

Electrodeposition of Metal Wires onto a Molecular Scale Template:
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We have demonstrated that the intrinsic nanometer length scales of two-dimensional molecular assemblies can be exploited to electrodeposit metal nanostructures with regular spacing and orientation. We observed evidence for preferential deposition of metals into parallel lines on Au(111) surface with a periodicity of 4.5 nm as determined by the hemimicelles formed by sodium dodecylsulfate. The preferential deposition of metals in molecular templates was achieved under optimal electrode potentials and ionic concentrations. The observed metal structures provide insight into the interactions between metal atoms, organic functional groups as well as the aqueous environment. Understanding and tailoring these interactions will lead to more precise control and new strategies for nanoscale placement and for connecting organic molecules to metal nanostructures.

Introduction

There has been intense interest in studying and controlling self-assembled structures of organic molecules on surfaces.^{1–4} Through deliberate molecular design, assembly strategies, as well as the aid of real space characterization techniques such as scanning probe microscopy, self-assembled structures formed by molecular adsorbates are being developed with increasing levels of sophistication.^{1–4} An interesting question is whether these two-dimensional (2D) molecular adlayers, which are one to a few molecules thick and have controllable lateral arrangements, can function as templates to pattern metal structures in the surface plane. Compared to typical self-assembled templates that are inherently bulk structures and offer little or no control over the lateral arrangement of the nanostructures produced,^{5,6} the 2D adlayers can produce nanostructures not only of desired dimensions but also with precise lateral arrangements according to the spatial registry of the adlayers. Metals have been deposited onto diblock copolymer and organic nanotube templates to grow nanowires perpendicular to a surface.^{7,8} Molecules can also direct the growth of nanostructures aligned along the surface. Self-assembled multilayers have been shown to function as resists that result in metal structures with gaps precisely defined by the sizes of the resist molecules.^{9,10} Biopolymers such as proteins and DNA

have been used to either nucleate electrodeposition¹¹ or to block electrodeposition in select sites.¹² Mao and co-workers produced copper sulfide wires in the presence adlayers through reaction between copper ions and hydrogen sulfide gas.¹³ However, the real space growth dynamics of the nanostructures in molecular scale templates remained unexplored. Hence, the nanoscale interaction between metal atoms and organic molecules remained largely unknown. Such interactions become more important as the requirements for precision in nanofabrication approaches the atomic scale. We demonstrate a new approach that utilizes the molecular scale features of 2D self-assembled structures to pattern electrodeposited metals and allows in situ visualization of the atomic scale process.

The present work focuses on the surface aggregates derived from a surfactant molecule.^{14,15} The hydrophobic chains of sodium dodecylsulfate (SDS) aggregate on surfaces to form hemicylinders, exposing the hydrophilic head groups to the aqueous environment (Figure 2A) even at concentrations below the bulk critical micelle concentration (8 mM).¹⁶ SDS molecules in the first surface layer lie flat to form rows with a head-to-head, tail-to-tail configuration (Figure 2A).¹⁷ The unit cell of the ordered structure is 4.4 nm long and 0.5 nm wide.¹⁷ The sulfate head groups are about 0.8 nm apart.¹⁷ It was found that SDS hinders Cu electrodeposition on Au electrodes.¹⁸ With ex situ electron microscopy and X-ray diffraction, Choi et al. found that electrodeposited ZnO in the presence of SDS formed layered structures.¹⁹ However, the techniques they used could not unambiguously determine the structures of surfac-

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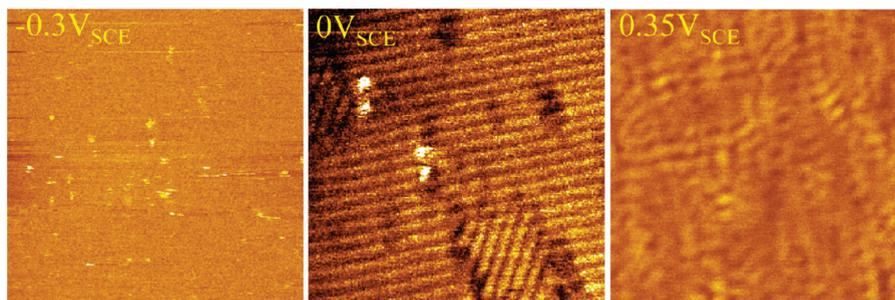


