Electrochemical Deposition of Metal Nano-Disk Structures Using the Scanning Tunneling Microscope

by

W. Li, T. Duong, J.A. Virtanen, and R.M. Penner

Prepared for Publication in the Proceedings NATO ASI 1993

University of California, Irvine
Department of Chemistry
Irvine, CA 92717-2025

July 12, 1994

Reproduction in whole or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.
Silver nanodisk structures were electrochemically deposited on graphite surfaces using a scanning tunneling microscope (STM). The deposition of metal occurs via a two-step mechanism involving the fast (2-5 μsec) formation of a 7Å-deep pit in the graphite surface, followed by nucleation and diffusion limited electrochemical deposition at this pit. An electrolysis time of 50 μsec produces diffusion-limited nanostructure dimensions of ≈200-400Å in diameter and 20-50Å in height. Silver nano-disk structures are stable in dilute aqueous solutions containing Ag⁺ at small (=20mV) sample-negative imaging biases, but are unstable with respect to dissolution at sample positive biases or when immersed in a pure water ambient (irrespective of the applied bias). The mechanism of discharge of a nanometer-scale battery consisting of copper anodes and silver cathodes is examined.
ELECTROCHEMICAL DEPOSITION OF METAL NANO-DISK STRUCTURES USING THE SCANNING TUNNELING MICROSCOPE

Wenjie Li, Tim Duong, Jorma A. Virtanen, and Reginald M. Penner*

Institute for Surface and Interface Science and,
Department of Chemistry
University of California, Irvine
Irvine, CA 92717-2025

ABSTRACT. Silver nanodisk structures were electrochemically deposited on graphite surfaces using a scanning tunneling microscope (STM). The deposition of metal occurs via a two-step mechanism involving the fast (2-5 μsec) formation of a 7Å-deep pit in the graphite surface, followed by nucleation and diffusion limited electrochemical deposition at this pit. An electrolysis time of 50 μsec produces diffusion-limited nanostructure dimensions of ~200-400Å in diameter and 20-50Å in height. Silver nano-disk structures are stable in dilute aqueous solutions containing Ag⁺ at small (~20mV) sample-negative imaging biases, but are unstable with respect to dissolution at sample positive biases or when immersed in a pure water ambient (irrespective of the applied bias). The mechanism of discharge of a nanometer-scale battery consisting of copper anodes and silver cathodes is examined.

1. Introduction.

The chemistry and physics of small silver particles having an agglomeration number, n, in the range 1<n<10⁶ have been intensively studied.¹⁻¹² To date, experimental investigations have been carried out exclusively on suspensions of colloidal particles. Measured physical properties for such suspensions represent averages over a particle size and shape distribution and a persistent problem has been the deconvolution of effects due to particle size and shape polydispersity from these experimental data.⁴ An alternative approach, which in principle circumvents the polydispersity problem, is to observe the properties of single metal particles. Until now, however, it has been impossible to prepare single metal particles under circumstances permitting the observation of these particles in chemically relevant ambients (e.g., aqueous solutions).

Here we describe an electrochemical method for preparing nanoscopic particles of silver and copper on single crystal graphite surfaces by performing an electrolysis of an aqueous metal-ion containing solution between the tip of a scanning tunneling microscope (STM) and a graphite surface.¹³,¹⁴ Disk shaped silver and copper particles having typical dimensions of 200-400Å in diameter and 20-50Å in height are produced by this method. These particles were produced during a 50 μsec electrolysis (occurring between the STM tip and surface) via a two-step mechanism in which a shallow, 7Å-deep pit is first induced in the graphite surface, followed immediately (i.e., within 1-2 μsec) by nucleation and electrochemical growth of metal at this pit. Once formed, the silver nanostructure is firmly anchored to the pit on the graphite surface on which it nucleated and the nanostructure exhibits no tendency to translate on the surface even during repetitive STM imaging at high tunneling currents of up to 1.0 nA.

*Address correspondence to this author.
Because these metal particles are disposed on the atomically smooth, and electrochemically inert graphite basal plane, the metal particles produced by this method constitute an extremely versatile “laboratory” for in-situ STM investigations of stability, electronic structure, inter-particle reactivity, and molecular adsorption in a variety of chemically relevant ambients.


