Ethylene diamine promotes Cu nanowire growth by inhibiting oxidation of Cu(111)

Myung Jun Kim, † Patrick F. Flowers, † Ian E. Stewart, † Shengrong Ye, † Seungyeon Baek, † Jae Jeong Kim, ‡ and Benjamin J. Wiley*†‡

† Department of Chemistry, Duke University, 124 Science Drive, Box 90354, Durham, North Carolina 27708, United States
‡ School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea

ABSTRACT: The synthesis of metal nanostructures usually requires a capping agent that is generally thought to cause anisotropic growth by blocking the addition of atoms to specific crystal facets. This work uses a series of electrochemical measurements with a quartz crystal microbalance and single-crystal electrodes to elucidate the facet-selective chemistry occurring in the synthesis of Cu nanowires. Contrary to prevailing hypotheses, ethylenediamine, a so-called capping agent in the synthesis of Cu nanowires, causes anisotropic growth by increasing the rate of atomic addition to (111) facets at the end of a growing nanowire relative to (100) facets on the sides of a nanowire. Ethylenediamine increases the reduction rate of Cu(OH)$_2^-$ on a Cu(111) surface relative to Cu(100) by selectively inhibiting the formation of Cu oxide on Cu(111). This work demonstrates how studying facet-selective electrochemistry can improve the understanding of the processes by which atoms assemble to form anisotropic metal nanostructures.

INTRODUCTION

One-dimensional nanowires of gold (Au), silver (Ag), and copper (Cu) have been extensively researched owing to their size-dependent electrical, catalytic, mechanical, and optical properties. 1−5 Cu nanowires are of particular interest due to the relatively large abundance of Cu, its low cost, and its high electrical and thermal conductivities. 6−10 For example, solution-deposited networks of Cu nanowires potentially offer a low-cost alternative to vapor-deposited indium tin oxide (ITO) as the transparent conductor 11−13 in solar cells, 14−16 organic light-emitting diodes (OLEDs), 18 touch screens, 19 and electrochromic windows. 20 Whereas ITO is brittle, composites of Cu nanowires in an elastomer exhibit little deterioration of their electrical conductivity after mechanical bending and stretching, demonstrating their potential for flexible and stretchable electronics. 18,21,22 The use of Cu nanowires has also been demonstrated in a variety of electrochemical applications, including batteries, 23−25 electrocatalysts, 26−28 and sensors. 29

Cu nanowires have been synthesized by chemical vapor deposition, 30 a template-assisted method, 31 electrospinning, 32 and several solution-phase syntheses. 33−35 Among these methods, the low-temperature solution-phase synthesis is perhaps the simplest method and has been scaled up to produce grams of Cu nanowires. 35 The solution for the synthesis of Cu nanowires consists of a metal precursor, a reducing agent, and a so-called capping agent (i.e., a ligand that selectively blocks a particular facet or group of facets). 31−33−38 The oxidation of the reducing agent provides electrons for the reduction of the metal precursor, and the capping agent directs the growth of the metal nanostructure into nanowires instead of nanoparticles.

The formation of Cu nanowires is due to the difference in the growth rate of the Cu crystals along different crystallographic directions. 11,12 Cu nanowires grow to be tens of micrometers long via the selective reduction of ionic Cu species onto the end of the nanowires, which consists of a pentagonal pyramid with five (111) planes. 11,12,39 In comparison, the addition of Cu to the (100) planes on the sides of the nanowire is so minimal that the diameters of the nanowires are typically between 20 and 150 nm. 11,12,15,34 It has been hypothesized that the difference in the observed growth rate between the (100) and (111) planes may be due to the capping agent preferentially adsorbing on the (100) surface and physically blocking the addition of Cu to that surface. 11,12,37,40 Similar hypotheses have been suggested to account for the growth of Ag and Au nanowires in the presence of capping agents. 24−6

The capping agents for the syntheses of Cu nanowires usually have an amine functional group and include such chemicals as ethylenediamine (EDA), 19,34,37−40 hexadecylamine (HDA), 36,41,42 and octadecylamine (ODA). 43

