Understanding the Solution-Phase Growth of Cu and Ag Nanowires and Nanocubes from First Principles

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solution-phase chloride enhances Cu nanowire growth due to a synergistic interaction between adsorbed chloride and hexadecylamine (HDA), which leaves the $\{111\}$ nanowire ends virtually bare while the $\{100\}$ sides are fully covered with HDA. For each of these topics, a synergy between theory and experiment led to significant progress.

INTRODUCTION

Shape control of metal nanocrystals will enable many applications that influence health and our overall quality of life. Although many shapes have been synthesized through solution-phase routes, the syntheses are generally not well controlled with regard to selectivity and yield to a particular shape. Input from theory and simulations is useful in this regard, and in this feature article, we provide an account of the motivations, the experiments, and the theory discussed in the Langmuir Lecture "Theory of Shape-Selective Metal Nanocrystal Synthesis from First-Principles" delivered by Kristen Fichthorn at the Fall 2020 Virtual Meeting of the American Chemical Society.

Numerous applications will be enabled or enhanced by achieving shape control of metal nanocrystals. In heterogeneous catalysis, for example, the activity and selectivity of a chemical conversion can be highly sensitive to the particular facet of the material that catalyzes it. With shape control, it has become possible to synthesize catalysts that express the most active and selective facets. A nice example (among many^{1–8}) of particular relevance to our research is from the work of Xiao et al., who studied the deoxygenation of *trans*-stilbene oxide catalyzed by various Cu nanomaterials.⁹ As we see in Figure 1A, the product of this reaction could be either *cis*- or *trans*-stilbene, with the particular isomer depending on the shape of

the Cu catalyst. The product was overwhelmingly *cis*-stilbene (Figure 1B) when the reaction was catalyzed by cubes (Figure 1C) or wires (Figure 1D), which both express a predominance of Cu(100) facets. However, when Cu nanoplates (with mostly $\{111\}$ facets) were used as the catalyst (Figure 1E), they observed a mix of cis and trans isomers, a product distribution comparable to that obtained with a support containing no catalyst. Thus, by designing the catalyst shape it is possible to dictate the outcome of a chemical transformation.

A second example illustrating the importance of shape control is in the synthesis of penta-twinned Cu and Ag nanowires with high aspect ratios. Ag nanowires have been researched extensively for use in flexible, transparent conducting thin films,^{10–13} which find application in touch-screen panels, flexible displays, and solar cells. Significant research is also underway to facilitate their use in flexible and transparent heaters,¹⁴ artificial skin,^{15,16} smart windows,^{14,17} and wearable or implantable health-monitoring applica-

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Figure 1. (A) The deoxygenation of *trans*-stilbene oxide can produce two isomers: *cis*-stilbene and *trans*-stilbene. (B) The selectivity to either *cis*-stilbene or *trans*-stilbene for various catalytic nanomaterials. When the reaction was catalyzed by Cu nanocubes (C) and Cu nanowires (D), which contain a majority of $\{100\}$ facets, the product was mostly *cis*-stilbene. When the reaction was catalyzed by Cu nanoplates (E), with a majority of $\{111\}$ facets, the product contained a majority of *trans*-stilbene. Reproduced with permission from ref 9. Copyright 2015 American Chemical Society.

tions.^{16,18} Copper is slightly less conductive than silver, but it is more earth-abundant and less expensive. Thus, Cu is seen as an alternative to Ag in many of the applications mentioned above.^{19–23}

A recent review by Ye and colleagues demonstrates nicely why nanowires with high aspect ratios are beneficial.²⁰ Devices that require optical transparency and high conductivity use thin films of nanowires in random orientations, as seen in Figure 2A. The conductivity in such films arises from nanowire



Figure 2. (A) Example images of Cu nanowire thin films for two different aspect ratios (L/D) and area fractions (AFs). (B) Plot of transmittance (T) versus sheet resistance for networks consisting of Cu and Ag nanowires with different L/D values and for different materials, including carbon nanotubes (CNT) and indium tin oxide (ITO). (A) Reproduced with permission from ref 20. Copyright 2016 American Chemical Society. (B) Reproduced from ref 24 with permission from The Royal Society of Chemistry.

contacts, and it increases (sheet resistance decreases) as the area fraction of nanowires in the film increases. However, increased conductivity comes with a decline in optical transparency (transmittance), which decreases with increasing nanowire area fraction. If the nanowires have a high aspect ratio (length-to-diameter ratio), then they can achieve many contacts at relatively low area fractions as well as high transparency. Figure 2B shows the transmittance as a function of resistivity for networks of Cu nanowires with different L/Dand for different materials, including carbon nanotubes (CNT) and indium tin oxide (ITO), the most commonly used transparent conductor. Here, we see both the transmittance and conductivity improve for Cu nanowires as their aspect ratio increases from 330 up to around 1860, and then these properties level off. With sufficiently long and thin Cu and Ag nanowires, nanowire films possess transmittance and sheet resistance comparable to or better than those of ITO.

