**Crystal Shape Control**

DOI: 10.1002/anie.200702432

# Elucidation of an Overpotential-Limited Branching Phenomenon Observed During the Electrocrystallization of Cuprous Oxide**

*Matthew J. Siegfried and Kyoung-Shin Choi**

We recently demonstrated the rational synthesis of $Cu_2O$ crystals with a vast array of new morphologies by independently and simultaneously controlling the habit and branch formation during electrodeposition ($2\,Cu^{2+} + H_2O \leftrightarrow Cu_2O + 2\,H^+$).[1–3] We achieved habit control by taking advantage of the preferential adsorption of sodium dodecyl sulfate ions on the {111} and $Cl^-$ ions on the {100} planes[1,2] and shape control by systematically altering the relative growth rate along the ⟨100⟩ direction with respect to the rate along the ⟨111⟩ direction. This was possible by varying the amount of $Cl^-$ ions in solution, which allowed for the growth of $Cu_2O$ crystals with shapes ranging from octahedral, truncated octahedral, cuboctahedral, and truncated cubic to cubic.[4] We regulated the degree of branching by controlling the deposition potential/current.[3] Thus, as the deposition potential became more positive the degree of branching gradually increased until the deposition potential/current no longer allowed for the deposition of $Cu_2O$ (Figure 1).

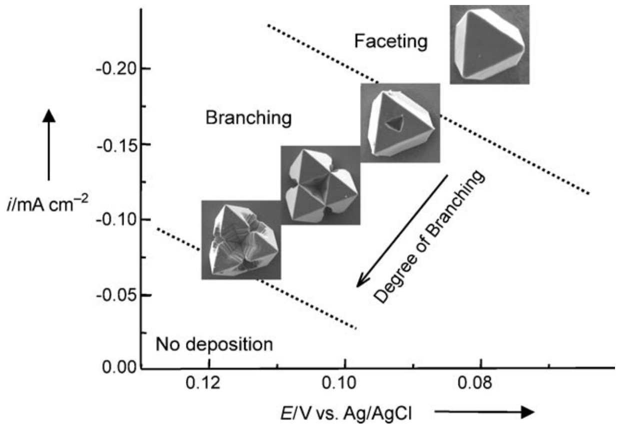

*Figure 1.* A morphology diagram showing the unusual potential- and current-dependence of $Cu_2O$ branching growth observed in a previous study.[3]

An overpotential is generated for the cathodic deposition of $Cu_2O$ when a deposition potential more negative than the reduction potential of $Cu^{2+}$ to $Cu^+$ ions is applied, and this overpotential increases as the applied potential becomes more negative. The relationship between the overpotential ($\eta$), the deposition potential applied ($E_{appl}$), and the reduction potential ($E_{red}$) is given by Equation (1).

$$\eta = |E_{appl} - E_{red}| \qquad (1)$$

The potential/degree of branching relationship shown in Figure 1 enabled us to precisely predict and systematically tailor the degree of branching of $Cu_2O$ crystals. However, we could not explain the trend whereby more severe branching growth is stabilized at a lower overpotential by conventional diffusion-limited branching mechanisms as this trend is exactly the opposite of what would normally be expected for diffusion-limited branching.

Diffusion-limited branching occurs when the initial growth rate of a crystal is faster than the diffusion rate of nutrient ions, which results in a depletion zone around the crystal.[5–8] The crystal growth and crystal shape are limited by diffusion when such a depletion layer is formed. Since the apexes of a polyhedral crystal protrude further into the region of higher concentration they can grow faster than the central parts of the facets, thus forming branches. In electrodeposition, the crystal growth rate is exponentially related to the overpotential, therefore, diffusion-limited branching during electrocrystallization is expected to occur at overpotentials higher than those that stabilize faceted crystals (in other words, at a more negative applied potential for cathodic deposition).[9,10] In this case, the degree of branching is expected to become more pronounced as the overpotential increases.