A commercial air/liquid STM in the normal two-electrode mode was employed for the deposition and imaging experiments described here. Polymer-insulated STM tips were employed for all measurements. These were fabricated from electrochemically etched platinum wires by coating with poly-a-methyl styrene, as described previously. The residual faradaic currents present with these tips, measured at a tip-sample separation of ≈5 μm, never exceeded 50 pA in these experiments. Electrochemical deposition of silver and copper were accomplished using a commercial scanning tunneling microscope (Park Scientific Instruments, Autoprobe CP) using the conventional two electrode mode (i.e., STM tip and sample). The deposition of silver was accomplished using aqueous plating solutions containing 0.5 mM of either silver fluoride (Aldrich, 99.95%), or copper sulfate (Aldrich, 99.95%). CuNO\(_3\) and CuCl\(_2\), employed for short circuit coulometry measurements, were >99% from Aldrich. All solutions were prepared using Nanopure water (p > 18MW). Single bias pulses for nanostructure deposition were supplied by a Hewlett Packard 214B pulse generator; coulometric transients were measured using a Keithley 428 current amplifier in conjunction with a Tektronix 2240 digital storage oscilloscope. The STM was equipped with a liquid cell, constructed of Kel-F, which enabled the immersion of the tip and sample in 50 μl of solution and which allowed for the exchange of solutions during STM imaging. Highly oriented pyrolytic graphite substrates were cleaved immediately prior to use. All STM images were obtained in constant current mode and represent raw data except for the subtraction of a linear background.

3. Investigations of the Mechanism of Metal Deposition.

![STM image of a silver nano-disk structure on graphite in aqueous 0.5 mM AgF immediately following deposition. STM tip-sample bias and tunneling current were 0.6 nA and +20 mV, respectively.](image)

**Figure 1.** STM image of a silver nano-disk structure on graphite in aqueous 0.5 mM AgF immediately following deposition. STM tip-sample bias and tunneling current were 0.6 nA and +20 mV, respectively.
Figure 1 shows a silver nano-disk structure which was deposited from an aqueous solution containing 0.5 mM AgF. Deposition of this structure, which has dimensions of ~500Å in diameter and ~50Å in height, was effected by applying a +6.0V x 50 μsec bias pulse while the STM tip was tunneling with an applied bias, \( E_B = +20 \text{ mV} \), and tunneling current, \( I_t = 0.6 \text{ nA} \). Prior to the application of the bias pulse, the graphite surface at this location was atomically smooth and defect free. Silver nanostructures, like that shown in Figure 1 are strongly adherent to the graphite surface as indicated by the fact that the structure exhibits no tendency to translate even during repetitive STM imaging at tunneling currents has high as 1.0 nA.

The mechanism of silver nanostructure nucleation and growth is depicted in the schematic diagrams of Figure 2. Figure 2A represents the STM tip and surface at the initiation of the silver deposition by the application of a +6.0V x 50 μsec bias pulse - the graphite surface is initially atomically smooth and defect free at the deposition site and the STM tip is tunneling with X and Y scans turned off. Following 5 μsec at 6.0V (Fig. 2B), a shallow pit is observed in the graphite surface. The typical dimensions of this pit are 100Å diameter and 7Å in depth. Pit formation on graphite surfaces was reported first by Quate and coworkers 1 and subsequently by a number of other groups. More recently, Penner et al. demonstrated that a well-defined 4.0V pulse threshold exists for bias pulse-induced pit formation in the STM for graphite surfaces immersed in aqueous solutions. The electrochemical deposition of silver is first observed at the circumference of the pit at approximately 10 μsec following a step-wise increase of the imaging bias to +6.0V, as shown in Fig. 2C. The most probable "counter-electrode" reaction at the platinum STM tip is the oxidation of water, as shown. In Fig. 2D, the silver nanostructure has attained diffusion-limited dimensions of 200-400Å in diameter and 20-50 Å in height. Further increases in the dimensions of the nanostructure are not observed with longer electrolysis times of, for example, 100 μsec. This fact suggests that the observed nanostructure dimensions are diffusion limited, and that following a 50 μsec electrolysis, silver ion is depleted from the volume of solution which is sandwiched between the STM tip and the graphite surface.