In this Feature Article, we will focus on understanding the syntheses of basic shapes of Cu and Ag nanocrystals. These shapes are shown in Figure 3 and include octahedra, truncated octahedra, cuboctahedra, truncated cubes, and cubes, a continuum of shapes that can be observed as we change the area fraction of $\{111\}$ facets relative to $\{100\}$ facets. We also see two possible shapes for penta-twinned nanowires in Figure 3. Table 1 shows a survey of various solution-phase syntheses for Cu nanowires and nanocubes. Here, we see that it is almost always the case that the precursor salt is a chloride, either CuCl or CuCl₂. When Cu(OAc)₂ salt was used as a precursor, CTAC was introduced as a chlorine-containing surfactant.



Figure 3. Various nanoshapes of interest in this work: (A) octahedron, (B) truncated octahedron, (C) cuboctahedron, (D) truncated cube, (E) cube, (F) penta-twinned Ino decahedron and associated nanowire, and (G) penta-twinned Marks decahedron and associated nanowire. Dark facets are fcc $\{100\}$, and light facets are fcc $\{111\}$.

Table 1. Various Solution-Phase Syntheses for Copper Nanowires and Nanocubes a

shape	metal salt	additives	medium	ref
nanowire	$Cu(NO_3)_2$	EDA	NaOH, aqueous	25, 26
	CuCl ₂	alkylamines	aqueous	27-29
	CuCl	CTAC	NaOH, aqueous	30
	$Cu(acac)_2$	CTAB, HDA	aqueous	22
nanocube	CuCl ₂	HDA	aqueous	27
	CuCl	OLA, TOP	OLA + TOP	31
	$Cu(OAc)_2$	CTAC	aqueous	32
^{<i>a</i>} EDA. ethylenediamine:		CTAC/CTAB.	cetyltrimethylammonium	

chloride/bromide; HDA, hexadecylamine; OLA, oleylamine; and TOP, trioctylphosphine.

Similarly, when $Cu(acac)_2$ was used as a salt, CTAB, which is a bromine-containing surfactant, was added. In almost all of these cases, long-chain additives such as alkylamines, oleylamine, CTAC, and CTAB have been used as capping agents. An exception is the case for which Cu nanowires were synthesized using $Cu(NO_3)_2$ salt with the short linear alkylamine EDA as a capping agent and no halide. For such a synthetic condition, EDA inhibited the oxidation of Cu(111)but not Cu(100), causing the selective deposition of copper to the {111} facets on the ends of nanowires.²⁵

Various solution-phase synthetic conditions for Ag nanowires and nanocubes are presented in Table 2. We note PVP is a common capping agent in Ag nanocrystal synthesis. Also, we see that the case for the involvement of halide as a shapedirecting agent is not as clear as for Cu, although chloride and bromide are frequently present in such syntheses.

A combination of theory and experiments is useful in understanding these systems. Unfortunately, no theoretical method or experimental analysis can probe all aspects of these complex syntheses in an integrated way. However, both theoretical and experimental studies can generate and test hypotheses to lead to a deeper understanding of these systems. Below, we will discuss how a synergy between theory and experiments has led to a fundamental understanding of these shape-selective syntheses.

Table 2. Various Solution-Phase S	Syntheses :	for Silver
Nanowires and Nanocubes ^a		

	shapes	metal salt	additives	medium	ref
	nanowire	AgNO ₃	PVP, NaBr, NaCl	EG	33
		AgNO ₃	PVP, NaCl, Fe ³⁺	EG	34
		AgNO ₃	CTAB, NaOH	aqueous	35
		AgNO ₃	PVP w/and w/o NaBr	EG	36
		AgNO ₃	PVP, NaCl	EG	37, 38
		AgNO ₃	sodium citrate	aqueous	39
		AgNO ₃	sodium citrate, NaOH	aqueous	40
c	cube	CF ₃ COOAg	CTAC, FeCl ₃	aqueous	41
		CF ₃ COOAg	PVP, NaHS, HCl	EG	42
		CF ₃ COOAg	PVP, NaHS, HCl	DEG	43
		AgNO ₃	PVP, HCl	EG	44
		AgNO ₃	PVP, NaBr	EG	45
		CF ₃ COOAg, AgNO ₃	PVP w/ and w/o HCl	EG	46
	a				

^aEG, ethylene glycol; DEG, diethylene glycol.

THERMODYNAMICS AND KINETICS OF Ag NANOSTRUCTURES

Ag Cubes. In early synthetic studies of Ag nanocubes and nanowires, these shapes were attributed to stronger binding of PVP to {100} than to {111} facets of Ag.⁴⁷ We confirmed this binding preference in our first-principles calculations based on density-functional theory (DFT).^{48,49} Later experimental studies by Xia and colleagues sought to quantify the role of PVP in determining the cubic shapes of Ag nanocrystals.⁴⁶ In these studies, they began with initially cubic Ag seeds in EG solution with PVP at two different concentrations, as indicated in the scanning electron microscope (SEM) images in Figure 4. If they further grew the cubic seeds in a 2.5 mM PVP solution, they continued to grow as cubes. If they continued to grow the seeds in a 0.3 mM PVP solution, the cubes evolved to cuboctahedra with further growth.

In efforts to understand the role of PVP, our group performed a series of molecular-dynamics (MD) simulation studies^{50–52} based on our empirical metal–organic many-body force field.⁵³ Though we reviewed this work previously,^{54,55} we discuss it here briefly to provide a complete account of the Langmuir Lecture. We posed the question of whether the nanostructures seen experimentally in Xia's study⁴⁶ (Figure 4) were kinetic or thermodynamic in origin. Our efforts were centered on applying the Wulff construction illustrated in Figure 5.

