

Modulating the Growth Rate, Aspect Ratio, and Yield of Copper Nanowires with Alkylamines

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Supporting Information

ABSTRACT: This article shows how the chain length of alkylamine capping agents and the corresponding stability of their self-assembled monolayers on a Cu surface determines the growth rate, yield, and dimensions of Cu nanowires produced in a solution-phase synthesis. Of the 10 linear alkylamines that were tested, only those with 12 or more carbon atoms induced growth of nanowires. The length, yield, and growth rate of nanowires were larger for shorter alkylamines. As the Cu nanowire growth rates were up to 1050 times smaller than the calculated diffusion-limited growth rates-and the alkylamine chain length had no significant effect on the in situ generation of the reducing agent-we conclude the rate of alkylamine-



mediated Cu nanowire growth is limited by charge transfer. Electrochemical measurements indicate longer alkylamines form more effective passivation layers that greatly decrease the rate at which Cu-alkylamine complexes are reduced onto a Cu surface. Molecular dynamics simulations show that the energy required for removal of octadecylamine from a self-assembled monolayer on the Cu surface is much larger (3.59 eV) than for removal of tetradecylamine (2.06 eV). Thus, the more stable self-assembled monolayer formed by longer-chain alkylamines leads to greater inhibition of Cu addition, slower growth, reduced yield, and reduced nanowire aspect ratio.

■ INTRODUCTION

Gold (Au),^{1,2} silver (Ag),³ and copper (Cu)⁴ nanowires have unique dimension-dependent electrical, catalytic, and optical properties that have potential benefits for many applications, including transparent electronics, ⁵⁻¹³ flexible/stretchable con-ductors, ¹⁴⁻¹⁶ photonics, ¹⁷ solar cells, ^{18,19} wearable devices, ^{20–22} sensors, ^{23,24} electrocataysts, ^{25,26} lithium ion batteries, ^{27,28} and air filters.²⁹ The performance of devices containing nanowires is often dependent on the diameter D, length L, and aspect ratio (L/D) of the nanowires. For example, nanowires with smaller diameters will increase the surface area available for electrocatalysis.^{30,31} Ultrathin nanowires can also improve the transmittance of transparent conductors due to their reduced scattering cross section.³²⁻³⁴ The aspect ratio of nanowires generally determines the electrical conductivity of 2D or 3D nanowire networks as a function of area and volume fraction in transparent conductors^{35,36} and polymer-nanowire composites.³⁷ Therefore, improving the accuracy, precision, and range of dimensional control of nanowires is an important goal for synthetic development as it will facilitate efforts to understand and use the properties of nanowires in a broad range of applications.

Cu nanowires are particularly attractive for commercial applications because Cu is 100 times less expensive than Ag, 1000 times more abundant, and only 6% less conductive. The

main disadvantage of Cu nanowires is that, unlike Ag and Au, they are easily oxidized by atmospheric oxygen. Therefore, many research articles have been devoted to the synthesis of Cu nanowires, as well as coating methods to protect Cu nanowires from oxidation.³⁸⁻⁴¹ Methods to make Cu nanowires include chemical vapor deposition,^{42,43} electrochemical deposition in templates,^{44,45} and solution-phase syntheses.⁴⁶⁻⁶¹ Among these methods, solution-phase synthesis has the greatest potential for producing large quantities of nanowires at low cost.⁵³ The solution-phase synthesis of Cu nanowires requires low reaction temperatures (60-100 °C) and can proceed at atmospheric pressure. The reaction solutions generally consist of Cu ion precursors, reducing agent(s), and additional organic additives that promote growth of Cu nanowires.

