Zuschriften

Zwei Wachstumsprozesse sind kristallformbestimmend: die Habitusbildung und das Auftreten von Verzweigungen. Gelingt es, diese beiden Prozesse methodisch zu beeinflussen, so wird eine Vielzahl von Architekturen gezielt zugänglich. K.-S. Choi und M. J. Siegfried zeigen dies in der Zuschrift auf den folgenden Seiten für das Beispiel elektrochemisch erzeugter Kupfer(I)-oxid-Kristalle.

DOI: 10.1002/ange.200463018

Crystal Engineering

Directing the Architecture of Cuprous Oxide Crystals during Electrochemical Growth**

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A basic crystal shape is determined by two growth processes: habit formation and branching growth.[1–7] Crystal habit is determined by the relative order of surface energies of different crystallographic planes of a crystal.[1,2] The fastest crystal growth will occur in the direction perpendicular to the face with the highest surface energy. This results in elimination or reduction of higher energy surfaces, while lower energy surfaces increase in area. Therefore, a habit can be modified when the relative order of surface energies can be altered or when crystal growth along certain directions is selectively hindered.[3] Alternatively, branching growth is created by a diffusion effect.[4,5] When a crystal grows, ions or molecules near the surface are consumed by the growing crystal and a concentric diffusion field forms around the crystal.[6,7] This makes the apexes of a polyhedral crystal, which protrude further into the region of higher concentration, grow faster than the central parts of facets, thus forming branches. The branching growth, however, generates rough and unstable surfaces between branches that have many surface dangling bonds. This can rapidly increase the growth kinetic coefficient in these regions and compensate for the diffusion effect to result in faceting growth that develops flat and smooth faces.[4,5] Therefore, preference for branching and faceting can be altered by growth conditions that amplify or minimize the diffusion effect.

The ability to tune the shapes of materials directly relates to the ability to tune their properties and stabilities because the crystal shape dictates the interfacial atomic arrangement of the material. To date, many efforts have been made to stabilize various habits or branching growth of inorganic materials.[3,8–17] However, most earlier efforts focused on stabilizing specific forms rather than providing a strategy to systematically and freely direct the crystal morphology. Recently, we reported a methodical habit modification of electrochemically deposited Cu_2O crystals by using the pH-dependence of preferential adsorption of sodium dodecyl sulfate (SDS) on the {111} faces of Cu_2O crystals.[18] We have been specifically interested in understanding and controlling the shape-guiding processes in electrodeposition because electrodeposition allows the growth of various semiconducting and metallic crystals directly from a conducting substrate with good electrical contact, which can be easily integrated into devices. Here, we elucidate synthetic parameters that can systematically control branching or faceting growth in electrodeposition. By coupling this understanding with an ability to independently control habit, we demonstrate a new level of programmability and freedom in directing the morphology of Cu_2O crystals.

For supersaturation-based crystallization, temperature and concentration are the main factors that affect the basic shape-guiding processes. For example, in nature snow crystals can grow into thousands of different forms with varying crystal habits and degrees of branching by subtle changes in temperature and humidity.[19–25] Therefore, we first investigated the effects of the temperature of deposition and the concentration of Cu^{2+} ions on the branching or faceting growth of Cu_2O crystals on an ITO (indium tin oxide) working electrode. Figure 1 shows scanning electron microscopy (SEM) images of crystals of Cu_2O grown from the medium that stabilizes an octahedral habit (see Experimental Section for detailed conditions)[18] at varying deposition temperatures (40, 50, 60, and 70 °C) by using both potentiostatic deposition (constant potential) and galvanostatic deposition (constant current density). When potentiostatic deposition is used ($E = 0.09$ V), branching is more pronounced as the temperature increases. However, under galvanostatic deposition ($I = 0.1$ mA cm^{-2}) the degree of branching diminishes as the temperature increases. Similar conflicting trends were observed for crystals of Cu_2O deposited from a range of concentrations of Cu^{2+} ions (0.005, 0.01, 0.02, and 0.04 M; images not shown). When potentiostatic deposition was used ($E = 0.09$ V), branching was favored in a more dilute solution (≤ 0.02 M), while under galvanostatic deposition ($I = 0.1$ mA cm^{-2}), more-pronounced branching was observed as the concentration increased (≥ 0.01 M). These opposite tendencies for potentio- and galvanostatic depositions indicate