In the Wulff construction,⁵⁶ facets in an equilibrium crystal shape follow the relation

$$\frac{h_i}{\gamma_i} = \lambda \tag{1}$$

where γ_i is the interfacial free energy of facet *i* for a crystal grown in solution, which is the liquid–solid interfacial free energy, h_i is the distance along a vector originating at the Wulff point of the crystal that is normal to facet *i*, and λ is a constant. Figure 5 shows the Wulff shapes predicted using eq 1 for an fcc crystal that can have {100} and {111} facets. Here, we see if the ratio $\gamma_{\{111\}}/\gamma_{\{100\}} \leq 1/\sqrt{3}$, the shape will be an octahedron. If $\gamma_{\{111\}}/\gamma_{\{100\}} \geq \sqrt{3}$, the shape will be a cube. Between these two limits, a continuum of shapes occurs, ranging from the



Figure 4. SEM images of Ag polyhedra grown in EG solution from 100 nm cubic Ag seeds in the presence of (A-C) 2.5 mM PVP10, where the final products are cubes, and (D-F) 0.3 mM PVP10, where the final products are cubes (D), truncated octahedra (E), and cuboctahedra (F). PVP10 refers to a PVP polymer with a molecular weight of approximately 10 000. Reproduced with permission from ref 46. Copyright 2012 American Chemical Society.



Figure 5. Thermodynamic $(\gamma_{\{111\}}/\gamma_{\{100\}})$ or kinetic $(G_{\{111\}}/G_{\{100\}})$ Wulff shapes for an fcc crystal containing two different types of facets: $\{111\}$ and $\{100\}$. $\{111\}$ facets are light blue, and $\{100\}$ facets are dark blue.

truncated octahedron to the cuboctahedron to the truncated cube as $\gamma_{\{111\}}/\gamma_{\{100\}}$, and the fraction of $\{100\}$ facets increases. There is also a kinetic Wulff construction^{57,58} that is analogous to eq 1. Kinetic Wulff shapes are dictated by the linear facet growth rates, which for facet *i* is G_i , such that

$$\frac{h_i}{G_i} = \lambda \tag{2}$$

The linear facet growth rate is the rate of growth normal to facet i and can be viewed in terms of the accumulation of atoms on facet i. It is important to recognize that when atoms accumulate on facet i they increase the area of the facets adjacent to i. As we see in Figure 5, we can simply substitute the ratio of linear facet growth rates for the ratio of interfacial free energies to predict kinetic Wulff shapes.

To predict thermodynamic equilibrium or kinetic crystal shapes, we need to calculate liquid—solid interfacial free energies or linear facet growth rates, respectively. We obtained these using MD simulations.^{50–52,59} To calculate $\gamma_{\{111\}}$ and $\gamma_{\{100\}}$, we developed a six-step, multischeme MD method based on thermodynamic integration.^{52,59} In our approach to ascertaining kinetic Wulff shapes, we equated the linear facet growth rate for facet *i* to the solution-phase Ag atom flux to facet *i*, which is tantamount to assuming that the inter-facet surface diffusion is negligible. This should be a reasonable assumption for crystals of the sizes shown in Figure 4. Using MD-based umbrella sampling, we calculated the mean first-passage time $t_{\rm M}$ for a solution-phase Ag atom at an experimental concentration to diffuse through EG-PVP solution and through the PVP capping layer to the Ag(100) and Ag(111) substrates.^{50,51} The linear facet growth-rate ratio, relevant to predicting the kinetic Wulff shape (cf. eq 2), was then taken as $G_{\{111\}}/G_{\{100\}} = t_{\rm M}\{100\}/t_{\rm M}\{111\}$.

Figure 6 shows the thermodynamic and kinetic Wulff shapes predicted in our calculations with PVP 20mers in EG solvent.



Figure 6. Ratio of liquid—solid interfacial free energies $\gamma_{\{111\}}/\gamma_{\{100\}}$ (blue) and linear facet growth rates $G_{\{111\}}/G_{\{100\}}$ (orange) for Ag(111) and Ag(100) facets in four different environments: vacuum, EG solution, EG-PVP solution with half of an adsorbed PVP layer, and EG-PVP solution with a full adsorbed PVP layer. Predicted Wulff shapes are shown for each set of conditions, with blue and orange shapes corresponding to the bars and with {100} facets shown darker and {111} facets shown lighter. Adapted from data in refs 50 and 52.