The purpose of this study is to elucidate the origin of the unusual branching growth of $Cu_2O$ that we observed in overpotential regions lower than those that enable faceting growth. The deposition mechanism of $Cu_2O$ can be broken down into two steps. The first step is the electrochemical reduction of $Cu^{2+}$ ions to $Cu^+$ ions [Eq. (2)] and the second step is the precipitation of $Cu_2O$ due to the solubility limit of $Cu^+$ ions at a given pH value [Eq. (3)].[11]

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \quad E^\circ = 0.159\ V \qquad (2)$$

$$2\,Cu^+ + H_2O \rightarrow Cu_2O + 2\,H^+ \quad \lg(Cu^+) = -0.84 - pH \qquad (3)$$

Equation (3) shows that the precipitation of $Cu_2O$ involves the generation of protons. This situation means that an increase in overpotential affects both the reduction

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[*] M. J. Siegfried, Prof. K.-S. Choi
Department of Chemistry
Purdue University, West Lafayette, IN 47907 (USA)
Fax: (+1) 765-494-0239
E-mail: kchoi1@purdue.edu

[**] This work was supported by the U.S. Department of Energy (DE-FG02-05ER15752), the Alfred P. Sloan Foundation, and the donors of the American Chemical Society Petroleum Research Fund. This work made use of the Life Science Microscopy Facility at Purdue University.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

rate and depletion of $Cu^{2+}$ ions and the local pH value around the crystals as it will speed up the rate of precipitation. Since pH value can also affect the shape formation of crystals in various ways,[12,13] its effect can interfere with diffusion-limited growth and lead to results that may appear to be due to a new phenomenon. Therefore, to verify whether the observed low overpotential branching is truly a new phenomenon and not conventional diffusion-limited branching, the effects of potential and pH value on branching growth need to be investigated separately. We address this issue herein by exploiting acetate buffers compatible with our deposition conditions to keep the pH value near the working electrode constant, regardless of the deposition potential/rate. This allows us to study the role of both pH value and potential on branching and propose a plausible mechanism that can explain the dependence of branching growth on various synthetic parameters.

We first studied the effect of pH value on branching growth by depositing $Cu_2O$ crystals from copper(II) acetate solutions buffered at pH 3.8, 4.7, and 5.1 at the same potential ($E = 0.07$ V). The scanning electron microscope (SEM) images of the resulting $Cu_2O$ crystals show that the pH value itself has a distinctive effect on branching, with the degree of branching decreasing systematically with pH value (Figure 2).

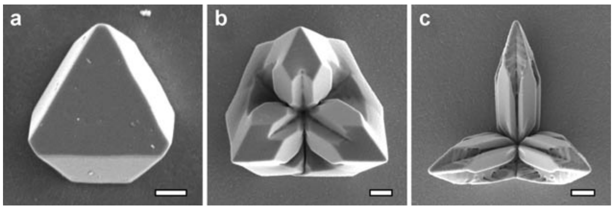

***Figure 2.*** SEM images of $Cu_2O$ crystals grown at $E = 0.07$ V at 60 °C for 10 min in acetate buffer solutions containing 0.02 M copper acetate; a) pH 3.8, b) pH 4.7, and c) pH 5.1 (scale bar: 1 μm). Low-magnification images showing the distribution of crystals on the working electrode and the uniform tendency of faceting/branching growth in each condition can be found in the Supporting Information.

This effect of pH value can be straightforwardly understood by considering the pH-dependence of the $Cu^+$ ion's solubility. Thus, the increase in solubility of $Cu^+$ ions at lower pH values allows these ions to remain in solution [Eq. (2)] until they find a thermodynamically favorable place to attach, which results in the formation of a smoother surface with a low surface energy. Under these conditions, even if $Cu^+$ ions are initially attached to a thermodynamically unfavorable place (such as formation of branches), they can easily redissolve and reprecipitate to achieve a thermodynamically more favorable shape (for example a faceted shape with flat surfaces). However, at higher pH values, where the solubility of $Cu^+$ ions is extremely limited, $Cu^+$ ions rapidly precipitate out of solution as soon as they are generated electrochemically, which means that they will crystallize where they are produced even if this results in shapes that are not thermodynamically favorable.