Figure 1. Surface charge-dependent structure of SDS on Au(111) in a 10 mM SDS solution. Image size: $100 \times 100 \text{ nm}^2$.

tant molecules in the layered structures, and the precise role of the surfactant molecules remains uncertain.¹⁹ Because of the limited interfacial control employed, more elaborate structures, such as one-dimensional wires oriented along the surface, were not formed under those conditions. In this work, we use in situ scanning probe microscopy to directly investigate the dynamic electrodeposition processes in the presence of SDS hemimicelles. We have determined the conditions that allow the 2D molecular assemblies to template electrodeposited metal nanostructures. We have found that the deposition of metal nanostructures follows a nucleation and growth mechanism. Our study demonstrates that, in order to achieve the desired nanoscale placement in the physisorbed template, the stability of the molecular template must be maintained by careful control of the electrode potential. In addition, we have found that kinetic control can be utilized to limit the deposition of metal atoms to preferential sites. The observed metal structures provide insight into the interactions between metal atoms, organic functional groups, and the aqueous environment. An interdigitated bilayer structure of SDS is proposed to form on top of the electrodeposited silver nanowires. Understanding and tailoring these interactions will lead to more precise control for atomic scale patterning as well as new strategies to connect organic molecules to metal nanostructures.

Methods

An Au(111) single crystal disk (Monocrystals Co., Richmond Heights, OH) was used as the substrate. The electrochemical cell was made of Teflon. An O-ring (Chemraz, Ace Glass) was used to prevent the leakage of the surfactant solution. A silver wire was used as the quasi reference electrode. The potential is quoted against SCE. A platinum wire was used as the counter electrode. AFM images were obtained with a PicoScan SPM system (Molecular Imaging) with oxide sharpened Si_3N_4 AFM tips (Digital Instruments). The cantilever with a nominal spring constant of 0.06 N/m was selected for imaging. The tips were cleaned in hot piranha solution (1:3 H_2O_2 (J.T.Baker, CMOSTM) and H_2SO_4 (J.T.Baker)) prior to imaging. Images were acquired mainly in the deflection mode, which is more sensitive to the contour of the electric double layer force and yields superior resolution of SDS surface aggregates.^{14,15} Topographic mode images showed similar basic features, but the resolution was poorer. Scanning tunneling microscopy (STM) images were obtained with the same SPM system. Electrochemically etched tungsten tips insulated by polyethylene were used. A bipotentiostat (Molecular Imaging) was used to control the sample and tip potential independently.

All chemicals, including SDS (Fluka, >99%), sodium perchlorate monohydrate (Fluka, puriss grade), and silver perchlo-

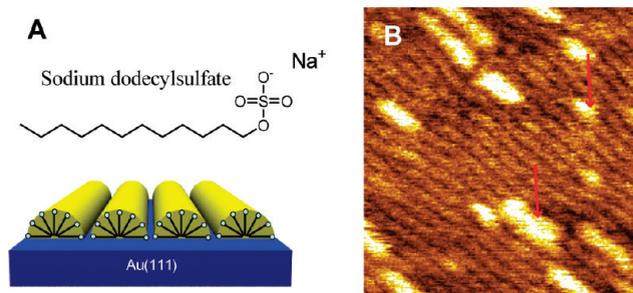


Figure 2. (A) Proposed model of hemicylinders of SDS on Au(111).¹⁵ (B) AFM image of Au(111) in a 10 mM SDS solution containing $1 \mu\text{M}$ AgClO_4 ; Image size: $80 \times 80 \text{ nm}^2$; electrode potential: $0.3 \text{ V}_{\text{SCE}}$. Elongated islands (arrows) were observed to grow along the surface hemicylindrical structures.

rate monohydrate (Aldrich, 99.999%) were used as received. Ten millimolar SDS solution was used within 24 h after preparation to minimize the effect of slow hydrolysis in aqueous solution.²⁰ No additional supporting electrolyte was used.