The two main solution-phase syntheses for Cu nanowires involve the use of (1) ethylenediamine (EDA) in an alkaline (8–15 M NaOH) aqueous solution^{4,7,10,15,46–53} and (2) alkylamines (e.g., hexadecylamine or octadecylamine) in a neutral aqueous solution. 54-61 In the first synthesis, electrons from the oxidation of hydrazine (N_2H_4) reduce tetrahydroxocuprate(II) and dihydroxocuprate(I) complexes

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while EDA promotes anisotropic growth by selectively inhibiting oxidation on the (111) facets at the end of a growing Cu nanowire.⁵² The dimensions of Cu nanowires can be controlled by changing the concentrations of NaOH, EDA, N_2H_4 , reaction temperature, and stirring during the reaction.^{10,46–50} For example, a decrease in the reaction temperature from 70 to 60 °C can increase the aspect ratio from 1860 to 5700, and a decrease in N_2H_4 below 5.7 mM can decrease the diameter from 65 to 35 nm.⁴⁶ Higher concentrations of EDA can reduce the nanowire aspect ratio and can also result in the formation of tapered Cu nanowires.⁴⁶

The alkylamine-mediated synthesis is more cost-effective compared to the EDA-NaOH synthesis; the total material cost for the production of 1 g of nanowires from the alkylaminemediated reaction is 1.6 times lower than for the EDA-NaOH synthesis (Table S1). The diameters of Cu nanowires synthesized with alkylamines are between 25 to 200 nm and can have aspect ratios >10 000.⁶⁰ It has been proposed that anisotropic growth of Cu nanowires in this system is due to alkylamines, including tetradecylamine (TDA),⁵⁴ hexadecyl-amine (HDA),^{55–60} and octadecylamine (ODA),⁵⁸ selectively adsorbing to the (100) facets on the sides of the nanowires, and selectively inhibiting atomic addition to those facets, while leaving the (111) facets at the ends of the nanowire open to atomic addition. This hypothesis is supported by simulations that show HDA forms self-assembled monolayers on Cu(100) and Cu(111) and that the binding energy for HDA on Cu(100)is higher (2.01 eV) than for Cu(111) (1.89 eV).^{62,63} Glucose is usually used as the reducing agent; however, it was shown that glucose alone cannot reduce Cu ions to metallic Cu.⁵⁹ It has been proposed that a Maillard reaction takes place between alkylamines and glucose and that this reaction is necessary to produce the reductones which in turn reduce Cu ion complexes.⁵

Despite previous reports on the use of alkylamines for the synthesis of Cu nanowires, it is not clear what effect different alkylamines have on the yield, dimensions, and growth rate of nanowires. In this article, 10 alkylamines with different chain lengths $(C_6 - C_{18})$ were examined to get a deeper understanding of what role(s) alkylamines play in Cu nanowire growth. We found a minimum alkyl chain length of 12 was needed to produce Cu nanowires. For alkylamines between $C_{12}-C_{18}$ nanowire aspect ratio increased with decreasing alkylamine chain length, and the yield of nanowires produced with TDA (C_{14}) was 9 times higher (54%) than the more commonly used ODA (C_{18}) capping agent (6%). Alkylamine chain length had a remarkable effect on the growth rate of the Cu nanowires, which ranged from 5 nm s^{-1} for ODA up to 69 nm s^{-1} for TDA. As these growth rates were 460-1050 times smaller than diffusion-limited growth rates, we determined the growth of Cu nanowires in this synthesis is charge-transfer-limited. We hypothesized that longer alkylamine chains slow Cu nanowire growth because they form a more effective passivating layer on the (111) facets at the ends of the nanowires. This hypothesis was supported by electrochemical measurements which show that increasing alkylamine chain length decreased the current from reduction of CuCl₂ onto a Cu surface derivatized with alkylamines. In addition, molecular dynamics (MD) simulations show the barrier for desorption of ODA from Cu(111) is greater (3.59 eV) than for desorption of TDA (2.06 eV), again indicating longer alkylamines can more effectively passivate a Cu(111) surface. Taken together, these results reveal how changing the structure of an organic additive can change the

rate of nanowire growth, which in turn changes the yield and aspect ratio of nanowires obtained from a given reaction.