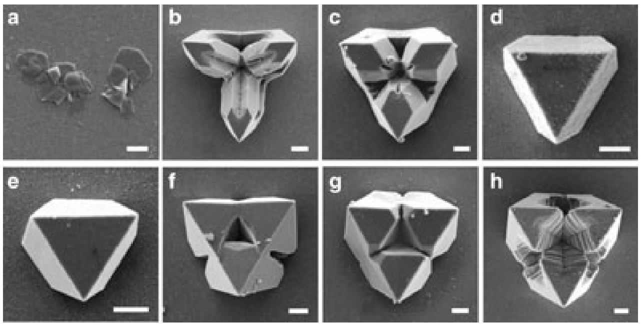

Figure 1. SEM images of octahedral Cu_2O crystals grown at varying deposition temperatures showing opposing trends of branching or faceting for potentio- and galvanostatic depositions. Potentiostatic depositions ($E = 0.09$ V) at a) 40 °C (no crystalline Cu_2O can be deposited under this condition), b) 50 °C, c) 60 °C, and d) 70 °C. Galvanostatic depositions ($I = 0.1$ mA cm^{-2}) at e) 40 °C, f) 50 °C, g) 60 °C, and h) 70 °C (scale bar = 1 μm). See Supporting Information for low-magnification SEM images that show the uniformity of crystal morphology over the electrodes.

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[**] This work was supported by the Purdue Research Foundation and 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.

that temperature and concentration are not the primary factors that exert homogeneous effects on branching in electrocrystallization. As the deposition temperature and the concentration of Cu^{2+} ions affect the deposition potential and current in a systematic manner, the changes in deposition potential and current caused by the variation of the temperature and concentration of Cu^{2+} ions needed to be examined in conjunction with the degree of branching.

Figure 2 shows the deposition potential and current used to deposit each crystal shown in Figure 1. In this plot, the effect of temperature on the potentials for galvanostatic deposition and the currents for potentiostatic deposition is clearly illustrated. Generally speaking, an increase in the temperature improves the reaction kinetics and results in an increase in reaction rates, which in electrodeposition translates into an increase in deposition current. Therefore, when potentiostatic deposition is used, an increase in temperature causes an increase in deposition current (solid line in Figure 2). Accordingly, when galvanostatic deposition is used, an increase in temperature causes a decrease in the deposition potential; with a faster deposition rate, less potential (equivalent to a more positive potential for cathodic depositions) is required to keep the same level of deposition current (dashed line in Figure 2).

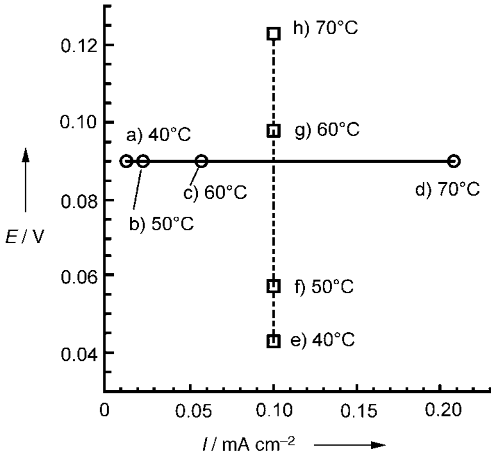

Figure 2. Plot of the deposition potential versus the current used to deposit each crystal shown in Figure 1. The effects of temperature on the deposition potential for galvanostatic deposition (-----) and the current for potentiostatic deposition (——) are clearly shown.