Results and Discussion

Potential Dependent Structures of SDS at the Electrochemical Interface. As a control experiment, we studied the stability of the SDS at different electrode potentials, free of silver ions. In agreement with Burgess et al.,¹⁷ atomic force microscopy (AFM) images suggest that the highly ordered stripes are only present within a certain potential range (Figure 1). The ordered structure disappeared at potentials below $-0.3 \text{ V}_{\text{SCE}}$, presumably because the sulfate ionic headgroups experience repulsion from the surface charge, leading to desorption of SDS molecules. Above $0.35 \text{ V}_{\text{SCE}}$, the structures become more disordered. It was suggested that the SDS may start to form a condensed bilayer, in which the hydrocarbon chains in two molecular layers are placed next to each other, with the sulfate groups exposed to the surface and the electrolyte, respectively.^{17,18} This is assumed to be a consequence of increased attraction between the substrate and sulfate headgroups as well as the hydrophobic effect of the hydrocarbon chains.^{17,18}

Electrodeposition of Silver in the Presence of SDS. After $1 \mu\text{M}$ AgClO_4 was added to the 10 mM SDS solution, islands appeared in addition to stripes due to the hemicylinders (Figure 2B). The islands were clearly elongated along the direction of hemicylinders. The apparent widths of the islands were about 5–10 nm, limited by AFM resolution. It is to be noted that such features appear at a potential above the reduction potential of $1 \mu\text{M}$ Ag^+ , calculated to be $\sim 0.19 \text{ V}_{\text{SCE}}$ according to the Nernst equation. The underpotential deposition of silver on gold is well established. Because of the strong interaction between silver and gold, silver can form a limited

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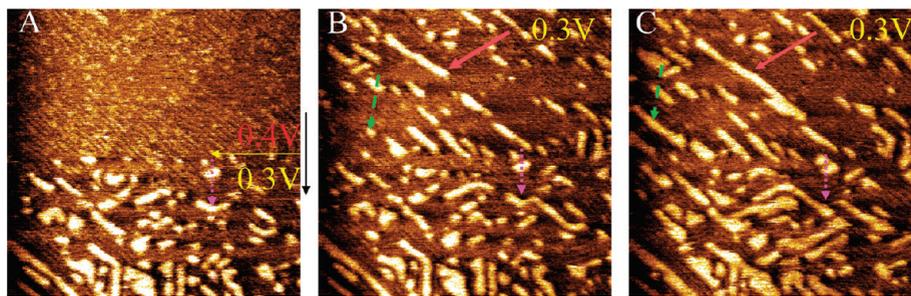


Figure 3. Time-dependent AFM images of electrodeposition on Au(111) under $1 \mu\text{M}$ AgClO_4 , 10 mM SDS. Image size: $225 \times 225 \text{ nm}^2$. The electrode potential was stepped from 0.4 to $0.3 \text{ V}_{\text{SCE}}$ in the middle of image A. B and C are the subsequent frames. Image acquisition speed: 80 s/frame . Solid, dashed, and dotted arrows identify the same spots in different images. All images were scanned downward.

number of atomic layers on a gold substrate at potentials above the reduction potential of Ag^+ .²¹ The features suggest that a strong interaction between the silver and the surface persists even in the presence of the SDS molecules.

Plausible reasons for the apparent preferential deposition in between the hemicylinders are as follows: (1) The Ag^+ concentration used was very low. Even if all the silver ions in the electrochemical cell (0.2 mL) were electrodeposited onto the gold surface, the coverage of silver would be only 0.35 ML . (2) Electron transfer is more facile at the sites in between the hemicylinders rather than on top of the insulating alkyl chains. (3) The Au substrate is exposed at these sites so that the silver atoms deposited there interact with the Au substrate and the sulfate anions.

The time-dependent image, Figure 3A, suggests that, after stepping the potential from 0.4 to $0.3 \text{ V}_{\text{SCE}}$, when the tip was scanning in the middle of the image, Ag islands grew. The sequence of images (Figure 3) suggests that Ag electrodeposition in the presence of the micellar structures followed a nucleation and growth mechanism.²² The island identified by a dashed arrow in Figure 3B was elongated into a 40 nm line in Figure 3C. Some islands merged as coverage increased (solid arrows in Figure 3B and C). However, the growth was also accompanied by reorganization. The right segment of an elbow marked by a dotted arrow in Figure 3 disappeared in Figure 3C, whereas the left segment merges with a wire of the same orientation.