RESULTS AND DISCUSSION

Effect of Alkylamines on Cu Nanowire Yield and Dimensions. We examined 10 different alkylamines to determine which alkylamine chain lengths promote Cu nanowire growth. Figure 1 shows the result of varying the



Figure 1. Cu nanostructures synthesized with (A) hexylamine, (B) heptylamine, (C) octylamine, (D) nonylamine, (E) decylamine, (F) undecylamine, (G) dodecylamine (DDA), (H) tetradecylamine (TDA), (I) hexadecylamine (HDA), and (J) octadecylamine (ODA). The concentrations of CuCl₂, alkylamines, and glucose were 16.4, 49.4, and 888 mM, respectively. The reaction took place at 90 °C for 16 h.

carbon chain length of alkylamines from 6 to 18. Alkylamines with a carbon chain length of 12 or more were required for the anisotropic growth of Cu nanowires. The shortest alkylamines $(C_6 - C_8)$ produced nanoparticle aggregates with sizes ranging from 6 to 13 μ m. The C₉-C₁₁ alkylamines produced individually dispersed Cu nanoparticles with a diameter of 111 ± 12 nm. Molecular dynamics simulations by Liu et al. for C_{5} , C_{10} , and C_{16} alkylamines on Cu(111) and Cu(100) surfaces show that C_{10} and C_{16} form ordered monolayers while C_5 (pentylamine) does not.^{62,63} Reduced interactions between the shorter hydrocarbon tails and the increased solubility of shorter alkylamines may prevent formation of an adsorbed alkylamine layer on Cu (100) facets in solution, leading to growth of nanoparticles instead of nanowires. The hypothesis that shorter chain alkylamines adsorb less strongly to the surface of Cu nanoparticles is supported by the observation that aggregation of the nanoparticles increased with decreasing chain length. As the main purpose of this article is to understand the role of alkylamines in Cu nanowire growth, we hereafter focus only on alkylamines which produced Cu nanowires $(C_{12}-C_{18})$.

Figure 2 shows a matrix of reaction solutions at 0, 2, and 16 h with 16.4 mM CuCl₂, 888 mM glucose, and different amounts of alkylamines. Note that no significant Cu reduction occurred unless the molar ratio of alkylamine:Cu was greater than 2:1. This suggests that alkylamine may complex with Cu ions in a 2:1 ratio to form a dialkylaminedichlorocuprate(II) complex. Excess alkylamine can react with glucose through the Maillard reaction to form reductones, which are the most likely reducing agent in the reaction.^{59,64–66} Ascorbic acid is the best known reductone, and it can reduce Cu ions.⁵⁷ We have chosen the 49.4 mM concentration of alkylamines as the control for most of the time-dependent and chain-length-dependent studies in this work because it is an intermediate concentration that readily produces nanowires.

Figure 3 presents the conversion of Cu ions to Cu nanowires and Cu nanoparticles as a function of time and the type of alkylamine. No data is shown for HDA and ODA at 4 h because it was not possible to reproducibly separate the small amount of



(mM) 0 16.4 32.8 49.4 65.6 82.0

Figure 2. Images showing the color of the reaction solutions containing different types and concentrations of alkylamines before and after heating at 90 $^\circ C$ for 2 and 16 h.



Figure 3. Conversion of Cu and yield of nanowires as a function of reaction time. The concentrations of alkylamines were 49.4 mM.

reduced Cu from HDA and ODA solutions at this time point. Clearly, the Cu reduction was much faster and more complete with shorter alkylamines. The reduction of Cu was complete in 4 h with DDA versus 12 h with HDA and ODA. Longer reaction times did not increase the yield of nanowires, presumably due to the conversion of reductones to melanoidins (see Figure S1 and the discussions in the Supporting Information). The final conversions of Cu were 92% for DDA, 76% for TDA, 60% for HDA, and 54% for ODA. However, the trend for the yield of Cu nanowires was TDA > DDA > HDA > ODA, different from the trend for the overall yield of Cu. Although shorter reaction times and higher yields of Cu nanowires were observed for DDA and TDA, HDA and ODA are more frequently used in literature reports of Cu nanowire syntheses.^{55–60} This result suggests that the use of shorter chain alkylamines such as TDA may improve the yield of Cu nanowires and thus the economics of the Cu nanowire synthesis.