This experiment clearly shows that pH value has a significant effect on the degree of branching and that decreasing the pH value promotes faceting growth. It also demonstrates the importance of maintaining a constant pH value to identify the true effect of the potential on branching growth.

We next performed an experiment to study the effect of the applied potential on branching growth at a fixed solution pH value of 4.7. Figure 3 a,b shows that low overpotential branching still exists even when the effect of pH changes during deposition are removed: almost faceted crystals are formed at 0.05 V and the degree of branching increases as the deposition potential becomes more positive (0.09 V). An additional interesting discovery from this experiment is the presence of another branching growth pattern that appears at deposition potentials more negative than 0.05 V (Figure 3 c). This branching growth fits well with the typical characteristics of the diffusion-limited branching in that it occurs at a higher overpotential than required to stabilize faceted crystals. A more pronounced diffusion-limited branching pattern can be obtained when the deposition rate is further increased by elevating the deposition temperature from 60 °C to 70 °C, which creates more severe depletion layers (Figure 3 d). The branching pattern in this region looks more complicated (for example with multiple side branching) and dendritic than the branching patterns stabilized at lower-potential regions, which have a more tailored shape with a symmetric polyhedral framework.

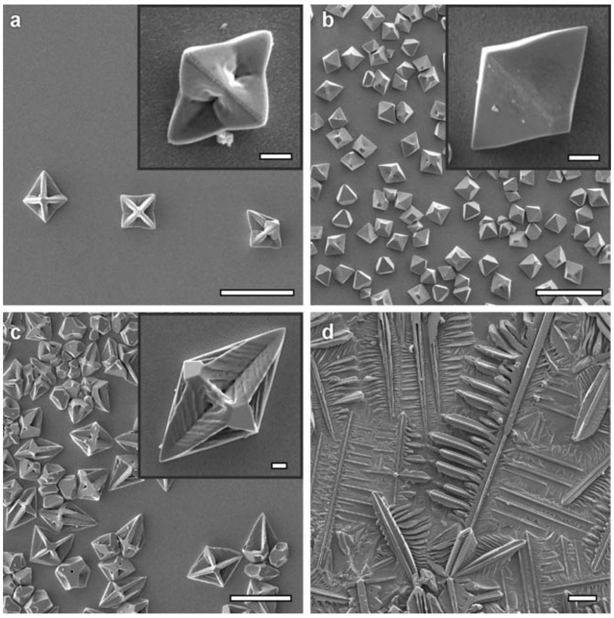

***Figure 3.*** SEM images of $Cu_2O$ crystals grown at a) $E = 0.09$ V, b) $E = 0.05$ V, and c) $E = 0.01$ V at 60 °C for 10 min in an acetate buffer solution containing 0.02 M copper acetate at pH 4.7 (the insets show higher magnification images). d) The more severe pattern of diffusion-limited branching obtained by increasing the temperature to 70 °C while using the same conditions as in (c) (scale bar: 10 μm; scale bar in insets: 1 μm).

We did not observe this diffusion-limited branching of $Cu_2O$ in our previous studies using unbuffered media because increasing the potential/current necessary to create dendritic $Cu_2O$ results in the deposition of Cu metal instead. Even when the initial applied potential was chosen to produce pure $Cu_2O$, the pH drop that accompanies fast production of $Cu_2O$ triggered the deposition of Cu metal during $Cu_2O$ deposition (the formation of Cu is more feasible at lower pH value).[11] Therefore, performing the reaction in a buffered medium broadens the deposition-potential window in which pure $Cu_2O$ can deposit with faster deposition rates, thus making the dendritic growth of pure $Cu_2O$ possible.

The fact that two different branching regions emerge at deposition potentials above and below the potential region where faceting growth occurs unambiguously confirms that the branching growth at low overpotential is truly a new phenomenon that is independent from diffusion-limited branching. Herein we propose a new branching mechanism, namely overpotential-limited branching, that can explain the origin of branching growth in low overpotential regions. This mechanism is based on the generation of an overpotential gradient across a crystal that allows the tips of crystals to possess a higher overpotential than the centers of the facets. To explain this mechanism we must first explain the relationship between the reduction potential of $Cu^{2+}$ ions and their concentration.