In principle, the difference in atomic addition to different facets due to the presence of a capping agent can be measured with appropriate electrochemical measurements on Cu(111) and Cu(100) single crystals in the reaction solution. This article...
reports the first such experiments and demonstrates that although EDA does promote the growth of Cu nanowires, it does not do so in the way that has previously been hypothesized. Rather than blocking electrochemical reactions from happening on (100) facets, EDA preferentially promotes reduction of Cu(OH)$_2$ on (111) facets by keeping them relatively free of Cu oxide. It is the presence of Cu oxide on (100) facets that hinders atomic addition to the sides of the nanowire. Thus, we show that EDA is a facet-selective promoter of Cu nanowire growth rather than a true capping agent. A similar electrochemical approach can likely be applied to a variety of metal nanostructure syntheses to determine the precise role of so-called capping agents and thereby greatly improve the understanding of how such nanostructures form.

## RESULTS AND DISCUSSION

### Identification of Relevant Electrochemical Reactions

Prior to clarifying the role of EDA, it is important to establish the basic characteristics of the electrochemical reactions in the Cu nanowire synthesis. The synthesis of Cu nanowires is performed by a sequential addition of Cu(NO$_3$)$_2$, EDA, and N$_2$H$_4$ in concentrated NaOH solution (Figure 1a). When Cu ions were introduced to the NaOH solution, the solution color turned blue and remained this color after EDA was added. Previously, it was confirmed that this blue color is due to the formation of Cu(OH)$_2$ instead of a Cu–EDA complex. After heating the solution at 70 °C and adding N$_2$H$_4$ as the reducing agent, the solution became colorless and bubbles formed due to the reduction of divalent Cu(OH)$_2$ to monovalent Cu(OH)$_2$ by N$_2$H$_4$. After 20–30 min at 70 °C, the color of the solution changed to a copper color due to the formation of Cu nanowires via the reduction of Cu(OH)$_2$ to metallic Cu.

The growth of Cu nanowires depends on two redox reactions: the oxidation of N$_2$H$_4$ and the reduction of ionic Cu species. In addition, a surface oxide can be continuously produced on the Cu nanowires due to a large amount of OH$^-$ in the reaction solution; this surface oxide is in turn reduced by N$_2$H$_4$. These reactions can be observed in Figure 1b, which shows I–V curves for a polycrystalline Cu electrode in NaOH solutions with either Cu(NO$_3$)$_2$ or N$_2$H$_4$. For oxidation, a single peak near −0.65 V vs Hg/HgO was assigned to N$_2$H$_4$ oxidation due to the linear relationship between the concentration of N$_2$H$_4$ and the peak current density (see Figure S1). For reduction, the polarization curve shows that four reactions could take place. The first sharp peak around −0.52 V is due to the reduction of surface oxide on the Cu electrode. Strong support for this assignment comes from the fact that such a peak was observed in the NaOH solution without any reagents (see Figure S2a). This peak nearly disappeared after the first voltage sweep because the majority of surface oxide was removed during the first sweep. The small current between −0.6 and −0.8 V is due to the reduction of Cu species (Cu(OH)$_2$, Cu(OH)$_4$), and the broad peaks over −0.8 V are due to the reduction of NO$_3$$. Evidence for these assignments was obtained by comparing the polarization curves for NaOH solutions containing Cu(NO$_3$)$_2$, CuSO$_4$, and NaNO$_3$ (see Figure S2b).

The change in the solution color suggests that Cu(OH)$_2$ $\rightarrow$ Cu + 2OH$^-$ is the main reduction reaction for Cu nanowire growth and that the oxidation of N$_2$H$_4$ (N$_2$H$_4$ + 4OH$^-$ $\rightarrow$ N$_2$(g) + 4H$_2$O + 4e$^-$) provided electrons for this reduction reaction. Therefore, the most direct way to clarify the effect of EDA on Cu nanowire growth would be to measure the reduction rate of Cu(OH)$_2$ with different concentrations of EDA. However, in order to make Cu(OH)$_2$ $\rightarrow$, it is necessary to add N$_2$H$_4$ because the reduction of Cu(OH)$_2$ to Cu(OH)$_2$ requires one electron. Figure 1c shows that the current for N$_2$H$_4$ oxidation overlaps with the current associated with the reduction of Cu(OH)$_2$, meaning that the usual linear sweep and cyclic voltammetry cannot distinguish between the currents that arise from the reduction of Cu(OH)$_2$ and the oxidation of N$_2$H$_4$. 