In addition to yield and reaction time, the dimensions of nanowires that can be obtained in a reaction is also important. Figure 4A,B show data for the length and diameter of Cu nanowires as a function of alkylamine type and concentration. Representative images used for measuring the average length and diameter of Cu nanowires are shown in Figure S2 and S3, respectively. Figure 4A shows the length of Cu nanowires decreases with increasing alkylamine concentration. High concentrations of alkylamine increased the rate of reductone generation (Figure S4), resulting in a greater nucleation density and therefore shorter nanowires (Table S2). For example, Figure S4 shows that the amount of reductone present at 2 h increased 1.3 times when the concentration of TDA was increased by 1.7 times (from 49.4 to 82.0 mM). Table S2 shows that the number of nanowires per unit yield increased by 4.9 times, resulting in a length decrease of 3.7 times when the TDA concentration was increased from 49.4 to 82.0 mM. At lower concentrations of alkylamine, the length of the Cu nanowires went as DDA > TDA > HDA > ODA. The diameter did not vary much with alkylamine type and concentration. The average diameters of nanowires were in the range of 30 to 60 nm, and all averages were within 2 standard deviations. Given the change in length and relatively constant diameter, the aspect ratio could be tuned from 280 (65.6 mM DDA) to 2830 (32.8 mM DDA). Representative images of nanowires with high and low aspect ratios are shown in panels C and D of Figure 4, respectively.

Understanding the Role of Alkylamine Chain Length. Now that we have established that the type and concentration of alkylamine used in the synthesis of Cu nanowires can affect the yield and aspect ratio, we turn to the difficult question of why this occurs. We have shown that higher concentrations of alkylamines lead to a faster reduction rate and produce shorter nanowires. This can be explained by the high concentrations of alkylamine increasing the rate of reductone generation (Figure S4), resulting in a greater nucleation density (Table S2). We have also shown that shorter alkylamines lead to a faster Cu reduction rate but produce longer nanowires. In an attempt to reconcile this contradiction and understand why shorter alkylamines produce longer nanowires, we turned to in situ visualization to measure the rate of Cu nanowire growth with TDA and ODA. Figure 5A,B show the representative images taken during growth of Cu nanowires. These images, along with supplementary videos 1 and 2, show that Cu nanowires grow from both ends in the alkylamine-mediated synthesis. This is in contrast to the EDA-mediated synthesis, in which the Cu nanowires grow through addition to one end. $^{\rm 51}$ The changes in the length of individual nanowires versus reaction time with TDA and ODA are presented in panels C and D of Figure 5, respectively. The initial time (t = 0 s) is from when nanowires were first observed. The average growth rate of Cu nanowires with TDA (69 \pm 14 nm s⁻¹) was 13.8 times faster than with ODA (5.0 \pm 1.5 nm s⁻¹). This result suggests that the reason why Cu nanowires grew longer with shorter alkylamines was due to their faster growth rate.



Figure 4. (A) Length and (B) diameter of Cu nanowires synthesized with different concentrations of alkylamines. Representative images of Cu nanowires with (C) high and (D) low aspect ratios which were synthesized with 32.8 and 65.6 mM DDA, respectively. The reaction time was 16 h.