This understanding revealed that it was not the temperature but the deposition potential and current varied by the temperature that were directly responsible for the systematic change in the degree of branching. The most-significant branching is produced in regions of low potentials or currents (Figure 2b,h), below which no crystalline cuprous oxide can be deposited. As the overpotential or current increases (to increase the overpotential for cathodic depositions is equivalent to shifting the deposition potential toward more-negative values), the degree of branching decreases by a more-pronounced filling-in process to seal the gaps between the branches (Figure 2c,f,g). When the potential and current values reach $I = 0.2\,\mathrm{mA\,cm^{-2}}$ and $V = 0.05$ V (Figure 2d,e), crystals grow as perfectly faceted polyhedra with no sign of branching. An identical trend was observed for the experiments with varying concentrations of Cu^{2+}; an increase in Cu^{2+} concentration causes an increase in deposition current for the potentiostatic deposition while causing a decrease in the deposition potential for the galvanostatic deposition. This observation again confirms that it is the changes in potential and current caused by the variation of concentration of Cu^{2+} that affect the degree of branching in a consistent manner.

On the basis of this realization, we attempted to control the preferences for branching or faceting solely by manipulating the deposition potential and current. Figure 3 shows branched crystals obtained under constant temperature (60 °C) and concentration of Cu^{2+} (0.02 M) by applying deposition conditions that were identified from Figure 2 to induce branching growth ($0.10\,\mathrm{mA\,cm^{-2}} \leq I \leq 0.12\,\mathrm{mA\,cm^{-2}}$ and $0.08\,\mathrm{V} \leq E \leq 0.12\,\mathrm{V}$). Various stages of branching and filling-in processes were captured by finely tuning the conditions, modes (i.e. galvano- or potentiostatic), and times of deposition. All the deposition conditions we have investigated and their effect on branching and faceting are summarized in Figure 4, which composes a well-defined potential–current (I vs. V) diagram for faceting and branching growth. The degree of branching in the branching region diminishes gradually as the potential and current move toward the border of the faceting region.

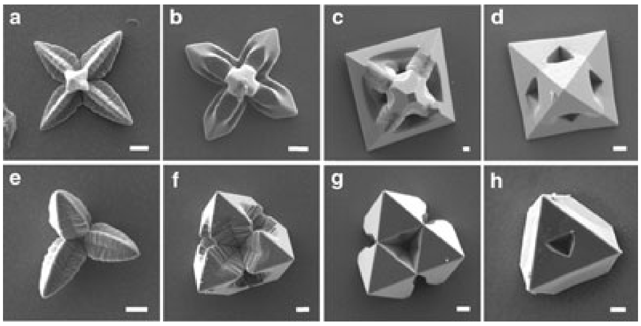

Figure 3. SEM images of deposited octahedral Cu$_2$O crystals that display systematically varying degrees of branching with (100) planes parallel to the substrate (a–d) and with (111) planes parallel to the substrate (e–h; scale bar = 1 μm). These crystals were obtained at a constant temperature (60 °C) and concentration of Cu^{2+} (0.02 M) and by applying deposition conditions of $0.10\,\mathrm{mA\,cm^{-2}} \leq I \leq 0.12\,\mathrm{mA\,cm^{-2}}$ and $0.08\,\mathrm{V} \leq E \leq 0.12$ V.

This tendency for branching and faceting is quite the opposite of what one would normally expect for electrodeposition in which only the concentration of the species to be reduced creates a diffusion-limited condition. For example, dendrite or branching growth of metals will most likely occur at a high potential or deposition rate owing to a rapid depletion of M^{n+} ions near the growing crystals ($\mathrm{M}^{n+} + n\mathrm{e}^- \leftrightarrow \mathrm{M}^0$). However, deposition of Cu$_2$O is quite unique in that it involves two distinctive processes for crystallization: reduction of Cu^{2+} ions ($\mathrm{Cu}^{2+} + \mathrm{e}^- \leftrightarrow \mathrm{Cu}^+$, $E^0 = 0.153$ V) and precipitation of Cu$^+$ ions ($2\,\mathrm{Cu}^+ + \mathrm{H_2O} \leftrightarrow \mathrm{Cu_2O} + 2\,\mathrm{H}^+$, $\log(\mathrm{Cu}^+) = -0.84 - \mathrm{pH}$; (Cu^+) = activity of Cu$^+$ ion).[26] Therefore, changes in concentrations of Cu$^+$