To complement the AFM investigation, we image the SDS adlayer on Au(111) in the presence of a small amount of Ag^+ with in situ electrochemical STM. Figure 4 shows alternate bright and dark stripes with a periodicity of 4.5 nm . The height difference between the bright and dark areas is only 0.2 \AA , consistent with the STM investigation of SDS adlayer by Burgess et al.^{17,18} According to Burgess et al., the lower regions correspond to the spacing between headgroups, and the higher regions correspond to alkyl chains that are adsorbed parallel to the surface.^{17,18} Electrons only have to tunnel a few angstroms through the alkyl chains to reach the electrode.⁴ Hence the molecules are conductive enough to be imaged by STM. The SDS molecules in another part of the hemicylinder, i.e., on top of the molecular monolayer template, have a much longer conduction path and hence are not conductive enough to be imaged by STM. In the presence of silver, we observed additional features. Some small islands, a few angstroms wide and 1.5 \AA high, appeared in the image. Because the STM image reflects the local density of states of surface structures,²³ metallic structures, with

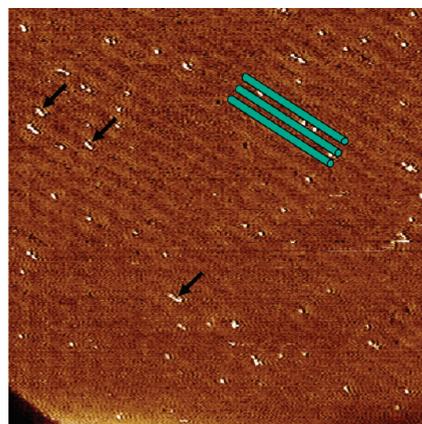


Figure 4. STM image of surface micelles on Au(111) under 10 mM SDS with $\sim 0.1 \mu\text{M}$ Ag^+ . Image size: $125 \times 125 \text{ nm}^2$. Electrode potential 0.2 V . Sample bias: 0.3 V . Tunneling current: 0.5 nA . Some islands are resolved. The black arrows indicate elongated islands. The three cylinders overlaid with the surface micelles suggest that the islands grow in the groove sites.

significantly higher conductivity than the hydrocarbon chains of SDS, appear as protrusions under STM. Therefore we attribute these features to small monolayer islands of silver. Upon close inspection, these islands appear *exclusively* in the lower regions. Most of the islands appear slightly elongated along the direction of the stripes. The width of these islands is about 1 nm , close to the 0.8 nm distance between the sulfate groups in adjacent unit cells. This provides direct evidence that the silver ions prefer to deposit onto the grooves between hemimicelles to form nanoscale wires. It is to be noted that these islands appear much thinner under STM. This is a reflection of the different contrast mechanisms. As STM is sensitive to the conductivity of the surface structures, it is capable of imaging the metal atoms with a high resolution. The conductivity through the upright alkyl chain of SDS is expected to be low.²⁴ At 1 V tip bias, a tunneling current of 10 pA or less (equivalent to transconductance of $10^{-11} \Omega^{-1}$ or less) must be maintained to image a dodecanethiol monolayer on gold without significant tip perturbation.²⁴ The tunneling transconductance, G , through an organic film decays exponentially with the increasing thickness, h , of the film $G = Be^{(-\beta h)}$ where B is a constant dependent on the electronic coupling between the molecule and the electrode, and β is the tunneling decay constant (1.2 \AA^{-1} for alkyl chains). As $10^{-11} \Omega^{-1}$ is already at the limit of many existing low current STMs, a bilayer structure of SDS, with almost double the thickness and poor electronic coupling between the top and

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bottom layers, would not be conductive enough to be imaged. To maintain a detectable tunneling current, the tip must temporarily displace the SDS molecules adsorbed on the silver nanostructures. Just like the solvent molecules, the SDS on Ag structures may appear transparent to STM. Therefore only the underlying silver nanostructures are resolved. By contrast, AFM is more sensitive to variation of the double layer force caused by the presence of SDS molecules associated with the nanostructure.²⁵ Therefore the islands appear much higher and wider under AFM.

Stability of the Electrodeposited Structures: Nanoscale Interaction between Metal Atoms and Organic Molecules.

To gain further insight into the nature of the features, we studied the stability of these stripes at more negative potentials. When the electrode potential was stepped to 0 V, these elongated islands were transformed into circular islands (Figure 5) in the subsequent frame taken 80 s later. These high aspect ratio structures are inherently unstable.²⁶ Absent of stabilizing interactions, the wires are expected to collapse into circular islands to minimize line tension.²⁶ Two factors may contribute to the collapse:

(1) At sufficiently low potentials, the stability of the molecular template is reduced due to increased repulsion of the negative surface charge of the gold substrate, as the potential (0 V) is well below the potential of zero charge of the interface.¹⁷ Therefore, the molecular template can no longer support the elongated structures of Ag.