The growth of Cu nanowires in this reaction is the result of two electrochemical reactions: the oxidation of reductones and the reduction of Cu-alkylamine complexes. One of two reactions should be the rate-determining step for Cu nanowire growth, and the rate-determining reaction will be either mass transport-limited or charge-transfer-limited. In order to determine the mechanism by which shorter alkylamines lead to faster nanowire growth rates, we first measured whether shorter alkylamines generated more reductones. As described in the Supporting Information (see also Figure S1 and S5), this was found not be the case. Next, we determined whether the reaction was mass transport-limited or charge-transfer-limited. As explained in the Supporting Information (see also Figure S6,S7 and Table S3), the diffusion-limited growth rates with TDA and ODA were calculated to be 31.4 and 5.26 μ m s⁻¹, respectively, which is 460 and 1050 times larger than the actual growth rates determined from in situ visualization. In addition, Figure S8 shows that the activation energy for TDA-mediated nanowire growth is 89.5 kJ/mol, which is 7.8 times larger than the activation energy for mass transport-limited Cu nanowire growth using EDA as a facet-dependent promoter (11.5 kJ/ mol).^{51,52} These results indicate that, in contrast to the EDAmediated synthesis, the growth of Cu nanowires in the alkylamine synthesis is not limited by the diffusion of the Cualkylamine complex. Thus, by process of elimination, the alkylamine-mediated growth of Cu nanowires is chargetransfer- limited.

Given that the rate of Cu nanowire growth is charge-transferlimited, it is possible that the reduction rate of the different Cualkylamine complexes was affected by the stability of the complex and/or the passivating effect of alkylamines adsorbed on the Cu surface. Figure 6A shows how the type of alkylamine affects the reduction of Cu-alkylamine complexes on a glassy carbon electrode. Two reduction peaks were observed, which corresponded to the reduction of Cu²⁺ to Cu¹⁺ and Cu¹⁺ to Cu⁰. The leftmost reduction peaks in Figure 6A show that the presence of alkylamines, and the resulting complexation with Cu^{2+} resulted in a negative shift in the onset potential for Cu^{2+} reduction by 150 mV relative to the reduction of Cu ions without alkylamimes. Since more stable complexes are reduced at more negative potentials, this result shows Cu-alkylamine complexes are more stable than free Cu ions or Cu-chloride ion complexes. However, as the onset potential for reduction of different Cu²⁺ complexes were within 5 mV, there is no significant effect of alkylamine chain length on the stability of Cu²⁺-alkylamine complexes. The difference in the peak current for the different alkylamines was due to the different diffusion coefficients of the complexes (see Table S3). In contrast, the alkylamine chain length had a dramatic effect on the onset potential and current for the reduction of Cu¹⁺ to Cu⁰. TDA, HDA, and ODA shifted the onset potential of Cu deposition by 430, 660, and 650 mV relative to the reduction of \overline{Cu}^{1+} without alkylamine. It is difficult to determine whether the peak shift for the reduction of Cu1+-alkylamine complexes was due to the higher stability of the complexes or the improved passivation of the electrode surface by longer alkylamines. Deposition of Cu onto the carbon electrode may take place through the growth of Cu nuclei. These Cu nuclei can potentially be covered with



Figure 5. In situ visualization of the growth of Cu nanowires with (A) TDA and (B) ODA. Longitudinal growth of individual nanowires versus time with (C) TDA and (D) ODA. The scale bars in the insets of (B) represent 2 μ m. Time *t* = 0 s is the point at which nanowires were first observed.

an alkylamine monolayer, making it impossible to rule out the effect of surface passivation. Nevertheless, these negative shifts in onset potential suggest the alkylamine chain length will affect the rate of Cu deposition onto the end of a nanowire, with longer chain lengths resulting in slower growth.

In order to further explore whether surface adsorption of alkylamine can inhibit Cu ion reduction in the absence of a dissolved Cu–alkylamine complex, we measured the reduction of Cu ions without alkylamines in solution onto a Cu surface derivatized with different alkylamines. The surface of a Cu electrode was derivatized by dipping the electrode in alkylamine solutions for 5 min, which was enough time for the open circuit potential to stabilize. Excess alkylamine was removed by dipping the electrode in DI water. Linear sweep voltammetry was performed immediately after transferring the electrode to a $CuCl_2$ electrolyte. Figure 6B shows the current for Cu reduction was suppressed by the presence of alkylamines adsorbed onto the Cu surface (red arrow in Figure 6B), indicating the adsorption of alkylamine can inhibit the deposition of Cu. The suppression of the reduction current

increased with chain length, indicating longer alkylamines are more effective inhibitors of Cu reduction. It is possible that the passivation layer can also physically inhibit the approach of reductones, but it is difficult to investigate this possibility because of the complexity of the Maillard reaction and the fact that both the concentrations of reductones and alkylamines will change with time.