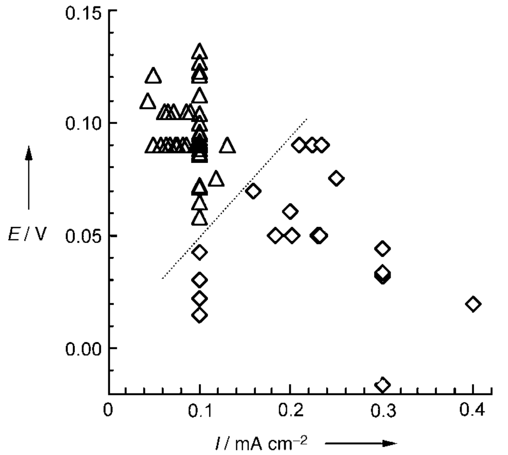

Figure 4. A deposition potential–current diagram summarizing the effect of electrochemical conditions on branching (△) and faceting (◇) growth. The electrochemical conditions plotted here were obtained either by directly adjusting the potential or current or by changing them indirectly through variation of temperature and concentrations of Cu^{2+} ion. The medium that stabilizes an octahedral habit was exclusively used to collect the data shown here.

and H^+ as well as Cu^{2+} and the site of reduction or deposition need to be studied in conjunction with changes in deposition potential and current to understand branching or faceting growth of Cu_2O crystals. More experiments are currently being carried out to derive a precise mechanism for branching in regions of low potential or current.

All the crystals discussed up to this point display the same octahedral habit as the degree of branching was independently controlled from habit. By combining the deposition conditions identified in Figure 4 with chemical conditions to regulate crystal habit (see Experimental Section for detailed compositions of media),[18] simultaneous manipulation of habit and branching become possible. Figure 5 a–c show the results of branching control performed in a medium that stabilizes the {100} faces of Cu_2O crystals and, therefore, a cubic habit. Conversely, Figure 5 d shows branched crystals obtained by using a medium that precisely tunes the growth ratio, R (the growth rate along the ⟨100⟩ direction/growth rate along the ⟨111⟩ direction), to obtain a truncated octahedral habit as the final morphology.[18,27] To the best of our knowledge, this level of synthetic freedom and programmability in controlling both the degree of branching and habit has not previously been demonstrated for any semiconducting system.

More complexity can be introduced to the architecture of Cu_2O crystals when different media are used for the branching and filling-in processes. This strategy mimics the growth of snow crystals in nature that leads to thousands of unique crystal morphologies. When developing snow crystals fall from the sky, they pass through many atmospheric regions of varying humidity and temperature. As each region has different preferences for habit and branching, the journey of snow crystals creates complexity in their growth history and, therefore, complexity in their final morphologies.[19,25] Electrodeposition is ideal for creating an equivalent complex growth history because the crystal growth can be paused at any moment and resumed in a new medium. Figure 6 a–c show how branched octahedral crystals transform when the filling-in process is continued in a new medium that stabilizes {100} faces. Since the initial branches are positioned to form an octahedral skeleton, a quick transition to a single cube is extremely difficult. Therefore, the tips of the branches that would otherwise become the apexes of an octahedron rapidly develop {100} faces and each branch forms its own cube and expose only {100} faces at the interfaces. Then these individual cubes eventually fuse together to form one seamless cube to attain a minimum surface energy. Figure 6 d–f show the opposite case; branches were built in a medium that stabilizes cubic shapes, and the filling-in process was continued in a medium to grow octahedral crystals. Again various novel and exquisite surface patterns are generated when the crystals are forced to develop {111} faces by using branches that point to the apexes of a cube to eventually transform into a simple octahedral crystal. This observation implies endless possibilities of designing new crystal mor-

