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Elucidating the Effect of Additives on the Growth and Stability of Cu_2O Surfaces via Shape Transformation of Pre-Grown Crystals

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Morphological control of crystals provides a means of tailoring the interfacial arrangement of atoms and has a vital role in enhancing the desired reactivity or stability of a material.[1] A common method to manipulate crystal habit is to employ a growth medium containing additives that can preferentially adsorb on specific crystallographic planes.[2−6] This changes the direction and rate of crystal growth and results in crystals with different final morphologies.[7,8] Preferential adsorption has been studied by carrying out the crystallization process with various additives and examining the resulting morphologies, from which the effect of additives can be deduced. However, this method cannot methodically elucidate how the relative stabilities of various crystallographic planes change upon the addition of additives. Furthermore, if several additives result in identical final morphologies, it is difficult to study their abilities to stabilize a specific plane in a comparative manner.

In this study, we introduce a simple and straightforward approach for systematically studying additives' effects on the stability and growth of various crystallographic planes of growing crystals. In our method, we pre-form crystals with well-defined shapes (e.g., cubic, octahedral) and resume their crystallization in a medium that contains the additive to be studied. This method makes it possible to study additives' interactions with specific planes (e.g., {100} of a cube and {111} of an octahedron) that already exist. By monitoring how the original shapes transform over time, the role and strength of habit modifiers can be studied in a more methodical manner. Here, we describe our approach for the electrocrystallization of Cu_2O crystals, which enabled us to determine the relative stabilities of the {100}, {111}, and {110} planes of Cu_2O in various growth media. Through this study, a scheme to create new crystal morphologies that cannot be formed via preferential adsorption alone is also devised.

The cubic Cu_2O crystals used in this study were first galvanostatically deposited (constant current deposition, $I = 0.3$ mA/cm^2) in a 0.02 M $Cu(NO_3)_2$ solution for 5 min.[9] The effect of NO_3^- ions on stabilizing {100} planes of Cu_2O has been reported previously.[10] The resulting cubic crystals are uniform in shape and size, but their orientations are random due to the polycrystalline nature of the ITO electrodes used as working electrodes (Supporting Information). Therefore, crystal images with two different orientations ({100} and {111} planes parallel to the substrate) are shown for results discussed in this study to best demonstrate the crystal morphologies.

Figure 1 shows scanning electron micrographs (SEM) of Cu_2O crystals obtained when the galvanostatic deposition ($I = 0.3$ mA/cm^2 for 5 min) was resumed with the addition of 0.17 M $NaNO_3$, Na_2SO_4, NH_4NO_3, or $(NH_4)_2SO_4$ as a habit modifier to the original plating medium. Crystals grown in the presence of $NaNO_3$ maintain the same cubic morphology, indicating that Na^+ ions do not exert any noticeable effect that can overcome the effect of NO_3^- ions stabilizing {100} planes. The crystals obtained in the presence of Na_2SO_4 developed a fraction of {111} planes at the corners of the cubes, indicating that SO_4^{2-} ions can increase the stability of {111} planes. The most interesting results were obtained from media that contain NH_4^+ ions; {110} and {111} planes develop simultaneously, resulting in a rhombicuboctahedral morphology. The appearance of {110} planes of crystals with primitive cubic structures is not common, and to the best of our knowledge, conditions that artificially stabilize {110} planes of Cu_2O crystals (space group $Pn\bar{3}m$, No. 224) have not been reported. The observed phenomena can be considered an effect of NH_4^+ ions since both NH_4NO_3 and $(NH_4)_2SO_4$ lead to an identical morphology and the {110} planes do not appear when the NH_4^+ ions are replaced with Na^+.