(2) The step line tension of the nanostructures is dependent on the electrode potential.²⁶ A theoretical study suggests that the step line tension increases almost linearly with increasing negative surface charge density.²⁶ Hence as the electrode potential is reduced and the negative surface charge density is increased, the line tension increases and the nanostructures are destabilized. In addition, the interaction between sulfate and silver, which also lowers the line tension and stabilizes the high aspect ratio structures, is also expected to decrease as the surface charge is shifted in the negative direction.

We suggest that the combination of these two effects contributes to the collapse of the elongated islands. It is to be noted that the collapse of the elongated islands occur at a potential (0 V) above the threshold potential at which the surface aggregates disappear (-0.3 V). Even at a potential where the hemimicelles still exist, the potential may destabilize the surface aggregates as well as the silver nanostructures sufficiently to cause the collapse.

The collapse of the elongated islands also supports our previous assumption that the stripes contain both surface micellar structures and silver. The area of the islands was less than 50% of the area occupied by the stripes. If there were a monolayer of silver under the surface micellar structures, the coverage of the circular silver islands would be equal to the coverage of the stripes. We previously argued against silver forming monolayer islands below the micellar structures from the standpoint of height difference. This coverage is also inconsistent with the possibility.

A remaining question is the precise structure resulting from electrodeposition of silver in the presence of SDS. STM results suggest that it must contain monolayer silver. However, from the AFM results, the larger apparent height of these islands (~ 1 nm) suggests higher electrostatic repulsion with

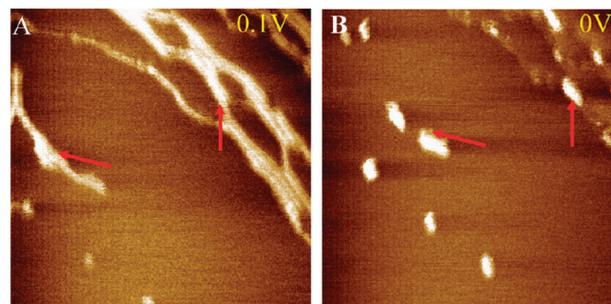


Figure 5. AFM images of electrodeposited islands on Au(111) under $1 \mu\text{M}$ AgClO_4 , 10 mM SDS. Image size: $200 \times 200 \text{ nm}^2$. (A) Isolated stripes, as indicated by arrows, are observed at $0.1 V_{\text{SCE}}$. (B) Stripes collapse to form more circular islands at $0 V_{\text{SCE}}$.

the tip and/or larger topographic height. This cannot be caused by monolayer silver islands alone, as silver islands are expected to be topographically lower than the neighboring hemimicelles and positively charged. In underpotential deposition of metals on more noble substrates, as a result of the lower work function of the metal overlayer, partial charge transfer to the substrate occurs.²¹ Without significant interaction between the silver islands and other molecules, we expect to observe depressions on the positively charged silver islands due to the attractive force with the negatively charged AFM tip.^{14,15} We propose that SDS molecules are adsorbed to form a bilayer on top of the monolayer silver islands (Figure 6). Such a model is consistent with the following considerations: (1) Sulfate has been observed to adsorb onto silver single crystal surfaces,²⁷ and the underpotentially deposited silver is expected to enhance adsorption of sulfate anions as has been observed with copper overlayer on gold.^{28,29} (2) A monolayer of SDS with headgroups interacting with the silver would expose the hydrophobic alkyl chains to the aqueous environment. The hydrophobic effect minimizing the exposure drives the formation of a bilayer.³⁰ (3) It explains the greater topographic height of such adduct (1 nm) over the neighboring hemimicelles. A monolayer of SDS would unlikely be imaged as protrusions surrounded by hemimicelles.