The two-step mechanism of nanostructure nucleation and growth is corroborated by experiments in which the nature of the modification produced on the graphite surface by +6.0 V...
bias pulses is investigated as a function of the bias pulse duration. Typical data are shown in Figure 3. Figure 3A shows the pit produced by the application of a +6.0V x 5 μsec bias pulse in an aqueous solution containing 0.5 mM AgF. The approximate dimensions of this pit are 150Å in diameter x 7Å in depth indicating the removal a single graphite atomic layer. No evidence for the electrochemical deposition exists, despite the fact that the applied bias is more than an order of magnitude greater than that which is thermodynamically required to deposit silver metal. We attribute the absence of observable silver metal to the rate limiting diffusional transport of silver on the 5 μsec time scale. This result establishes that pit formation is completed in less than 5 μsec. In other experiments, we have found that pits are reliably produced by bias pulses having durations

![Image of STM images](image_url)
as short as 1.0 μsec. This experiment demonstrates that pit formation is complete prior to the onset of significant silver metal deposition. In Figure 3B is shown an STM image of the same region of the graphite surface following the application of a bias pulse having a 50 μsec duration and an amplitude of just +3.0V. This bias pulse amplitude is too small to induce a modification to the graphite surface,

but of sufficient amplitude to simultaneously drive the reductive deposition of silver and the oxidation of water at the STM tip. It is observed in this image that silver metal has filled the pit produced in the experiment of frame A. This result confirms that the time scale associated with electrochemical deposition of metal is much longer than that associated with pit formation. That the protrusion of Figure 3B is, in fact, silver metal is confirmed by the experiment of Figure 3C in which the STM imaging bias was switched from ≅+25 mV (tip vs. sample) to -25 mV. Within 5 minutes, anodic dissolution of the silver nanostructure occurs, again revealing the pit produced in the experiment of frame A. This result establishes that the potential of the graphite surface in frame B is within a 50 mV window about the Nernst potential for silver as defined by equation (1):

\[ E_{\text{Nernst}} = E^0_{\text{Ag}/\text{Ag}} + \frac{RT}{F} \ln \frac{1}{[\text{Ag}^+]}. \]  

(1)

The effect of the imaging bias is to displace the potential of the graphite surface slightly either positively or negatively from the Nernst potential, and it is therefore possible to exert considerable control over the dimensions of nanoscopic silver particles even using the simple, two electrode (i.e., STM tip and surface) instrumentation employed here. In Figure 3D, for example, the pit produced in frame A has again been filled with silver by simply switching the imaging bias to +25 mV and applying a second, +3.0V x 50 μsec bias pulse. At this sample-negative bias, the silver nanostructure is completely stable while imaged in the STM repeatedly over the course of an hour or more.

The stability of silver nanodisk structures may be controlled via the STM imaging bias only when these structures are immersed in an aqueous solution containing silver ions. In the absence of silver ion, Equation (1) predicts that \( E_{\text{Nernst}} \) of the surface is undefined and the potential of the surface is then free to drift either positively or negatively from \( E_{\text{Nernst}} \). We have observed that silver nanodisk structures slowly dissolve away when transferred into a pure water ambient. As expected, the rate of this dissolution is not affected by application of very negative STM imaging biases because neither the STM tip nor the graphite surface (in the absence of silver metal) has an established Nernst potential.

4. The Mechanism of Discharge For a Nanometer-Scale Ag/Cu Galvanic Cell.

Metal particles, prepared by the technique described above, are ideally suited to investigations of stability. In particular, questions relating to metal corrosion, inter-metallic reactivity, and mechanisms of dealloying may be addressed by experiments involving pairs of dissimilar metals codeposited on a graphite surface. Figure 4 shows one example involving the spontaneous reaction of copper and silver nanostructures immersed in an aqueous 0.5 mM CuSO\(_4\) solution.\(^{14}\) In this experiment, the two silver nano-disk structures (shown at right in Figure 4) were first deposited from a 0.5 mM AgF solution. The silver plating solution was then removed.
and replaced with the copper electrolyte and the two copper nanostructures at left were deposited. The STM image of Figure 4 was then acquired and subsequently, over the next 45 minutes, a

![STM image of copper and silver nano-disk structures codeposited on a graphite surface prior to reaction.](image)

**Figure 4.** STM image of copper and silver nano-disk structures codeposited on a graphite surface prior to reaction.\(^\text{14}\) (Reprinted with permission of the ACS).