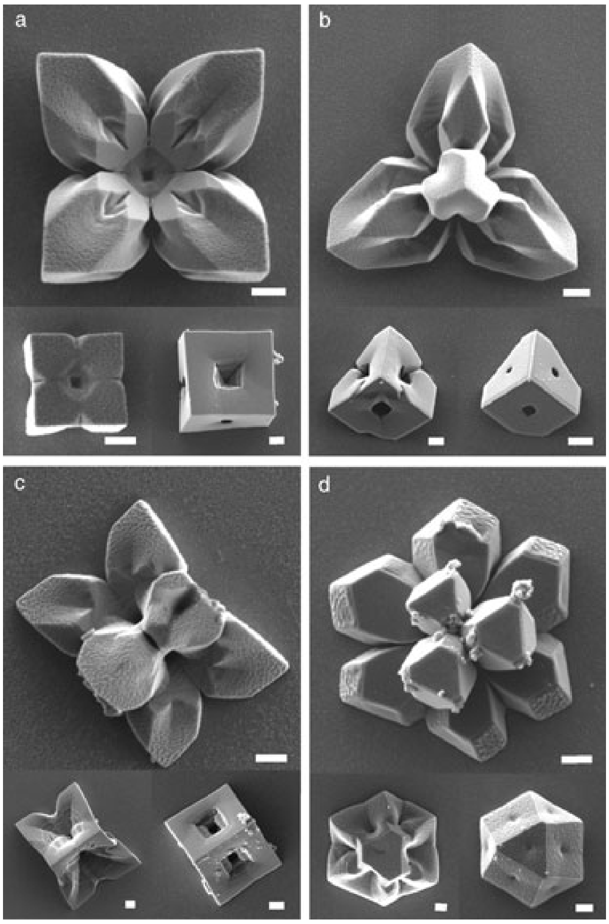

Figure 5. SEM images of branched Cu_2O crystals with varying crystal habit. Cubic crystals grown with a) (100) planes, b) (111) planes, and c) (110) planes parallel to the substrate. d) Cuboctahedral crystals with (111) planes parallel to the substrate. Insets for each image show crystals of the same habit and orientation with gradually increasing filling-in processes that are controlled by the deposition conditions identified in Figure 4 (scale bar = 1 µm). See Experimental Section for detailed compositions of the media.