We also measured the effect of adsorbed alkylamine on the oxidative dissolution of a Cu electrode as a way to measure the ability of alkylamine to prevent the approach of molecules (e.g., O_2 , Cl⁻, or reducing agents) to the Cu surface. Figure 6C shows adsorbed alkylamines greatly suppressed the oxidative current and were effective corrosion inhibitors. The efficiency with which alkylamines protect Cu against oxidative dissolution was calculated from the ratio of the oxidative current with and without alkylamines protect Cu against oxidative dissolution increases with chain length (TDA < HDA < ODA), with the efficiency of ODA approaching a remarkable 100% (Figure 6D). This result clearly shows ODA is more effective than TDA



Figure 6. Linear sweep voltammograms for Cu reduction on (A) a glassy carbon electrode and (B) a Cu electrode derivatized with alkylamines. (C) Linear sweep voltammograms comparing the oxidative current for a polycrystalline Cu electrode in NaCl-alkylamine electrolytes. (D) The efficiency with which alkylamines inhibit Cu oxidation was calculated from the oxidative currents in (C). The concentrations of $CuCl_2$, NaCl, and alkylamines used for the electrochemical measurements were 16.4, 32.8, and 49.4 mM, respectively.

at preventing the approach of molecules to a Cu surface and allowing electron transfer to occur and suggests that longer alkylamines will more effectively inhibit the oxidation of reducing agents. Similar chain-length-dependent corrosion resistance has previously been observed for *n*-alkanethiol monolayers on Au surfaces.⁶⁷

Effect of Alkylamine Chain Length on the Free Energy for Desorption. We expect that adsorbed alkylamine must desorb in order for Cu reduction and deposition to occur and that desorption becomes less favorable as chain length increases. In order to determine the extent to which chain length affects the energy required for desorption, we used MD simulations to calculate the free-energy profile or potential of mean force (PMF) for TDA and ODA chains to desorb from their self-assembled monolayers on Cu(111). We obtained the PMF using umbrella sampling simulations,^{68,69} in which we sample the center of mass of an alkylamine chain at various windows as it proceeds along a reaction coordinate (RC) normal to the aqueous phase. The center of mass is held at each window using a harmonic bias potential and the free energy is obtained from the sampling data using umbrella integration.⁷⁰ Details of our calculations can be found in the Supporting Information.

Figure 7 shows PMF profiles for the desorption of TDA and ODA chains from their self-assembled monolayers. We note that the PMF profiles have an oscillatory structure, with several local minima in addition to the global minimum associated with the binding position of the alkylamine in its equilibrium conformation within the layer. We observe six distinct minima for TDA and five for ODA, with an additional three "shelves" in the PMF profile for ODA. These features indicate that alkylamine desorption is a sequential process, in which a chain proceeds from one (partially) adsorbed state to another via a series of steps before it ultimately leaves the surface. We can associate these minima and steps with various conformations of alkylamine chains within the self-assembled layer.

As an alkylamine chain proceeds along the RC, it forms favorable and unfavorable structures that originate from the alignment of methylene hydrogens within the layer. As shown in Figure S9, the methylene hydrogens are in a staggered configuration in favorable structures but are aligned and in the process of passing one another in unfavorable configurations. The spacing between neighboring minima in Figure 7 is approximately 2.6 Å, which corresponds to the distance between alternating hydrogens in the chains. The six minima for TDA in Figure 7A correspond to the six possible favorable



Figure 7. Potential of mean force (PMF) profiles and corresponding images for the desorption of (A) TDA and (B) ODA from their monolayers on the Cu(111) surface.

configurations (Figure S9) as one chain moves past another. The eight possible favorable configurations for ODA correspond to the minima and shelf structures in Figure 7B. Thus, the chains in self-assembled alkylamine monolayers form a "gear" structure, in which methylene groups form interlocking teeth. As these molecules are pulled from their initial bound state, they proceed from one interlocked state to another, overcoming a series of free-energy barriers to reach their final free state in solution.