For the thermodynamic Wulff-shape calculations, shown in blue, the ratio of liquid–solid interfacial free energies in Figure 6 is constant and independent of the EG-PVP solution environment. For all of the different environments, the predicted thermodynamic shape is a truncated octahedron. The kinetic Wulff shapes in Figure 6 show more sensitivity to the EG-PVP solution environment. The predicted shape is a truncated octahedron in EG solution without PVP, a cuboctahedron in EG solution with half a layer of adsorbed PVP, and a truncated cube in EG solution with a full layer of adsorbed PVP. For the kinetic shapes, we found two factors contributed to the linear-facet growth-rate ratio.^{50,51} First, the



Figure 7. SEM images of Ag nanocrystals synthesized with 3 mM HNO₃ and (A) 0.03 mM NaCl, (B) 0.3 mM NaCl, and (C) 3 mM NaCl. In (D), we show the surface energies γ of Ag(100) and Ag(111) for different surface coverages of Cl as a function of the solution-phase Cl⁻ chemical potential μ_{Cl} . Colored lines indicate the minimum γ on each surface. Wulff shapes are shown for several values of μ_{Cl} . The vertical red line at μ_{Cl} = -2.68 eV denotes where the formation of bulk AgCl is thermodynamically favored over Ag surfaces containing adsorbed chlorine. Adapted with permission from ref 44. Copyright 2019 American Chemical Society.

stronger binding of PVP to Ag(100) leads to a larger freeenergy barrier for Ag atoms to reach the Ag(100) surface. Second, a more extended PVP layer on Ag(111), due to its weaker binding on this surface, leads to Ag atom trapping above the surface and promotes flux to Ag(111). Though the PVP oligomers in our calculations are smaller than those in the experiment (20 repeat units in our calculations vs 100 repeat units for the PVP in the experiments in Figure 4), the polymers should exhibit the same features as we observe here because the interaction of the repeat units with the substrate is similar. The kinetic Wulff shapes are consistent with the experimental results shown in Figure 4 and indicate the PVP-covered cubes are kinetic shapes. We note that subsequent to this study, Chen and colleagues measured equilibrium isotherms for PVP adsorption to Ag(100) and Ag(111) in EG solvent.⁶⁰ They also concluded PVP-covered Ag cubes in EG solution are kinetic structures.

Though cubic shapes can occur for Ag cubes in EG-PVP solution, Table 2 indicates chloride is a common additive in the synthesis of Ag cubes. What is the role of chloride? To understand this role, we performed a joint experimental—theoretical study.⁴⁴ Experimentally, we probed the synthesis of Ag nanocrystals in EG-PVP solution containing various additives. These experiments indicated the importance of Cl⁻ in establishing cubic crystal shapes and the importance of H⁺ in promoting a monodisperse shape distribution consisting of only cubes. The role of H⁺ was presumably to etch the initial seeds as they formed and prevent the formation of twinned nanowires.

By adding both HNO₃ (at 3 mM for the H⁺) and NaCl (for the Cl⁻) in addition to PVP to the synthesis, we could form a series of single-crystal shapes, as shown in Figure 7. We observed cuboctahedra, as shown in Figure 7A, when the

concentration of NaCl was 0.03 mM, whereas with the addition of 0.3 mM NaCl, truncated cubes formed (Figure 7B). As shown in Figure 7C, Ag nanocubes formed with the addition of 3 mM NaCl. Thus, the increase in Cl^- concentration led to a shape evolution from truncated octahedra to cuboctahedra, truncated cubes, and eventually cubes.

To probe the role of Cl⁻ in dictating Ag nanocrystal shapes, we carried out ab initio thermodynamics calculations to obtain the surface energies of Cl-covered Ag facets for various solution-phase chloride chemical potentials μ_{Cl^-} . In Figure 7D, we plot the surface energy of Ag(100) and Ag(111) as a function of μ_{Cl^-} . Predicted Wulff shapes are shown for selected values of μ_{Cl^-} . As μ_{Cl^-} increases, the area fraction of Ag(100) facets also increases, and the Wulff shape becomes more cubic, consistent with the experimental observation that Ag nanocrystal shapes evolve from truncated octahedra to cubes with increasing Cl⁻ concentration. These results indicate a thermodynamic tendency for Ag nanocubes to form in the presence of adsorbed chlorine/solution-phase chloride.

Thus, our calculations indicate the thermodynamics of PVP adsorption alone would not lead to cubes. On the other hand, Figure 6 shows that PVP alone could lead to kinetic Wulff shapes that are truncated cubes. Our study of the influence of solution-phase chloride shows if the concentration of Cl^- is high enough (the surface coverage of adsorbed Cl is around 0.5 ML) then Cl has the capacity to produce thermodynamic cubic shapes.

Âg Nanowires. A common hypothesis for penta-twinned Ag nanowire formation is the capping agent binds selectively to $\{100\}$ on the nanowire sides, leaving the $\{111\}$ ends free for metal-atom addition.⁴⁷ Our studies indicate that this is unlikely to be the case for Ag nanowires.^{50,61} As we see in Figure 6, the

flux ratio $G_{\{111\}}/G_{\{100\}}$ we predict is sufficient to grow cubes, but theoretical estimates indicate that a significantly larger ratio, around 120, is required to grow nanowires with an aspect ratio of around 100.⁶¹ Moreover, Ag nanowires can grow under vapor-phase conditions devoid of any special additives,^{62,63} which seems to indicate that some specific feature of the material or seed structure leads to one-dimensional growth. It has been observed that nanowires grown in the absence of solution-phase halide do not achieve aspect ratios as high as those in the presence of halide.³⁶ Thus, it seems the basic mechanism of nanowire growth does not depend on any particular solution-phase additive, though such additives may influence facet growth rates.