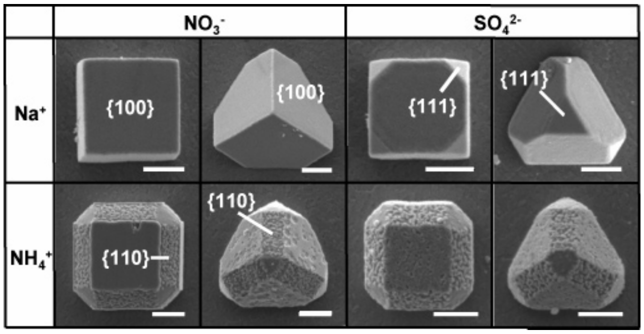

Figure 1. SEM images of Cu_2O crystals after the crystallization process of Cu_2O cubes was resumed in a 0.02 M $Cu(NO_3)_2$ solution containing 0.17 M $NaNO_3$, Na_2SO_4, NH_4NO_3, or $(NH_4)_2SO_4$ for 5 min. The anions and cations of the salts are separated into (columns and rows so that the effect of individual ions can be easily recognized. For each case, crystals viewed down on the ⟨100⟩ and ⟨111⟩ directions are shown on the left and right sides, respectively (scale bar = 1 μm).

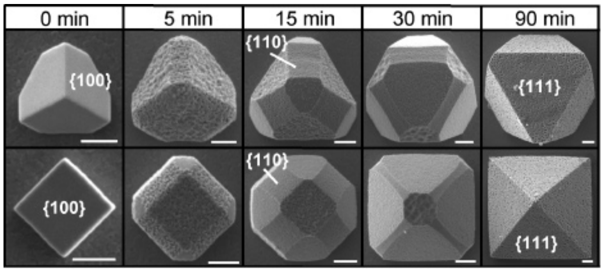

Figure 2. SEM images showing the transformation of pre-grown cubic Cu_2O crystals over time in a 0.02 M $Cu(NO_3)_2$ solution containing 0.17 M $(NH_4)_2SO_4$. Top: view down the ⟨111⟩ direction. Bottom: ⟨100⟩ direction; scale bar = 1 μm.

A time-dependent transformation of Cu_2O cubes in the presence of NH_4^+ ions provides more information regarding the effect of NH_4^+ ions on the relative stability of the {100}, {111}, and {110} planes, which is inversely proportional to the growth rate along the ⟨100⟩, ⟨111⟩, and ⟨110⟩ directions. Figure 2 shows that, while the {100} surfaces constantly decrease in area, the {110} surfaces reach a maximum area and then decrease. Concurrently, the {111} planes continually gain in area, eventually leading to an octahedral morphology. This result suggests that the most stable planes in the

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medium containing NH_4^+ ions are the {111} planes. The temporary appearance of {110} planes can be attributed to the relative stability of planes in this medium being in the order of {100} < {110} < {111}. In this case, both the {110} and {111} planes are more stable than {100} planes and initially gain in area, but eventually the crystal surface will be composed of only the most stable {111} planes. When NH_4NO_3 or $(NH_4)_2SO_4$ is present in the 0.02 M $Cu(NO_3)_2$ solution from the beginning of the crystallization process, Cu_2O crystals grow as octahedral crystals exposing only the {111} planes at the surface without any indication of forming {110} planes (Supporting Information). This experiment clearly demonstrates that the stabilization of {110} planes and the information on the relative stabilities of {100}, {110}, and {111} planes cannot be achieved without using pre-grown cubic crystals.

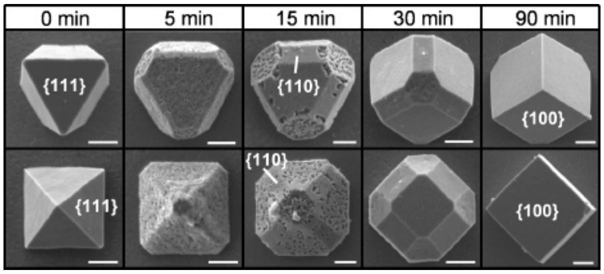

Figure 3. Transformation of pre-grown octahedral Cu_2O crystals over time in a 0.02 M copper nitrate solution containing 0.17 M SDS and 0.004 M NaCl. Top: view down the ⟨111⟩ direction. Bottom: ⟨100⟩ direction; scale bar = 1 μm.