We note that the first four minima in Figure 7, which occur when the alkylamine is close to the surface, are well-defined and that the minima become shallow and, in the case of ODA, degrade to shelves as the chain moves into solution. This degradation of the free-energy minima occurs when six or more of the alkylamine segments have reached the solution phase, as can be observed from the images of the desorption process in Figure 7. When a significant portion of the chain is in the solution phase, the chain can flex and bend to increase both its interaction with the terminal methyl groups in the layer and its entropy. This increasing flexibility, which is more prevalent for ODA (because it is longer) than TDA, leads to a departure of the chain from the solid-like behavior it exhibits when the large majority of its segments reside within the monolayer. Thus, the free-energy profiles transition from having oscillatory, solid-like structures when the large majority of chain segments reside within the self-assembled layer, to an increasingly liquid-like structure, as a greater portion of the chain segments reside in solution.

Comparing the PMF profiles for TDA and ODA, we see that the free-energy barriers for the first three steps of alkylamine desorption are larger for ODA than for TDA. This occurs because a greater number of methylene groups align for unfavorable ODA configurations than for TDA configurations. The overall free-energy change from the completely adsorbed state to the completely desorbed state is also larger for ODA than TDA. Both of these features indicate that the desorption rate for TDA will be larger than that for ODA. Thus, these calculation results support the hypothesis that longer alkylamines will more effectively passivate a Cu(111) surface.

CONCLUSIONS

This work contributes to the literature on the roles organic additives can play in a nanostructure synthesis by exploring how the length of alkylamines affects the outcome of a Cu nanowire synthesis. We found that shorter alkylamines (1) increase the rate of Cu reduction, (2) produce higher yields of nanowires, and (3) produce longer nanowires. In situ measurements showed nanowires grew 13.8 times faster (69 nm s⁻¹ vs 5.0 nm s⁻¹) with TDA ($C_{14}H_{31}N$) than ODA ($C_{18}H_{39}N$), indicating alkylamine chain length affects not only the aspect ratio and yield of Cu nanowires but also their growth rates.

In contrast to EDA-mediated Cu nanowire growth, which is diffusion-limited, we show that alkylamine-mediated growth of Cu nanowires is charge-transfer-limited. We further show longer alkylamines decreased the current for the reduction of $CuCl_2$ onto a Cu surface, and more effectively protect Cu

against oxidative dissolution in an alkylamine solution. Taken together, this electrochemical data indicates that increasing alkylamine chain length leads to adsorbed alkylamine monolayers acting as more effective inhibitors of electrochemical reactions. Molecular dynamics simulations show the greater passivation provided by longer alkylamines can be ascribed to the greater energy required to remove a longer alkylamine from its monolayer on a Cu(111) surface. The more effective inhibition of electron transfer provided by longer alkylamines translates into slower nanowire growth rates, reduced yields of nanowires, and shorter nanowires.

Several questions remain unanswered by this work. The process by which Cu-alkylamine complexes are transported through the alkylamine monolayer, are reduced, and added to the metal surface remains unclear. It is also not clear why the nanowires grow anisotropically through selective atomic addition to (111) facets at the ends of the nanowires. We expect that future studies combining simulations with electrochemical measurements will provide additional insights into the process by which anisotropic atomic addition occurs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.8b00760.

Experimental procedures, supplemental results, details of the molecular dynamics simulations, and supplementary figures (PDF)

Supporting video 1 for the growth of Cu nanowires with tetradecylamine (AVI)

Supporting video 2 for the growth of Cu nanowires with octadecylamine (AVI)

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Notes

The authors declare no competing financial interest.

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