In an effort to quantify the growth mechanism of Ag nanowires, we considered the diffusion of Ag atoms on the surfaces of nanowire seeds and the possibility their accumulation on the {111} facets could lead to the growth of the seeds into nanowires. In this analysis, we do not account for how penta-twinned seeds form initially, which is presumably due to a lack of oxidative etching during seed formation.⁶⁴ Penta-twinned nanowires grow from decahedral seeds that are almost always schematically depicted as shown in Figure 3F. Such seeds possess strain because the 5-fold structure is not space-filling (e.g., ref 65) and closure of the small gap among the five sections creates a complex strain field.⁶⁶ However, our calculations indicate that a Marks-like Dh, similar to that shown in Figure 3G, is energetically favored.⁶¹ The inset to Figure 8 shows a picture of our



Figure 8. MFPT for an atom to transit from {100} to {111} $\langle t_{\{100\} \rightarrow \{111\}} \rangle$ as a function of the nanowire length (lower axis) and aspect ratio (upper axis) for a constant nanowire diameter of ~28 nm. The inset depicts the seed geometry, with {111} facets in dark blue, {100} facets in aqua, and {110} facets in green. Adapted from data in ref 61.

predicted nanowire seed structure. In addition to possessing $\{111\}$ end facets, $\{100\}$ side facets, and $\{111\}$ "notches" running along the nanowire length, these seeds/nanowires possess $\{110\}$ "steps" leading from the notches to the end facets. The Marks-like structure relieves some of the strain associated with the 5-fold structure and has a lower surface-area-to-volume ratio compared to related shapes.

We considered the role of surface diffusion in nanowire growth beginning with the seed structure in Figure 8 for a seed with a diameter of approximately 28 nm.⁶¹ These were

multiscale calculations involving MD simulations, calculations of diffusion barriers and hopping rates, and, ultimately, the incorporation of the hopping rates into calculations based on the theory of absorbing Markov chains⁶⁷⁻⁷⁰ designed to predict the inter-facet mean first-passage time. The MD simulations and hopping-rate calculations were performed using the LAMMPS package⁷¹ with an empirical embeddedatom method (EAM) potential for Ag.72 From the MD simulations, we learned that aggregation on the {111} end facets occurred within nanoseconds, a time scale that proved to be much faster than the aggregation time on the $\{100\}$ facets for a seed of this size. Once a modest aggregate (i.e., a dimer) formed on the {111} end facets, the barrier for an atom to break away was large, as we elaborate below. Although the rapid aggregation on the $\{111\}$ facets is a consequence of the rapid diffusion on these facets, we found the most probable locations for the aggregates were at the twin edges of these facets and at the $\{111\}/\{110\}$ facet boundaries due to the strain distribution on the nanowire ends.

We calculated diffusion-energy barriers using the climbingimage nudged elastic band method,⁷³ as implemented in LAMMPS. Overall, we calculated 32 different diffusion barriers (16 forward and 16 reverse) for adatom hopping on the {100}, {111}, and {110} facets as well as in the notch and for diffusion between these different facets. The hopping rate for a diffusion barrier $E_{\rm B}$ is given by

$$r = v_0 \exp\left(-\frac{E_{\rm B}}{kT}\right) \tag{3}$$

where v_0 is the pre-exponential factor, which we took to be $v_0 = 10^{13} \text{ s}^{-1}$. A key rate with relevance to nanowire growth is diffusion in the {111} notch, which has a relatively low diffusion barrier of 0.16 eV. This low barrier, combined with the rapid aggregation on {111} facets and its effect of slowing {111} diffusion, is important in promoting nanowire growth. As for aggregation on the {111} facets, the notch forms as a consequence of strain and functions as a "super highway" to channel atoms from the nanowire sides to the ends. With a knowledge of hopping rates between various facets, we could calculate linear-facet growth rates *G*.

The linear-facet growth rates of the end $\{111\}$ and the side $\{100\}$ facets are given by the accumulation of atoms on those facets by

$$\frac{\mathrm{d}N_{100}}{\mathrm{d}t} = G_{\{100\}} = r_{\mathrm{dep},\{100\}} + R_{\{111\} \to \{100\}} - R_{\{100\} \to \{111\}}$$
(4)

and

$$\frac{\mathrm{d}N_{111}}{\mathrm{d}t} = G_{\{111\}} = r_{\mathrm{dep},\{111\}} + R_{\{100\} \to \{111\}} - R_{\{111\} \to \{100\}}$$
(5)

where $r_{\text{dep},\{100\}}$ and $r_{\text{dep},\{111\}}$ are the deposition rates on the $\{100\}$ and $\{111\}$ facets, respectively, $R_{\{111\}\rightarrow\{100\}}$ is the net rate at which atoms on the $\{111\}$ facet diffuse to the $\{100\}$ facet, and $R_{\{100\}\rightarrow\{111\}}$ is the net rate at which atoms on the $\{100\}$ facet diffuse to the $\{111\}$ facet. The total deposition rate is $r_{\text{dep}} = r_{\text{dep},\{100\}} + r_{\text{dep},\{111\}}$, and it can be obtained from experiment. A survey of the literature indicates r_{dep} is around 10^3-10^4 s⁻¹, considering various experiments run for just Ag and solution-phase additives other than those containing Cl.^{36,40} In our work, we used the theory of absorbing Markov chains to calculate $R_{\{100\}\rightarrow\{111\}}$ and $R_{\{111\}\rightarrow\{100\}}$.