![Image](https://example.com/image1.png)
Determination of the Electrochemical Potential and Redox Currents for Nanowire Growth. To separately determine the currents from reduction of Cu(OH)$_2^-$ and oxidation of N$_2$H$_4$, we used an electrochemical quartz crystal microbalance (EQCM) to simultaneously measure the changes in mass and reaction potential at an electrode in the nanowire growth solution. According to mixed potential theory, spontaneous redox reactions occur at a mixed potential ($E_m$) where their rates are identical.$^{46,47}$ For Cu nanowire growth, the redox reactions take place at a potential where the cathodic current from the reduction of Cu species exactly matches the anodic current from the oxidation of N$_2$H$_4$. Thus, the current from oxidation of N$_2$H$_4$ at this potential can be used for estimating the reduction rate of Cu species. In addition, the change in the mass of the electrode can be used to calculate the current due to reduction of Cu(OH)$_2^-$.

Comparing the EDA-Dependent Electrochemistry of Cu(111) and Cu(100) Single-Crystal Electrodes. It has previously been shown that the structure of synthesized Cu nanowires is 5-fold twinned such that the sides of the nanowire consist of (100) planes and the end is capped with a pentagonal pyramid consisting primarily of (111) planes.$^{11,12,39,40}$ It has been hypothesized that the adsorption of EDA on (100) facets results in anisotropic growth by preferentially capping the side of the Cu nanowire. Therefore, the role of EDA was investigated with two Cu single crystals, oriented and polished.
to show either the (100) or (111) surface. Since the reduction of surface oxide plays an important role in Cu nanowire growth, we first examined the open circuit potential of Cu(100) and Cu(111) crystals in NaOH−N2H4 solutions with and without EDA.

In the absence of EDA (Figure 3a), we observed a decrease in the potential over time that was roughly the same for both Cu(111) and Cu(100) electrodes. This decrease in potential corresponds to a decrease in the current from the oxidation of N2H4 and reduction of surface oxide. We believe that the rapid polarization occurring around 150 s, as with the similar potential change in Figure 2b, is associated with the partial exposure of the metallic Cu surface. In the presence of EDA, a second smaller polarization was observed, and this potential shift to −0.9 V occurred much more rapidly for Cu(111) than for Cu(100). It took only 54 s for the potential to drop to −0.9 V for Cu(111) after the first polarization, compared to 345 s for Cu(100). The oxidation rate of N2H4 is essentially zero at −0.9 V (see Figure 1b), meaning that the surface oxide is completely removed and no new oxide is being generated. Our interpretation of these results is shown in Figure 3c. After the first polarization, EDA started to adsorb on the surface of the metallic Cu and inhibit its further oxidation. Since EDA adsorbed more quickly on (111) than on (100), there was a period during which the surface oxide was completely removed on the (111) surface while the (100) surface was still oxidized.

The inhibition of surface oxidation by EDA suggests that EDA might also hinder electrochemical reactions from occurring on the electrode. To determine if this was the case, we measured the current from oxidation of N2H4 versus EDA concentration (Figure 4). Surprisingly, the peak current for N2H4 oxidation increased with an increase in EDA concentration. EDA promoted the oxidation of N2H4 likely by keeping the electrode surface metallic and free of oxide. This means that EDA does not behave like a traditional capping agent in that it does not physically block the approach of electrochemical reactants. In addition, the oxidation current of N2H4 was greater on Cu(111) than on Cu(100), indicating that EDA promotes the oxidation of N2H4 to a greater extent on (111) facets. These results suggest that EDA promotes anisotropic growth of Cu nanowires by keeping the (111) facets at the end.
of a growing Cu nanowire relatively more free of oxide than the (100) facets on the sides of Cu nanowire.

