



# Rusty Orzo with Lemon on the Side



## A Recipe for Citric Acid-Modified Akaganeite

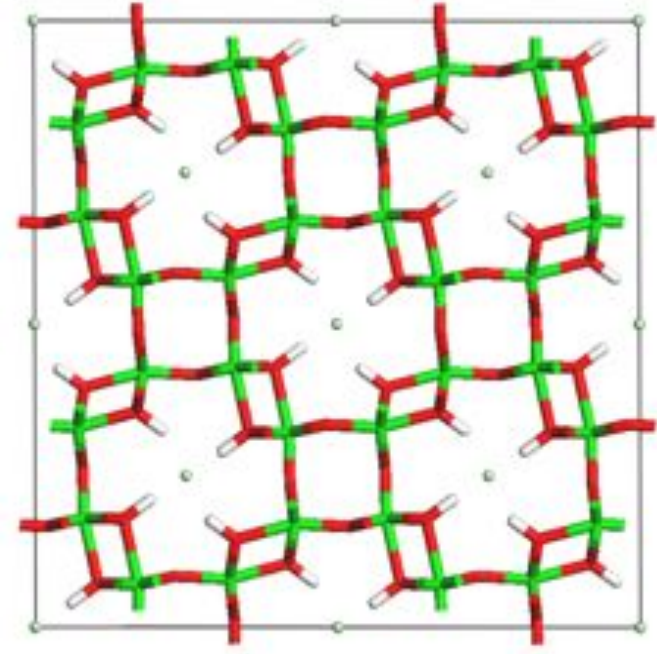
Erik D. Spoerke, Holly F. Zarick, Jill S. Wheeler, Dara Van Gough, Mark Rodriguez, and Bonnie B. McKenzie