The SDS hemimicelles are physisorbed on the surface. One would question whether such physisorbed structures can have any templating effect on the deposition of metal nanoscale structures at all, as previous studies only showed that surface aggregate structures simply suppress the electrodeposition or form layered electrodeposited structures.^{19,31–33} Our results suggest that, under optimal conditions, surfactant hemicylinders can induce anisotropic electrodeposition, in contrast to previous studies.^{19,31–33} An important reason is that we limited the final metal coverage to well below a monolayer by operating at bulk concentrations significantly lower than the mM concentrations that are typical in electrodeposition studies.³⁴ The electrodeposited surface coverage rapidly exceeds 1 ML in a few minutes at 1 mM Ag^+ .³⁴ Assuming the groove between the hemicylinders, where Ag deposits preferentially, to be 0.8 nm wide,¹⁷ and the periodicity of the surface micelles to be 4.4 nm , the coverage of

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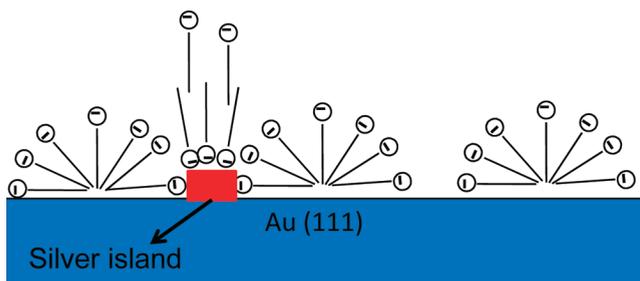


Figure 6. Proposed model for the SDS silver nanowire adduct. The sulfate headgroups are attracted to the positively charged silver islands. The hydrophobic chains interdigitate to form a bilayer on top of the silver island.

the groove sites is 0.18 ML. If the amount of metal deposited is higher than 0.18 ML, all the groove sites will be saturated, and the Ag must be deposited elsewhere. As the Ag^+ concentration is decreased, the electrode reaction becomes increasingly diffusion limited. The Cottrell equation provides an estimate of the quantity of deposited silver.³⁵ The integrated charge density, σ , is

$$\sigma(t) = \frac{2nFD_0^{1/2}C_0^*\sqrt{t}}{\pi^{1/2}}$$

where n is the number of electrons involved in the reduction (1 for Ag^+), F is the Faraday constant, C_0 is the bulk ion concentration, and D_0 (10^{-5} cm²/s for Ag^+) is the diffusion constant of Ag^+ .³⁵

Assuming $220 \mu\text{C}/\text{cm}^2$ is required to reduce 1 ML of Ag,³⁴ the maximum surface coverages of electrodeposited silver at different ionic concentrations are plotted as a function of time.

Figure 7 suggests that even without taking convection into consideration,³⁵ which increases the deposition speed relative to the values predicted by the Cottrell equation, the surface coverage is calculated to rapidly exceed 1 ML at 1 mM Ag^+ concentration within a few minutes, a typical concentration used for electrodeposition studies. By contrast, at 1 μM Ag^+ concentration, the surface coverage remains well below 0.1 ML.

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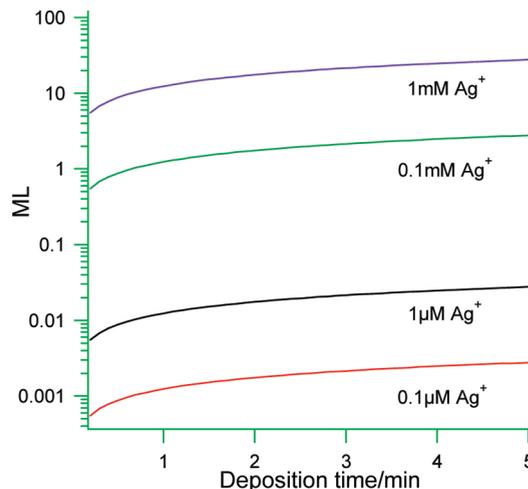


Figure 7. Time-dependent surface coverage of diffusion-limited electrodeposition of Ag at different concentrations of Ag^+ .

Our results also suggest that the electrode potential must be carefully controlled to achieve the desired nanoscale placement. A prerequisite to observe the template effect is that the hemicylinders must be stable at the electrodeposition potential. If the potential is too positive, SDS only forms a condensed layer instead of hemicylinders structures.¹⁷ If the potential is too negative, the stability of the SDS hemicylinders is reduced and the silver nanostructures collapse into circular islands.

We demonstrate that the intrinsic molecular features of a physisorbed molecular scale template can define the 2D electrodeposition of metal nanostructures. Our in situ study reveals atomic scale interactions between metal atoms and organic molecules and points to the importance of coverage control and electrode potential. Further high resolution studies and optimizations will reveal more details of the process and result in the growth of more uniform nanowires of silver and other noble metals relevant to electrocatalysis.

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