The standard reduction potential of $Cu^{2+}$ to $Cu^+$ ions is given in Equation (2). However, under nonstandard conditions, the reduction potential of $Cu^{2+}$ to $Cu^+$ ions is a function of the concentration of these ions, as shown in the Nernst equation [Eq. (4)].

$$E = E^\circ - 0.05916\,\lg([\mathrm{Cu}^+]/[\mathrm{Cu}^{2+}])\ \text{[at 298.15 K]} \qquad (4)$$

The concentration of $Cu^+$ ions in solution can be assumed to be constant and equal to the maximum solubility of $Cu^+$ ions at a given pH value once $Cu_2O$ starts to precipitate as a result of the supersaturation of $Cu^+$ ions [Eq. (3)]. At this point the reduction potential ($E_{\text{red}}$) depends mainly on the concentration of $Cu^{2+}$ ions. The relationship between $Cu^{2+}$ concentration and the $Cu^{2+}/Cu^+$ reduction potential can also be demonstrated experimentally by linear sweep voltammetry (LSV) performed with electrolytes containing various $Cu^{2+}$ concentrations (0.005, 0.01, and 0.02 M). Figure 4 shows that the onset potential for $Cu^{2+}$ reduction shifts gradually to more negative potentials as the concentration of $Cu^{2+}$ ions decreases, which means that the reduction of $Cu^{2+}$ ions is more difficult when fewer $Cu^{2+}$ ions are present. The arrows in Figure 4 indicate the reduction potentials calculated with the Nernst equation. These values (0.15, 0.17, and 0.19 V for a $Cu^{2+}$ ion concentration of 0.005, 0.01, and 0.02 M, respectively) show a good agreement with the onset potentials for $Cu^{2+}$ reduction observed experimentally by LSV.

This result implies that even if an identical external potential is applied, a working electrode immersed in a less-concentrated solution experiences less overpotential than one in a more-concentrated solution [Eq. (1)]. For example, when an external bias of 0.15 V is applied, the overpotential experienced by working electrodes immersed in solutions

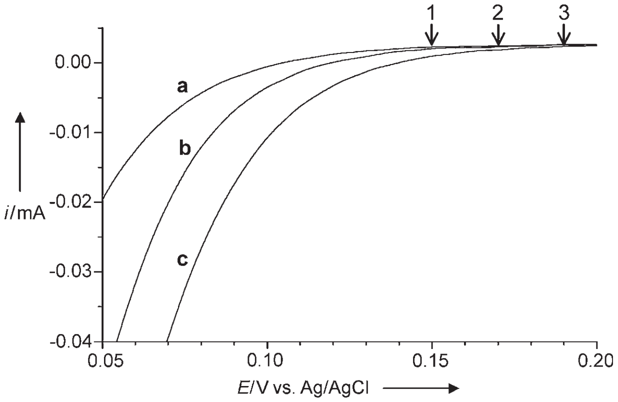

*Figure 4.* Linear sweep voltammetry carried out in an acetate buffer solution (pH 4.7) containing a $Cu^{2+}$ ion concentration of: a) 0.005 M, b) 0.01 M, and c) 0.02 M. The potential was scanned from 0.25 to 0.05 V at a scan rate of 10 $mV\,s^{-1}$ at 25 °C. The arrows indicate the reduction potentials of $Cu^{2+}$ ions calculated for each concentration using the Nernst equation.

with a $Cu^{2+}$ ion concentration of 0.02 and 0.01 M would be 0.04 and 0.02 V, respectively, both of which would result in the deposition of $Cu_2O$. However, a working electrode immersed in a solution with a $Cu^{2+}$ ion concentration of 0.005 M would not be able to reduce $Cu^{2+}$ ions because of the lack of overpotential.