To determine the difference in the reduction rates of Cu(OH)$_2$ on Cu(111) and Cu(100) electrodes, we compared the open circuit potential at single-crystal electrodes submerged in NaOH$-\text{EDA}-\text{N}_2\text{H}_4$ solutions with and without Cu(NO$_3$)$_2$. The electrons from N$_2$H$_4$ oxidation were completely consumed by the reduction of surface oxide in the absence of Cu(NO$_3$)$_2$ (red circles in Figure 5a,b), but they were consumed by both the reduction of Cu oxide and Cu(OH)$_2$ in the solution containing Cu(NO$_3$)$_2$ (blue squares in Figure 5a,b). Thus, the difference in the potential originates from the reduction of Cu(OH)$_2$. As shown in Figure 5a,b, the potential difference between the two solutions was much larger for the Cu(111) (125 mV at 100 s, 138 mV at 300 s) than for the Cu(100) (5 mV at 100 s, 42 mV at 300 s). The Coulombic efficiency of Cu(OH)$_2$ reduction was defined as the amount of electrons used for Cu(OH)$_2$ reduction divided by the total amount of electrons provided by N$_2$H$_4$ (see the Supporting Information).

Figure 5c shows that Cu(OH)$_2$ reduction was the dominant reaction on Cu(111), whereas oxide reduction was the dominant reaction on Cu(100). This difference between the (111) and (100) facets is responsible for the anisotropic growth of Cu nanowires. This phenomenon originates from the effect of EDA preferentially adsorbing to and inhibiting the oxidation of (111) facets.

We note the facet-selective chemistry is time-dependent in that the Coulombic efficiency of Cu(OH)$_2$ reduction on Cu(100) gradually increases over several hundred seconds. It was previously observed that, 300 s after Cu nanowires form, additional Cu can start to deposit on the sides of the nanowires, leading to an increase in the diameter of the nanowires. This phenomenon can now be understood in terms of the increase in the Coulombic efficiency of Cu(OH)$_2$ reduction on Cu(100) relative to Cu(111) that occurs over 400 s.

The schematic diagram summarizing our current understanding of EDA-assisted Cu nanowire growth is presented in Figure 5d. The electrons for reduction of both Cu oxide and Cu(OH)$_2$ are provided by the oxidation of N$_2$H$_4$. The degree to which adsorbed EDA prevents surface oxidation is larger on (111) than that on (100), leading to a larger reduction rate of Cu(OH)$_2$ on (111) facets at the end of the nanowire. Meanwhile, Cu oxide is continuously formed via reactions of Cu with OH$^-$ on the (100) facets and continuously reduced by N$_2$H$_4$. Thus, rather than acting as a capping agent, EDA acts as an anisotropic promoter of Cu nanowire growth by keeping the facets at the end of the nanowire electrochemically active and free of oxide.

It has previously been hypothesized that the 5-fold twinned crystal structure of metal nanowires plays an important role in inducing anisotropic growth. The model for the 5-fold twinned decahedra, five single-crystal tetrahedra oriented radially about a central axis, leaves an unfilled gap of 7.5°. This lack of a space-filling structure is thought to result in strain in the lattice that increases with increasing distance from the central axis of a 5-fold twinned nanowire, which in turn may

Figure 5. Potential behavior of (a) Cu(111) and (b) Cu(100) crystals in 15 M NaOH solutions containing 70 mM EDA and 5.5 mM N$_2$H$_4$ with and without 4.74 mM Cu(NO$_3$)$_2$. (c) Coulombic efficiency of Cu(OH)$_2$ reduction on Cu(111) and Cu(100) surfaces. (d) Schematic diagram of Cu nanowire growth in NaOH$-\text{EDA}-\text{Cu(NO}_3\text{)}_2-\text{N}_2\text{H}_4$ system.
make lateral growth of nanowires energetically unfavorable. It has also been hypothesized that the twin defects on the ends of the nanowire may serve as active sites for atomic addition. However, these crystal-structure-based mechanistic hypotheses do not explain the time dependence of anisotropic growth in the Cu nanowire system. In contrast, the time scale of the anisotropic efficiency of Cu(OH)⁴⁻ reduction on (111) versus (100) closely matches the time scale over which a change from longitudinal to lateral growth occurs for Cu nanowire growth, resulting in a reduction in aspect ratio of 1810 to 360. Thus, we believe the dominant driving force for anisotropic growth in the Cu nanowire system. In contrast, the time scale of the charge transfer of Cu(OH)⁴⁻ reduction and oxidation currents are presented in Figure 6b. Figure 6c shows the oxidation rate of N₂H₄ at Eₘ was measured with chronoamperometry (see Figure S3), and the average oxidation currents are presented in Figure 6a. Figure 6c shows the oxidation rate of N₂H₄ was linearly dependent on the concentration of Cu(NO₃)₂. As we have confirmed that the adsorption of EDA effectively prevented the formation of surface oxide on Cu(111), the oxidation rate of N₂H₄ at Eₘ is approximately equal to the rate of Cu deposition. Thus, we conclude that the reaction rate of Cu(OH)⁴⁻ was linearly dependent on the concentration of Cu(NO₃)₂.

