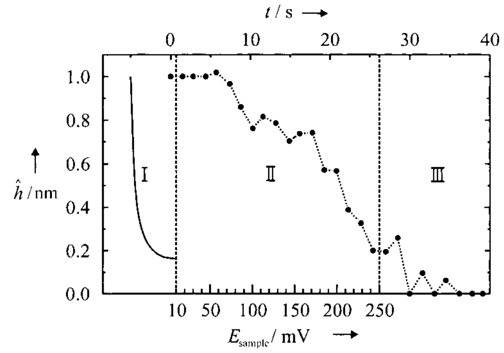

Figure 5. Normalized height ($\hat{h}$) of tip-induced Cu clusters as a function of time (normalized with respect to their initial height). Electrolyte: 0.05 M H_2SO_4 + 1 mM $CuSO_4$. Region I: $E_{\text{sample}} = +10$ mV vs. Cu/Cu^{2+}. Region II: E_{sample} increased from +10 mV to +250 mV vs. Cu/Cu^{2+} at 10 mVs^{-1}. Region III: $E_{\text{sample}} = +250$ mV vs. Cu/Cu^{2+}. For comparison, in region I, the result for the electrochemically grown cluster dissolving at +10 mV vs. Cu/Cu^{2+} (see Figure 3) is shown again.

We now turn to the question of how to explain the unusually high stability of small copper clusters on gold(111). For many in situ STM studies, the close proximity of the tip has been found to exert a noticeable influence on electrochemical reactions.[8] Early explanations for these stability effects suggested tip shielding.[2] Stability tests with tips that were retracted by about 3 μm during most of the time and only briefly engaged every few minutes for cluster height measurements, yielded the same result as studies with permanently engaged tips. Later explanations were based on kinetic or thermodynamic arguments. Assuming the small metal clusters to be more or less perfect single crystal units, a high overvoltage for dissolution was suggested due to lack of defects.[3] Lorenz et al.[9] coined the expression "zero-dimensional phase" for the small clusters. The stability of a metal increases in the order of three-, two- and one-dimensional forms, as bulk metal, UPD monolayers, and metal atoms at substrate steps, respectively. The "zero-dimensional phase" corresponds to a much more positive Nernst potential. None of the explanations were satisfactorily.

The concept of a metal electrode in equilibrium with its ion in solution, which stands behind the Nernst equation, requires electronic states at the Fermi level. These states are plentiful in common metals. For semiconductor electrodes, metal deposition and dissolution are no longer determined by the Nernst potential of the metal but rather by the availability of electronic states in the electrode. If the dimensions of the metal are reduced to those of the "electron in a box" problem (the nanometer range) the electronic states in the metal become discrete in their energy distribution. To a very simple approximation, the energy gap ΔE between the electron states in a small metal particle can be estimated by $\Delta E = E/N$, where E is the width of the energy band in the metal and N is the number of atoms per cluster.[10] For $E = 10$ eV[11] and $N = 100$ an energy separation of the order of 0.1 eV is obtained. This, of course, is a rather crude estimation, but it demonstrates that overpotentials (in this case in the thermodynamic sense) of 50 or 180 mV, as observed in the experiment, can result from quantum effects. Consider a redox potential, that is, the Fermi level of the redox system, lying within the energy gap of the metal cluster. Dissolution of the metal would only start after the energy states in the cluster have been shifted by a change in the electrode potential to match the redox potential. We thus propose that the stability range of our tip-induced copper clusters of at least 50 mV versus Cu/Cu^{2+} (which is quite significant in electrochemical terms) might be a consequence of quantum effects. An obstacle for such an interpretation is the fact that the copper clusters are on a metal rather than on an insulator surface, which raises the question of a quantum confinement normal to the surface. However, since the contact between copper cluster and the gold(111) substrate represents a discontinuity in structural as well as in electronic terms, this interface may well provide the necessary barrier for the electrons in the cluster.

Experimental Section

Both fabrication and imaging of the Cu clusters were performed with a PicoSPM (Molecular Imaging Corp., Tempe, Arizona). The electrolyte used in this study was 0.05 M H_2SO_4 with concentrations of Cu^{2+} between 0.05 and 1 mM, prepared from H_2SO_4 (Merck, 96 %), $CuSO_4 \cdot 5\,H_2O$ (Fluka, >99 %) and Milli-Q water (Millipore). Sample and tip potentials were controlled independently from each other by a bipotentiostat. As reference electrode, a Cu or a Pt wire was used, and the counter electrode was a Pt wire. The tip was made from a 0.25 mm diameter Pt/Ir (80/20) wire by electrochemical etching. All potentials are quoted against Cu/Cu^{2+} in the same solution. Other technical details are given in references [2, 3, 12].

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Synthesis of the (9*S*,18*R*) Diastereomer of Cyclamenol A**

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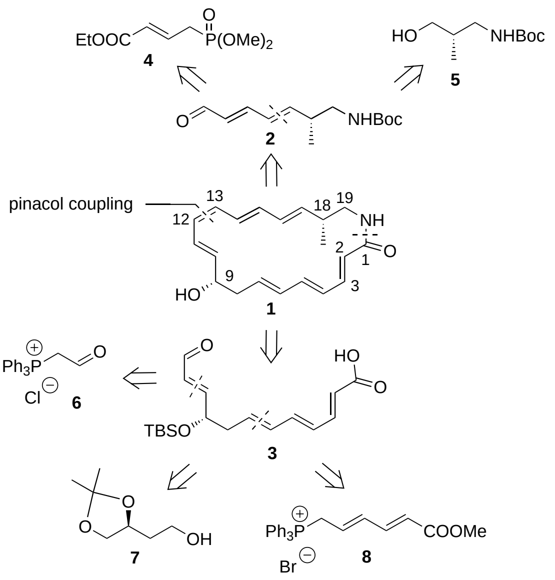
A key event in the humoral response to inflammation, tissue injury, and infection is the transport of leukocytes to the site of injury. It is facilitated by adhesion of the leukocytes to endothelial cells and their subsequent transmigration from the bloodstream through the wall of the blood vessel and the surrounding tissue.[1] Over-recruitment of these blood cells can result in the establishment of various diseases and disorders ranging from chronic autoimmune diseases to acute inflammation. Intervention of leukocyte recruitment by inhibiting their adhesion to endothelial cells is considered to be a new strategy for the development of antiinflammatory agents. This approach may offer entirely new and alternative opportunities for the treatment of, for example, reperfusion injuries, strokes, asthma, and arthritis. Thus, the development of peptide and carbohydrate derivatives as inhibitors of the selectin/sialyl Lewis X interaction has attracted considerable interest.[2] However, non-peptide and non-carbohydrate natural products have not been investigated so far.

Cyclamenol A (**1**) (Scheme 1), a macrocyclic polyene lactam isolated from *Streptomyces spec.* MHW 846 by chem-



Scheme 1. Retrosynthetic analysis of cylamenol A (**1**). Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl.

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