To perform our calculations, we make a map containing all sites on the {111} and {100} facets of an Ag nanowire. For a {100} facet, this map consists of all of the {100} binding sites, the {111} notch sites, the {110} sites, and the {111} sites on the border between the {100} and {111} facets. For a {111} facet, this consists of all of the {111} end-facet sites, the {110} sites, and the {100} and notch sides on the border between {111} and {100}. For both facets, the border sites are taken as absorbing states, and all the rest of the sites are considered to be transient states. The atoms in transient states can transit to other states, while atoms in absorbing states cannot transit; the absorbing state is a final state. We can then construct a transition matrix **A** for each facet, the elements of which are given by

$$A_{ij} = \begin{cases} \sum_{k} r_{ik}, \ ifi = j \\ -r_{ji}, \ ifi \neq j \end{cases}$$
(6)

for all sites *i* and *j*, where r_{ik} is the rate for an atom to hop from site *i* to site *k*, which takes the form given in eq 3.

We construct Markov matrix **M** from **A**. The Markov matrix has the form

$$\mathbf{M} = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{R} & \mathbf{T} \end{pmatrix} \tag{7}$$

For $N_{\rm T}$ transient states and $N_{\rm A}$ absorbing states, **I** is the identity matrix with dimensions of $N_{\rm A} \times N_{\rm A}$, **0** is the null matrix with dimensions of $N_{\rm A} \times N_{\rm T}$, **R** is the recurrent matrix with dimensions of $N_{\rm T} \times N_{\rm A}$, and **T** is the transient matrix with dimensions of $N_{\rm T} \times N_{\rm A}$, and **T** is the transient matrix with dimensions of $N_{\rm T} \times N_{\rm A}$. **R** contains information on the transitions from transient states to absorbing states, and **T** describes the transitions between transient states. Defining $\tau_i = A_{ii}^{-1}$, the elements of **R** and **T** are given by

$$R_{ij} = r_{ij}\tau_i \tag{8}$$

and

$$T_{ij} = \begin{cases} 0 \text{ if } i = j \\ r_{ij}\tau_i \text{ if } i \neq j \end{cases}$$
(9)

The mean first-passage time $t_{\rm M}$ and the probabilities of ending in different absorbing states $\vec{p}_{\rm exit}$ can be obtained from

$$t_{\rm M} = \vec{p}_0^T \cdot (\mathbf{I} - \mathbf{T})^{-1} \cdot \vec{\tau}$$
⁽¹⁰⁾

and

$$\vec{p}_{\text{exit}} = \vec{p}_0^T \cdot (\mathbf{I} - \mathbf{T})^{-1} \cdot \mathbf{R}$$
(11)

where \vec{p}_0^{T} is the transpose of the initial occupancy vector of the transient states.

We calculated $\langle t_{\{100\}\rightarrow\{111\}}\rangle$ and $\langle t_{\{111\}\rightarrow\{100\}}\rangle$ using eq 10. For wires of a constant diameter (= 28 nm), we found $\langle t_{\{111\}\rightarrow\{100\}}\rangle = 0.4555$ s. $\langle t_{\{100\}\rightarrow\{111\}}\rangle$ is a function of the nanowire length and is shown in Figure 8. Here, we see $\langle t_{\{100\}\rightarrow\{111\}}\rangle \ll \langle t_{\{111\}\rightarrow\{100\}}\rangle$, which means $R_{\{100\}\rightarrow\{111\}} \ll R_{\{100\}\rightarrow\{111\}}$. Taking $t_{dep} = r_{dep}^{-1} = 10^{-4}$ s, we see it is on the order of $\langle t_{\{100\}\rightarrow\{111\}}\rangle$. Considering the ramifications of this for eqs 4 and 5 and noting that $R_i = t_{M,i}^{-1}$, we have $G_{\{100\}} = r_{dep,\{100\}} - R_{\{100\}\rightarrow\{111\}} \approx 0$ and $G_{\{111\}} = r_{dep,\{111\}} + r_{dep,\{100\}} = r_{dep}$. Thus, our calculations predict Ag atoms deposited on the nanowire ends rapidly aggregate and accumulate there while atoms deposited on the sides diffuse to the notches, where they rapidly transit to the nanowire ends.

To predict nanowire lengths/aspect ratios, we note nanowires will grow to a length at which the deposition rate exceeds the inter-facet transport rate $(r_{dep,\{100\}} \ge R_{\{100\} \rightarrow \{111\}})$. After nanowires reach this length, accumulation occurs on the $\{100\}$ facets and the wires thicken. Considering there are five $\{100\}$ side facets on the nanowires, we predict nanowires with aspect ratios of around 40–180, which falls in the experimental range.⁶¹

THERMODYNAMICS AND KINETICS OF Cu NANOSTRUCTURES

As we see above in Table 1, chloride is present in nearly every synthesis of Cu nanowires and nanocubes. However, capping agents are also present, and prior to our work, the prevailing hypothesis was that the additive molecules in Table 1 bound selectively to Cu(100), which promoted the addition of Cu atoms to the $\{111\}$ ends of the wires. Figure 9, which is from the work of Yang and colleagues, illustrates this idea for their study of the growth of Cu nanowires from CuCl in oleylamine (OLA) solution.⁷⁴



Figure 9. Proposed growth mechanism for Cu nanowires. (A) Front view of penta-twinned seeds showing the $\{111\}$ facets. (B) Side view of penta-twinned seeds showing the $\{100\}$ facets. (C) Seeds grow to nanowires because OLA adsorbs preferentially on the $\{100\}$ side facets, allowing Cu atoms to deposit preferentially on the $\{111\}$ facets. Reproduced with permission from ref 74. Copyright 2014 American Chemical Society.