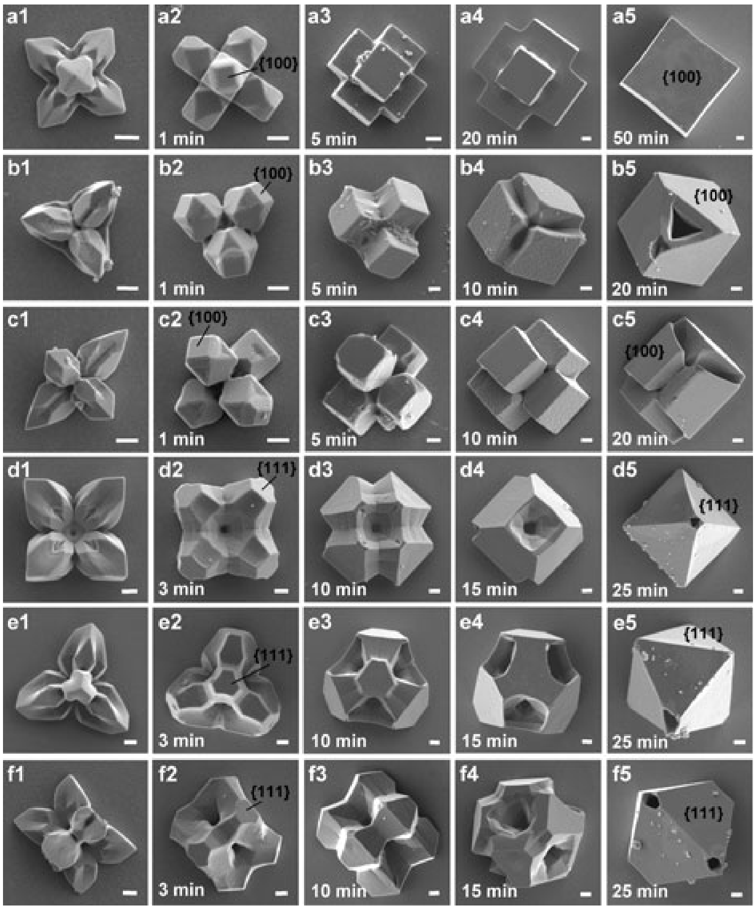

Figure 6. SEM images of novel Cu_2O crystal morphologies constructed through the addition of complex growth histories. a–c) Branched crystals were first deposited in a medium that stabilizes an octahedral habit for 3 minutes (column 1), and the filling-in process was resumed in a new medium that stabilizes a cubic habit for the time depicted in each figure (columns 2–5). d–f) Branched crystals were first deposited in a medium that stabilizes a cubic habit for 12 minutes (column 1), and the filling-in process was resumed in a new medium that stabilizes an octahedral habit for the time depicted in each figure (columns 2–5). Crystals are shown with (100) planes (a, d), (111) planes (b, e), and (110) planes (c, f) parallel to the substrate (scale bar = 1 μm). All the crystals shown here were grown under constant temperature (60 °C) and concentration of Cu^{2+} ion (0.02 M). Galvanostatic depositions of $I = 0.1$ mA cm^{-2} and 0.3 mA cm^{-2} were used for the initial branching and resumed filling processes, respectively.

phologies by combining multiple growth media and growth conditions.

In summary, we have demonstrated a methodical and simultaneous tuning of the habit and the degree of branching of Cu_2O crystals by elucidating and manipulating key conditions that control shape-guiding processes in electrocrystallization. By combining this understanding with the unique capability of electrodeposition to pause and resume crystallization at any stage, it was possible to assemble numerous unprecedented crystal architectures by rationally designing the growth conditions and growth history. The programmability and synthetic freedom demonstrated in this work will not only provide valuable information for the study of electrochemical crystal growth mechanisms[23,28,29] but also build a foundation for the study of directed crystal growth of various semiconducting crystals on a conducting substrate. These systems will be useful for a broad range of applications such as sensors, optoelectronics, and catalysis.

Experimental Section

Cu_2O crystals were prepared by cathodic deposition from aqueous solutions of 0.005–0.04 M $Cu(NO_3)_2$ ($2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+$) by 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 = 15 ± 5 Ω cm^{-2}), purchased from Delta Techologies, Limited, was used as a working electrode. The reference electrode was Ag/AgCl in a solution of KCl (4 M), against which all potentials reported here were measured. The electrolyte used to stabilize the octahedral shape (shown in Figures 1 and 3) contains 5 wt % sodium dodecyl sulfate (SDS) as a habit modifier (pH 4.9 before the addition of SDS) to stabilize {111} faces of Cu_2O crystals. The medium used to stabilize a cubic habit (Figure 5 a–c) was composed of a solution of $Cu(NO_3)_2$ (0.02 M) without SDS (pH 4.9), and the medium used to grow truncated octahedral habit (Figure 5 d) was composed of a solution of $Cu(NO_3)_2$ (0.02 M) and 5 wt % SDS (the pH was adjusted to 4.3 before the addition of SDS).[18] The range of deposition conditions to promote faceting growth in a solution of Cu^{2+} (0.02 M) is $E \leq 0.07$ V and $I \geq 0.15$ mA cm^{-2} at 60 °C. Branching growth can be stabilized at $0.07\,\text{V} < E \leq 0.14\,\text{V}$ and $0.04\,\text{mA cm}^{-2} \leq I < 0.15\,\text{mA cm}^{-2}$ with more-significant branching induced at a more-positive potential and lower current. Both potential and current are required to be in these specific ranges to stabilize branching growth. When $E > 0.14$ V and $I < 0.04$ mA cm^{-2}, no crystalline Cu_2O can be deposited. The compositional purity of the Cu_2O crystals shown in this study was confirmed by powder X-ray diffraction, details of which are provided in the Supporting Information.

Received: December 22, 2004

Keywords: crystal growth · electrochemistry · semiconductors · solid-state structures

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