When additives in a $Cu(NO_3)_2$ solution do not create any noticeable morphological changes in pre-grown cubic Cu_2O crystals, it is not possible to evaluate the strength of their ability to stabilize {100} planes relative to that of NO_3^- ions. In this case, a crystal morphology other than a cube can be used as a starting point to precisely determine the effect of the additives. Figure 3 demonstrates how NaCl, which does not alter the morphology of pre-grown cubes, interacts with pre-grown octahedral Cu_2O crystals. Octahedral Cu_2O crystals were first grown for 5 min in a 0.02 M $Cu(NO_3)_2$ solution containing 0.17 M sodium dodecyl sulfate (SDS), and the deposition resumed after 4 mM NaCl was added to the deposition solution. The effect of SDS stabilizing the {111} planes of Cu_2O has been previously reported.[10] Since Na^+ ions were already present in the medium (from SDS) before the addition of NaCl, any additional morphological change observed can be reasonably assigned as an effect of Cl^- ions. The concentration of NaCl used in this experiment (4 mM) is significantly lower than those of other additives discussed (0.17 M). This is necessary because we observed that Cu_2O was chemically not stable under the presence of excessive Cl^- ions and was converted to $Cu_2Cl(OH)_3$ or its hydrated form.[11]

The time-dependent transformation of octahedral crystals in Figure 3 shows that crystals initially developed both {110} and {100} planes, but only {100} planes remain in their final morphologies, leading to cubic shapes. From the final morphology, the effect of Cl^- ions can be explicitly determined; they stabilize {100} planes more strongly than NO_3^- ions (before NaCl is added, NO_3^- ions alone do not overcome the effect of SDS and octahedral shapes resulted). The temporary appearance of {110} planes again provides information regarding the relative stability of {100}, {111}, and {110} planes in this medium, which is in the order of {111} < {110} < {100}. When the crystallization process is initiated in the same solution without pre-grown octahedral crystals, information regarding {110} planes cannot be obtained because crystals adopt cubic shapes from the early stages of habit formation. This result, along with the result obtained with NH_4^+ ions, establishes that pre-forming certain crystal shapes and forcing them to grow in a medium where the initial shape becomes the most unstable morphology can be used as a general scheme to form planes with stabilities between those of the pre-existing planes and those of the final planes stabilized.

It is worth mentioning that the surface roughness observed in some images shown in Figures 2 and 3 is not due to the intrinsic nature of NH_4^+ or Cl^- ions as a habit modifier, but arises from changes in the growth mechanism (i.e., layer by layer growth to polynucleation growth on crystal surfaces).[8] When the composition of the plating medium changes, it can affect the reduction potential of Cu^{2+} ions and the deposition potential required to maintain the same current density, which alters the driving force for electrocrystallization and therefore the growth mechanism. However, the growth mechanism and surface roughness can be independently controlled from crystal habit by tuning electrochemical (deposition potential and current) and chemical (pH, ionic strength) conditions, which is not a scope of this study.

In summary, we demonstrated a new approach of using pre-grown crystals with well-defined shapes to systematically determine the role of habit modifiers and relative stabilities of Cu_2O planes in various growth media. Applying our method to study various crystal systems may enable us to classify common features of additives (e.g., charges, type of atoms) and crystallographic planes (e.g., atomic arrangement, surface termination, surface charge) that permit strong interactions between them, which would significantly improve our general understanding of preferential adsorption phenomena.

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Supporting Information Available: Representative XRD of Cu_2O crystals, SEM images of crystals grown using the same conditions in Figure 1 without using pre-grown cubes, low magnification SEM images of initial cubic and octahedral crystals depicting the random orientation of crystals, and low magnification SEM images of crystals presented in Figures 2 and 3 that show the uniformity of shape regulation obtained in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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