Cu Nanowires. We considered the growth of Cu nanowires in aqueous solution containing hexadecylamine (HDA) as a capping agent. Two different types of experiments were performed: synthesis experiments and electrochemical experiments on single-crystal electrodes. In the synthesis experiments, with SEM images depicted in Figure 10, we found when $CuCl_2$ is the salt, nanowires form (Figure 10A). When $Cu(NO_3)_2$ salt is used as the source of Cu, nanowires do not form (Figure 10B). However, nanowires form when $Cu(NO_3)_2$ is the salt and NaCl is added (Figure 10C).²⁹ In this latter case, the synthesized morphology is a function of the NaCl (Cl⁻) concentration: if the Cl⁻ concentration is too low, then spherical nanoparticles form (Figure 10B), and if the Cl⁻ concentration is too high, then the nanowires achieve a nonuniform cross-section, with javelin-like shapes.²⁹ Nano-



Figure 10. SEM images of Cu nanostructures synthesized from (A) $CuCl_2$, (B) $Cu(NO_3)_2$, and (C) $Cu(NO_3)_2$ with NaCl in the presence of HDA and ascorbic acid. Reproduced with permission from ref 29. Copyright 2018 American Chemical Society.

wires with high aspect ratios form over an intermediate range of Cl^- concentrations (Figure 10C).

Electrochemical experiments on single-crystal Cu(111) and Cu(100) surfaces indicate there is little difference in the rates at which Cu ions are reduced on the two Cu surfaces at low concentrations of Cl⁻; both reduction rates are low (cf. Figure 11A).²⁹ At intermediate Cl⁻ concentrations, where nanowires are observed, the rate of Cu ion reduction is larger on Cu(111)than on Cu(100); this is the region enclosed by the dotted line in Figure 11A. High Cu ion reduction rates occurred on both surfaces at high chloride concentrations, where the wires take on javelin-like shapes. Thus, experiments identify that chloride is needed for the growth of Cu nanowires, its concentration has to fall within a certain window for nanowire growth to occur, and the resulting morphology can be connected to reduction rates observed in single-crystal electrochemical experiments.²⁹ To address these results, we used first-principles DFT calculations.

Our DFT calculations indicate in the absence of adsorbed Cl, HDA forms self-assembled monolayers (SAMs) that cover both Cu(100) and Cu(111) if no solution-phase chloride is present.^{75–77} This is not consistent with the picture presented in Figure 9, which depicts the hypothesis that OLA, a similar molecule, exhibits highly selective binding to Cu(100) facets. We considered a possible synergistic interaction between chloride and HDA in promoting the growth of Cu nanowires. To do this, we used DFT-based ab initio thermodynamics to delineate the range of solution-phase Cl⁻ and HDA chemical potentials for which various surface environments are expected, based on coadsorption structures of Cl and HDA on Cu surfaces. We constructed a phase diagram by identifying various unique chemical-potential regions of surface configurations on the two surfaces.⁷⁷ Figure 12 shows a portion of this phase diagram that is relevant to experimental nanowire growth.

Since the concentration of HDA is a constant in the synthesis experiments with various chloride concentrations,²⁹ we find a region of HDA chemical potentials consistent with experimental observations, as shown in Figure 12. In particular, we expect to observe nanowire formation for sufficiently high $\Delta \mu_{\rm HDA}$. Figure 11B,C shows the predicted surface configurations of Cl (coverage of 0.33 ML) and HDA [0.33 ML on Cu(100) and 0 ML on Cu(111) in one of the regions where we predict wires will form on Figure 12. We associate these configurations with the region enclosed by the dotted line in the experimental electrochemical results in Figure 11A. Here, we see HDA is chemisorbed to Cu(100). In our DFT calculations, which are performed at 0 K, there is a weakly physisorbed HDA layer above Cu(111). At the finite temperatures of the experiments, such a layer would be too weakly bound to remain near the surface. Moreover, the HDA



Figure 11. (A) Experimental current densities at the mixed potential j_{MP} for Cu(100) and Cu(111) as a function of the solution-phase chloride concentration. (B and C) Side and top (showing Cl and N only) views of optimized binding conformations of Cl and HDA at Cl coverages of (B) 0.33 ML on Cu(100) and (C) 0.33 ML on Cu(111) (brown, Cu; dark blue, chemisorbed N; light blue, physisorbed N; green, Cl; gray, C; and white, H). Reproduced with permission from ref 29. Copyright 2018 American Chemical Society.