The schematic diagram for the diffusion-limited reduction of Cu(OH)⁴⁻ (blue line) and charge transfer-limited oxidation of N₂H₄ (red line) at various concentrations of Cu(NO₃)₂ is presented in Figure 6d. The opposite case, i.e., charge transfer-limited reduction of Cu(OH)⁴⁻ and diffusion-limited oxidation of N₂H₄ is shown in Figure S4. A diffusion-limited reaction is one in which the rate-determining step is the diffusion of reactants; thus, the reaction rate is dependent on the concentration of reactants, not the electrode potential. In contrast, the applied potential determines the rate of a charge transfer-limited reaction. The points at which the dashed line crosses the x-axis in both figures corresponds to Eₘ where the rates of the redox reactions are identical. As illustrated in Figure 6d, if the reduction of Cu(OH)⁴⁻ is diffusion-limited, we would expect that the reaction rate increases linearly and Eₘ shifts to more positive potentials as the concentration of Cu(NO₃)₂ increases. This prediction matches the experimental observations in Figure 6a,c. In contrast, the rate of the charge transfer-limited reduction of Cu(OH)⁴⁻ would be constant regardless of Cu(NO₃)₂ concentration (see Figure S4). Thus, we conclude
that the electrochemical reactions on the Cu(111) surface consist of diffusion-limited reduction of Cu(OH)\textsuperscript{2–} and charge transfer-limited oxidation of N\textsubscript{2}H\textsubscript{4}\textsuperscript{2–}. This conclusion agrees with previous results from the real-time visualization of Cu nanowire growth that show the growth rate of Cu nanowires was linearly dependent on the concentration of Cu(NO\textsubscript{3})\textsubscript{2}.\textsuperscript{40}

## CONCLUSIONS

We showed that EDA, a so-called capping agent in the synthesis of Cu nanowires, is actually a facet-selective promoter of Cu atomic addition to the (111) facets at the end of a Cu nanowire. Measurements with an electrochemical quartz crystal microbalance demonstrated that only 25% of electrons from N\textsubscript{2}H\textsubscript{4} oxidation go toward reduction of Cu(OH)\textsubscript{2} to metallic Cu; the remainder are consumed by the reduction of Cu oxides that are continuously formed due to the high pH environment. By comparing the rate of Cu oxide reduction on Cu(111) and Cu(100) surfaces, we showed that EDA passivates Cu(111) against further oxidation more quickly than for Cu(100). Although EDA passivates Cu(111) from oxidation, it actually promotes N\textsubscript{2}H\textsubscript{4} oxidation on Cu surfaces, likely by keeping the Cu surface metallic and relatively free of oxides. The EDA-enhanced passivation of the Cu(111) surface opens a ∼300 s window during which anisotropic growth of Cu nanowires can occur. If the Cu nanowire reaction continues outside of this window, Cu nanowires can grow laterally, resulting in larger nanowire diameters.\textsuperscript{48} The series of electrochemical experiments in this article can likely be applied to a wide variety of metal nanostructure syntheses to determine the precise role of so-called capping agents and thereby greatly improve the understanding of how anisotropic growth of metal nanostructures occurs.

## ASSOCIATED CONTENT

### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10653.

Experimental methods and calculations and additional results of electrochemical analyses (PDF)

## AUTHOR INFORMATION

### Corresponding Author

*benjamin.wiley@duke.edu*

**ORCID**

Benjamin J. Wiley: 0000-0003-0055-9018

**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by a National Science Foundation CAREER award (DMR-1253534) and the “R&D Center for Reduction of Non-CO\textsubscript{2} Greenhouse Gases (2013001690004)” funded by the Korea Ministry of Environment (MOE) as a “Global Top Environment R&D Program”.

## REFERENCES