Time-Dependent Growth of Zinc Oxide Crystals

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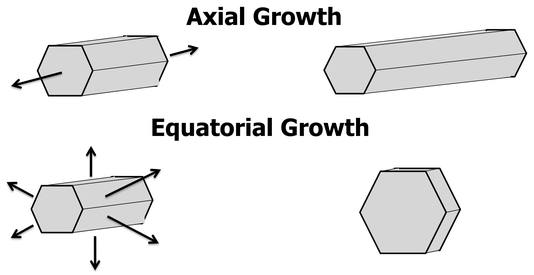
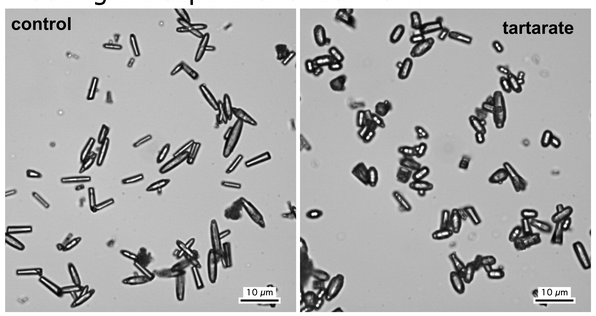
Background

ZnO crystals experience two different types of growth which control the aspect ratio (defined as length/width).



Organic ligands modify ZnO crystal shape by reducing the aspect ratio. But how?

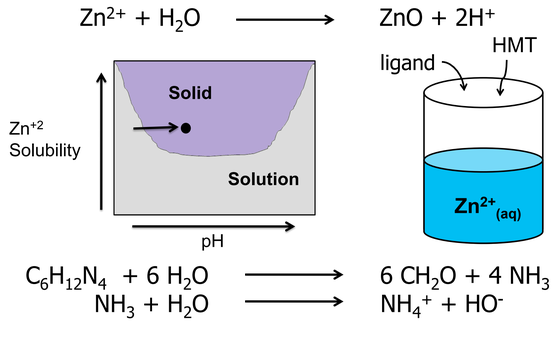


Question: Do ligands change axial growth or equatorial growth? How?

Strategy: Determine the growth rate for each crystal face without ligand (control) and with tartarate (treatment). Compare to elucidate the mechanism of shape control.

Methods

Zinc oxide crystals are grown in aqueous solution by exploiting its pH-dependent solubility. At neutral concentrations, Zn^{2+} is lesssoluble. Increasing the pH allows it to precipitate and form crystals.



$Zn^{2+} + H_2O \longrightarrow ZnO + 2H^+$

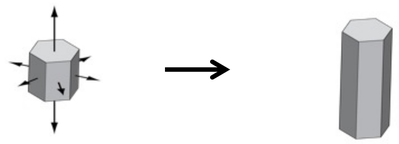
$C_6H_{12}N_4 + 6\ H_2O \longrightarrow 6\ CH_2O + 4\ NH_3$

$NH_3 + H_2O \longrightarrow NH_4^+ + HO^-$

Organic ligands are added to the growth solution to reduce the aspect ratio.

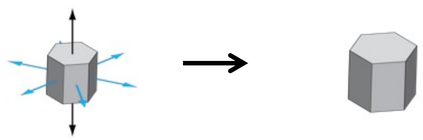
Two Mechanisms of Shape Control

Normal crystal growth leads to prismatic crystals with high aspect ratio.



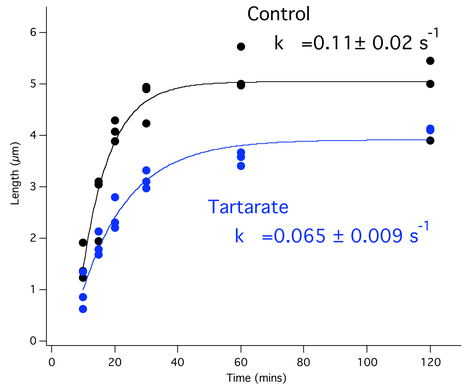
Inhibition of axial growth leads to reduced aspect ratio

Enhancement of equatorial growth leads to reduced aspect ratio.

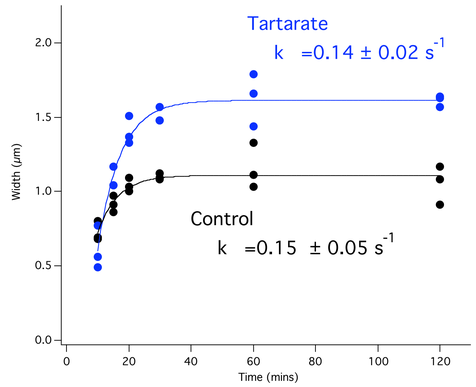


Time Dependence of Shape

Tartarate slows axial growth.



Equatorial growth is the same.



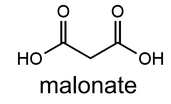
Consistent with inhibition mechanism.

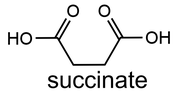
- Because the rate of equatorial growth remains the same, and the rate of axial growth decreases, the mechanism is consistent with inhibition of axial growth, not enhancement of equatorial growth.
- Assume 1st order accumulation kinetics:

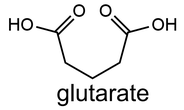
$$y(t) = y_{max}[\,1 - e^{-k(t-t0)}]$$

Which ligands inhibit axial growth?

Effect of bridge length


malonate — **no**

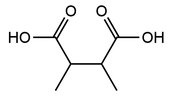

succinate — **no**

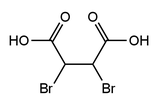

glutarate — **no**

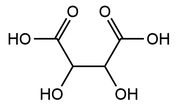
At first, bridge length appears to have no effect on shape.

But what about substitution on the ligand bridge?

Effect of substitution on succinates


strong

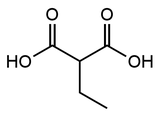

medium

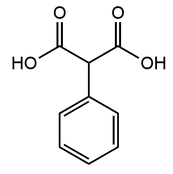

very strong

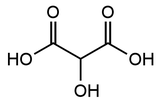
Substitution on ligand bridge enables shape control.

Does substitution affect malonates as well?

Effect of substitution on malonates


very weak


very weak


very strong

Both substitution and bridge length determine shape control.

Hydroxyl substitution is strongest.

Abstract:
The mechanism of shape control in zinc oxide crystal growth was elucidated by quantifying crystal dimensions over time. The final shape of a crystal is determined by the relative rates of axial and equatorial growth, where axial growth tends to elongate the crystal, and equatorial growth tends to widen the crystal. Bidentate carboxylate ligands, such as tartarate, reduce the aspect ratio (defined as length/width) of crystals. This effect is consistent with one of two mechanisms of shape control: inhibition of axial growth or enhancement of equatorial growth. To distinguish these possibilities, the time evolution of both crystal length and width were measured. From these data, the rate constants of axial and equatorial growth were determined in the absence and presence of tartarate. In the absence of tartarate, the rate constant for axial growth is 0.11 s^{-1}. Addition of 5-μM tartarate reduces the rate constant to 0.065 s^{-1}, a reduction of 40%. In contrast, tartarate has no significant effect on the rate constant for equatorial growth. These results support an inhibition mechanism for shape control, while ruling out an enhancement mechanism. The inhibition mechanism suggests that ligands specifically bind to the axial face and block deposition on that face. This mechanism will inform efforts to develop better photovoltaic materials.

Acknowledgments
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