Figure 12. Phase diagram indicating HDA ($\Delta \mu_{\text{HDA}}$) and chloride (μ_{Cl^-}) chemical potentials for which various surface environments occur. We predict solid CuCl will form for $\mu_{\text{Cl}^-} \geq -2.43$ eV. Adapted from the data in ref 77.

aggregate would gain entropy by existing in solution as a micelle. Thus, our calculations predict there is a narrow region of solution-phase chloride concentrations for which HDA is chemically adsorbed to Cu(100) and physically adsorbed to (or absent from) Cu(111). For lower chloride concentrations, HDA is chemisorbed to both surfaces, and there is low electrochemical activity on both surfaces in Figure 11A. Also, for higher chloride concentrations (higher μ_{Cl} -, cf., Figure 12), HDA is weakly physisorbed (or not adsorbed) on both surfaces, and experiments (Figure 11A) indicate similar electrochemical activity on both surfaces.

Thus, a synergistic interaction between adsorbed Cl and linear alkylamines creates a situation in which the HDA SAMs fully protect the sides of a penta-twinned Cu nanowire from Cu atom addition while weakly bound HDA (or no HDA at all) at the ends leaves them free for growth. Future studies could examine how to exploit this mechanism or how it might work in conjunction with other chemical additives (for example, O_2^{78}) to optimize the morphology in Cu nanowire growth.

Cu Cubes. Penta-twinned nanowires grow as kinetic structures from decahedral seeds.⁷⁹ If the initial seed is a single crystal, then single-crystal structures will form. For example, Jin et al. synthesized HDA-protected Cu nanocubes beginning with single-crystal seeds, which formed for relatively low HDA concentrations, likely due to a lack of HDA protection from the oxidative etching of these structures.²⁷ Using eq 1, we predicted Wulff shapes for single crystals based on their surface energies. Figure 13 shows $\gamma_{\{111\}}/\gamma_{\{100\}}$ as a function of the chloride and HDA chemical potentials for represent the full range of conditions probed in our studies.^{29,77} For the regions that lead to the growth of Cu nanowires from penta-twinned seeds (the two rightmost regions in Figure 12), we predicted cubic shapes consistent with those seen in experimental studies of Cu nanocube growth.²⁷ As we see in Figure 12, {100} facets are passivated by HDA, while {111} surfaces are unprotected in these regions. Hence, in addition to the thermodynamic driving force to grow nanocubes, there is a kinetic effect that arises from enhanced Cu ion flux to the {111} facets and hindered flux to the $\{100\}$ facets. This kinetic benefit could lead to the formation of "pointy" cubes when truncated cubes are predicted on the basis of thermodynamics. Thus, our DFT calculations predict either cube or wire formation, depending



Figure 13. Ratios of the surface energies of Cu(111) to Cu(100) $(\gamma_{\{111\}}/\gamma_{\{100\}})$, given by the scale bar, as a function of the HDA $(\Delta\mu_{\text{HDA}})$ and chloride (μ_{CI^-}) chemical potentials. For the largest values of $\gamma_{\{111\}}/\gamma_{\{100\}}$, we predict cubic nanocrystals (also see Figure 5), as seen in the experiment. The inset depicts SEM images of Cu nanocubes, reproduced with permission from ref 27. Copyright 2011 Wiley Publishing.

on the seed structure, which agrees well with experimental observations. $^{\rm 27}$

CONCLUSIONS

In this feature article, we discussed several instances for which multiscale theory and simulations based on first-principles DFT were useful in uncovering the intertwined influences of kinetics and thermodynamics on the growth of Ag and Cu nanowires and nanocubes. We saw how relatively modest differences in the binding of PVP to Ag(100) and Ag(111) surfaces were sufficient to produce Ag nanocubes based on deposition kinetics with limited inter-facet diffusion for large cubes.^{50,51} The addition of chloride to the synthesis, however, could promote thermodynamic cubic shapes.⁴⁴ On the other hand, our calculations indicate that Ag nanowires achieve high aspect ratios as a consequence of Ag atom surface diffusion on nanowires that grow from Marks-like decahedral seeds.⁶¹

We found Cu nanowire growth is enhanced in the presence of solution-phase chloride because for certain intermediate, solution-phase chloride concentrations we achieve the situation in which Cu(100) is completely covered by chemisorbed HDA SAMS while HDA is weakly physisorbed to Cu(111). This will promote a high flux of Cu ions to the nanowire ends, with virtually no flux to the nanowire sides, similar to the cartoon depicted in Figure 9 but different in the essential way that both chloride and HDA are needed for this scenario to occur.^{29,77} In addition to this kinetic driving force, we also find the thermodynamic driving force at which the surface energy of chlorine- and HDA-covered Cu(100) becomes lower than that of chlorine- and HDA-covered Cu(111). If growth commences from single-crystal seeds, then we predict cubic Wulff shapes will grow under solution-phase conditions similar to those that favor wire growth from pentatwinned seeds.

Thus, much progress has been made in understanding the kinetic and thermodynamic origins of metal nanocrystal shapes that grow given an initial seed. For every system that we investigated, there were possible kinetic origins for the final shapes. However, most of the shapes could have both thermodynamic and kinetic origins, depending on the synthesis conditions. These results highlight the significant role of kinetics, even at such small sizes, where diffusion lengths are relatively small and we might expect facile restructuring of the nanocrystals to achieve thermodynamic shapes. It is likely that kinetics is important at even smaller sizes than those for the structures investigated here, at sizes relevant to the seeds from which these various shapes were grown. A significant future challenge is understanding how seeds transform as they grow to assume their final shapes and how this might be controlled.⁸⁰ Synergy between theory and experiment could lead to significant progress on this topic.

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Notes

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