These results also suggest that if a concentration gradient is formed around a growing crystal during deposition, this will result in a reduction potential gradient, and therefore an overpotential gradient, across the crystal (the central part will experience a lower overpotential than the corners that protrude into more concentrated regions). Therefore, if a deposition potential is chosen such that the crystals have barely enough overpotential to reduce $Cu^{2+}$ ions based on the bulk $Cu^{2+}$ concentration, the central part will stop growing when a certain level of concentration gradient forms, which results in branching growth (Figure 5 a). For branching that originates from an overpotential limitation, the degree of branching would decrease when the deposition potential

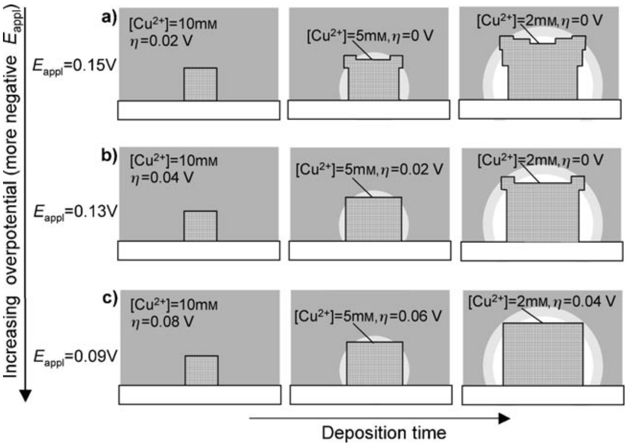

*Figure 5.* Evolution of overpotential-limited branching in a solution with a bulk $Cu^{2+}$ ion concentration of 10 mM. The overpotentials ($\eta$) given were calculated using Equation (4) with $T = 298.15$ K.

becomes more negative as the region that has enough overpotential to grow can expand toward the center of the facet. In other words, initiating overpotential-limited branching under a more negative applied potential would be more difficult as it requires a more significant decrease in concentration near the center of the crystal (Figure 5 b).

As the applied potential keeps shifting to more-negative values it eventually reaches a point where even the core part has enough overpotential to produce $Cu_2O$ regardless of the presence of a concentration gradient. In this case, faceted crystals can be formed even if the corners still have a higher overpotential than the core (Figure 5 c) as the shape of $Cu_2O$ crystals depends not only on the amount of $Cu^+$ ions generated but also on how easily they can attach themselves to the surface of $Cu_2O$ (in other words, the sticking coefficient).[14] Although the tips can produce more $Cu^+$ ions, the regions between the tips possess more rough and reactive surfaces than the smoother tips. As a result, $Cu^+$ ions can attach more easily in the regions between branches. This uneven distribution of sticking coefficients over a crystal's surface can compensate for the uneven reduction rates of $Cu^+$ ions and result in faceting growth with flat surfaces even in the presence of a concentration gradient.[14–16]

If the applied potential becomes more negative than that required to form perfectly faceted crystals, this results in an even higher reduction rate which will completely deplete $Cu^{2+}$ ions near the crystal. In this case, the crystal shape will depend entirely on diffusion and its effect cannot be fully compensated by the effect of an uneven sticking coefficient, which results in diffusion-limited dendritic branching.[14,17]

In light of the proposed mechanism, we expect that both the overpotential-limited and diffusion-limited branching of $Cu_2O$ can also be stabilized without changing the applied potential simply by varying the concentration of $Cu^{2+}$ ions, as this can increase or decrease the overpotential. Figure 3 a shows almost faceted crystals obtained from a solution with a $Cu^{2+}$ ion concentration of 0.02 M at an applied voltage of 0.05 V. Figure 6 shows the overpotential-limited and diffusion-limited branching obtained from solutions with $Cu^{2+}$ ion concentrations of 0.01 M and 0.04 M at the same applied potential. The overpotential applied to the crystal is diminished in the 0.01 M solution owing to the more-negative reduction potential created by the lower concentration of $Cu^{2+}$ ions, which results in overpotential-limited branching. In the 0.04 M solution, however, the increase in $Cu^{2+}$ ion concentration makes the reduction potential more positive, which increases the overpotential and results in diffusion-limited branching.