![Graph showing volume of metal structures over time.](image)

**Figure 5.** Plots of nanostructure volume, obtained from integration of STM line scans, versus time for the four metal nanostructures shown in Figure 4.\(^\text{14}\) (Reprinted with permission of the American Chemical Society).
monotonic decrease in volume of the copper nanostructures and an increase in volume of the silver nanostructures was observed. The volumes of all four electrodes - obtained from line scan integrations - are plotted as a function of time in Figure 5.14

It is proposed14 that the spontaneous and persistent volume changes observed in this experiment occur as a consequence of the underpotential deposition (UPD) of copper on the silver nanostructures, and the concomitant anodic dissolution of copper from the copper nanostructures over time. Although metal monolayer formation via UPD has been observed previously for many pairs of metals,22 the UPD of copper and silver has never previously been reported although Hubbard and coworkers have looked for this reaction at Ag(111) surfaces in aqueous trifluoroacetate electrolytes.23

The existence of this electrochemical reaction, however, is easily confirmed by performing a short-circuit coulometry experiment. This experiment, which is shown schematically in the inset

![Figure 6](image.png)

**Figure 6.** Plots of current versus time following the connection of copper and silver wires, immersed in 0.5 mM CuNO₃ (pH = 2.5), as shown in the inset. Both copper and silver wires had diameters of 0.125 mm and the numbers shown at upper right are distances of immersion of the silver wire into the copper nitrate electrolyte.

of Figure 6, essentially constitutes a macroscopic model for the nanometer-scale galvanic cell shown in the STM image of Figure 4. Copper and silver wires are immersed in a 0.5 mM CuNO₃ electrolyte and at time = 0, are shorted together through a sensitive picoammeter. The existence of faradaic discharge should be revealed by a current transient which is cathodic at the silver wire, and which scales linearly with the area of the silver wire exposed to the copper plating solution. As shown in Figure 6, this is qualitatively the behavior which is observed.
Integration of these current transients yields the data like that shown in Figure 7. The dependence of charge on the immersion of the silver wire is clearly linear and the slopes of the lines for the data shown in Figure 7 (square data points only) are $25.3 \times 10^{-5}$ C cm$^{-2}$ for the chloride electrolyte, and $8.15 \times 10^{-5}$ C cm$^{-2}$ for the nitrate electrolyte. Assuming the measured charge derives only from Faradaic discharge of copper at the silver surface, the equations of these lines are given by:

$$Q = nF \Gamma_{ads}A$$

where $\Gamma_{ads}$, the copper coverage (moles cm$^{-2}$), for chloride and nitrate are $1.31 \times 10^{-9}$ moles cm$^{-2}$ and $4.22 \times 10^{-10}$ moles cm$^{-2}$, respectively, corresponding to 0.70 and 0.23 monolayers in these two electrolytes assuming a radius for copper on the silver surface of 1.6Å. Although a detailed explanation of these numbers will not be attempted here, these results are consistent with the formation of partial monolayers of copper on the silver surface at short circuit as expected for UPD, and as previously proposed$^{14}$ to account for the galvanic discharge of the nanometer-scale cell shown in Figure 4.

5. Summary.

A general method for the electrochemical deposition of single silver and copper nanodisk structures on graphite surfaces has been developed. Following the application of a $+6.0V \times 50$
μsec bias pulse to the graphite surface in an aqueous Ag⁺ or Cu²⁺-containing solutions, the nucleation and growth of silver occurs via a two step mechanism involving the rapid formation of a monolayer-deep pit in the graphite surface, followed promptly by the nucleation and electrochemical growth of silver at this defect. Significantly, control over nanostructure dimension may be exerted via adjustments to the STM imaging bias. In principle, this strategy enables silver nanostructures of arbitrary dimensions to be prepared. Metal particles prepared by the procedure described here are likely to be useful for investigations of metal nanoparticle stability, inter-metallic reactivity, electronic structure, and adsorption.

6. Acknowledgment.
We thank Arthur Moore at Union Carbide for generous donations of highly ordered pyrolytic graphite. This work was supported by the donors of the Petroleum Research Fund administered by the ACS, and the Young Investigator Award programs of the National Science Foundation and the Office of Naval Research. RMP further acknowledges the generous financial support of the NATO Advanced Study Institute.

7. References.