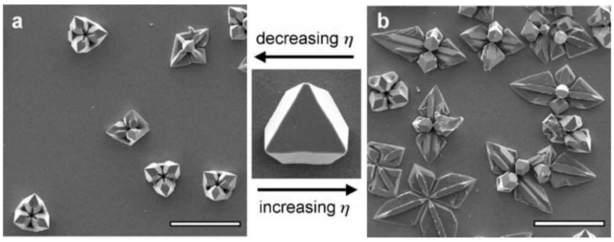

**Figure 6.** SEM images of $Cu_2O$ crystals grown at $E = 0.05$ V from an acetate buffer solution (pH 4.7) containing a $Cu^{2+}$ ion concentration of: a) 0.01 M and b) 0.04 M (scale bar: 10 μm).

In addition to the concentration gradient, another factor that may contribute to the formation of an overpotential gradient over a crystal is the shape-dependent charge distribution,[18,19] whereby charges accumulate more densely at sharp tips than on flat surfaces. This phenomenon means that the corners of crystals experience a higher applied potential than the core of the crystals, which will also result in a higher overpotential at the corners than the cores. However, we believe that the overpotential-limited branching described herein is mainly caused by the reduced potential gradient rather than by the applied potential gradient as low-potential branching cannot be initiated from an already grown faceted crystal simply by applying a potential that would normally create this type of branching. Low-potential branching occurs only when a crystal is grown without interruption as this creates a natural concentration gradient around the crystal. This finding indicates that the presence of a concentration gradient, and the resulting overpotential gradient, across a crystal is the key to triggering overpotential-limited branching.

In summary, we have investigated the effect of pH value and deposition potential on the branching growth of $Cu_2O$ crystals in buffered media. The results have enabled us to methodically study the effect of pH value and potential on branching growth and establish a plausible mechanism for the branching that occurs in the low overpotential region. The pH conditions play an important role in promoting faceted growth of $Cu_2O$ crystals by increasing the solubility of $Cu^+$ ions and altering the reversibility of the precipitation and dissolution processes. Both this new overpotential-limited branching and conventional diffusion-limited dendritic branching of $Cu_2O$ can be stabilized by keeping the pH value constant during the deposition process. The origin of the overpotential-limited branching and its dependence on the deposition potential and $Cu^{2+}$ concentration can be explained in light of the relationship between the $Cu^{2+}$ ion concentration, the reduction potential of $Cu^{2+}$, and the overpotential. This understanding offers further ways to control crystal growth in a rational manner.

## Experimental Section

$Cu_2O$ crystals were deposited cathodically at 60 °C without stirring using a conventional three-electrode setup. For the counter electrode, 100 Å of titanium followed by 500 Å of platinum were deposited on clean glass slides by sputter coating. ITO (sheet resistance: 8–12 $\Omega\,cm^{-2}$), purchased from Delta Technologies, Ltd., was used as a working electrode. The reference electrode was a double-junction Ag/AgCl electrode in 4 M KCl with a bridging solution of saturated $KNO_3$, against which all potentials reported herein were measured. All electrochemical studies were performed with a Princeton Applied Research VMP2 Multichannel Potentiostat/Galvanostat under the conditions described in the text. The plating media were aqueous solutions containing 0.005–0.04 M copper(II) acetate and an acetic acid buffer. The pH value of these solutions was adjusted to 3.8, 4.7, or 5.1 by adding the appropriate amounts of NaOAc or HOAc. The sum of acetate and acetic acid concentrations was kept constant at 0.2 M in each case.

Linear sweep voltammetry was performed at room temperature (25 °C) with 0.005–0.02 M copper(II) acetate solutions containing an acetate buffer at pH 4.7. The potential was scanned from 0.25 to 0.05 V at a scan rate of 20 mV s$^{-1}$.

The scanning electron microscope (SEM) images were obtained with a JEOL JSM-840 SEM operating at 5 kV. A thin layer of platinum (approx. 20–30 Å) was thermally evaporated onto all samples before imaging to reduce charging. X-ray diffraction patterns obtained with a Bruker D4 diffractometer (Cu$_{K\alpha}$ radiation) showed that the $Cu_2O$ crystals discussed in this study were pure $Cu_2O$.

Received: June 4, 2007
Revised: August 9, 2007

**Keywords:** copper · crystal growth · electrochemistry · electrocrystallization · topochemistry

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