Sandia National Laboratories, Albuquerque, NM USA

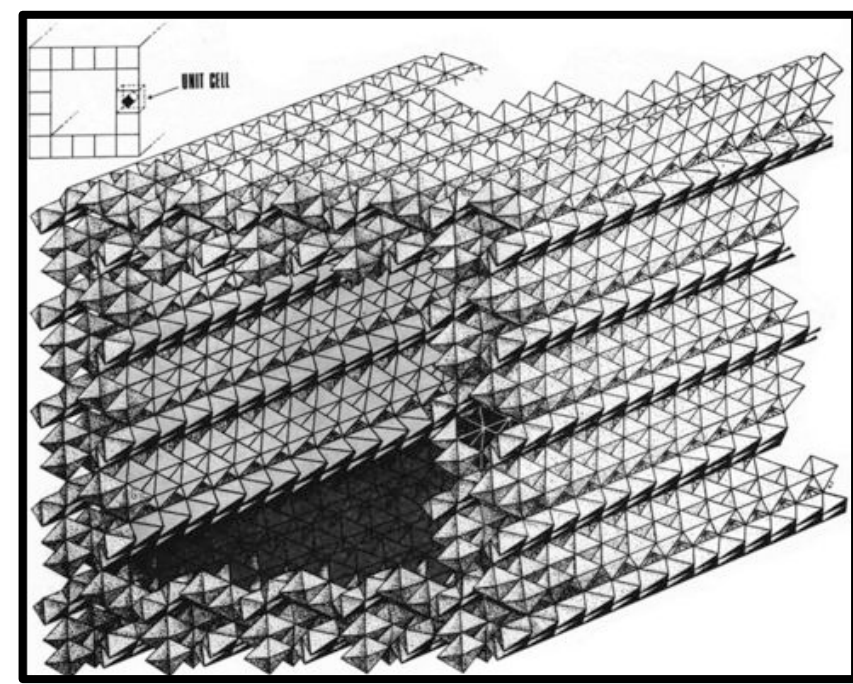
SAND2013-2793C

### Background

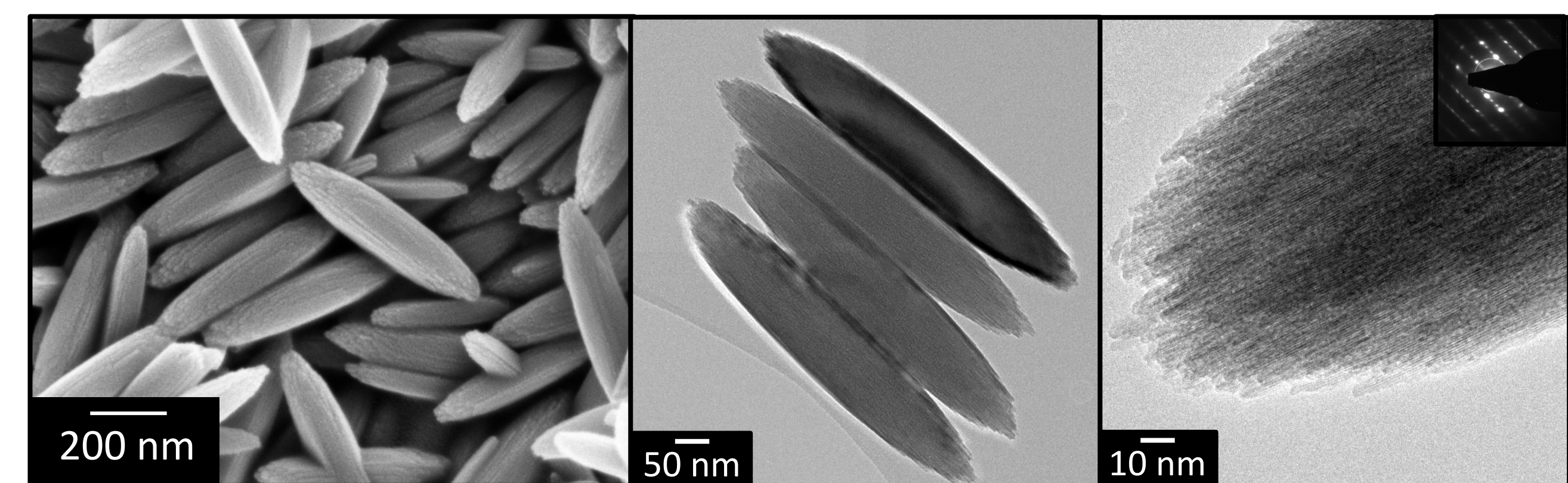
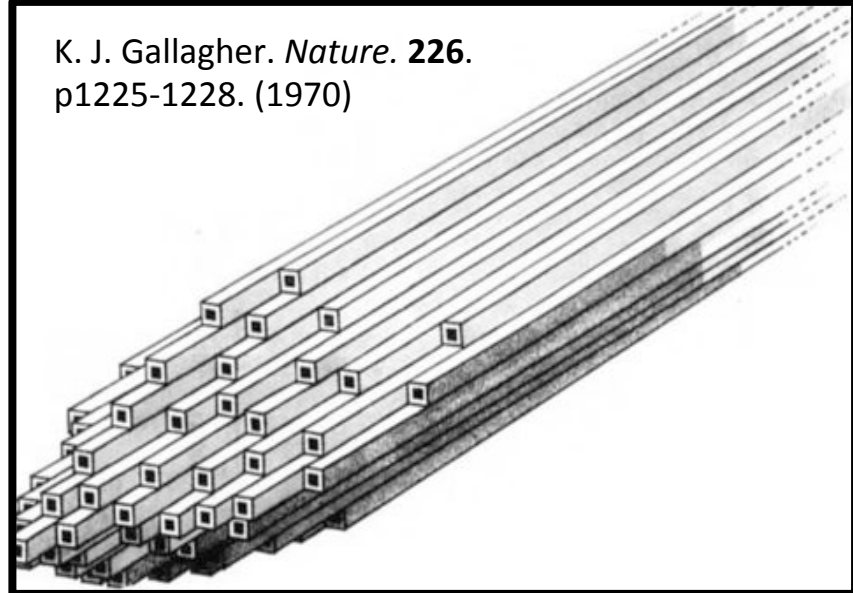
Akaganeite is a polymorph of iron oxy-hydroxide ( $\beta$ -FeOOH) with a tunneled hollandite structure.



Unit cells of these crystals assemble into unusual secondary crystalline tubules with inner pore diameters of 3-4 nm.



These crystalline nanotubules further organize into densely-packed nanoporous bundles.



To some, these nanoporous  $\beta$ -FeOOH crystal bundles resemble orzo pasta!

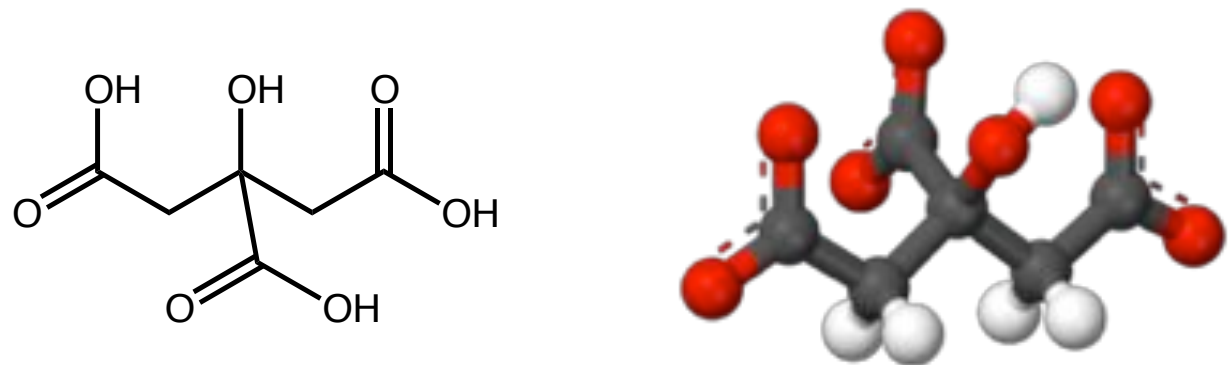
These nanoporous materials have potential applicability as catalysts, sorbents, pigments, ion-exchangers, and even electrochemical materials.

Naturally, the properties of these materials will depend on the crystal chemistry and nanoscale morphology of the  $\beta$ -FeOOH crystal aggregates.

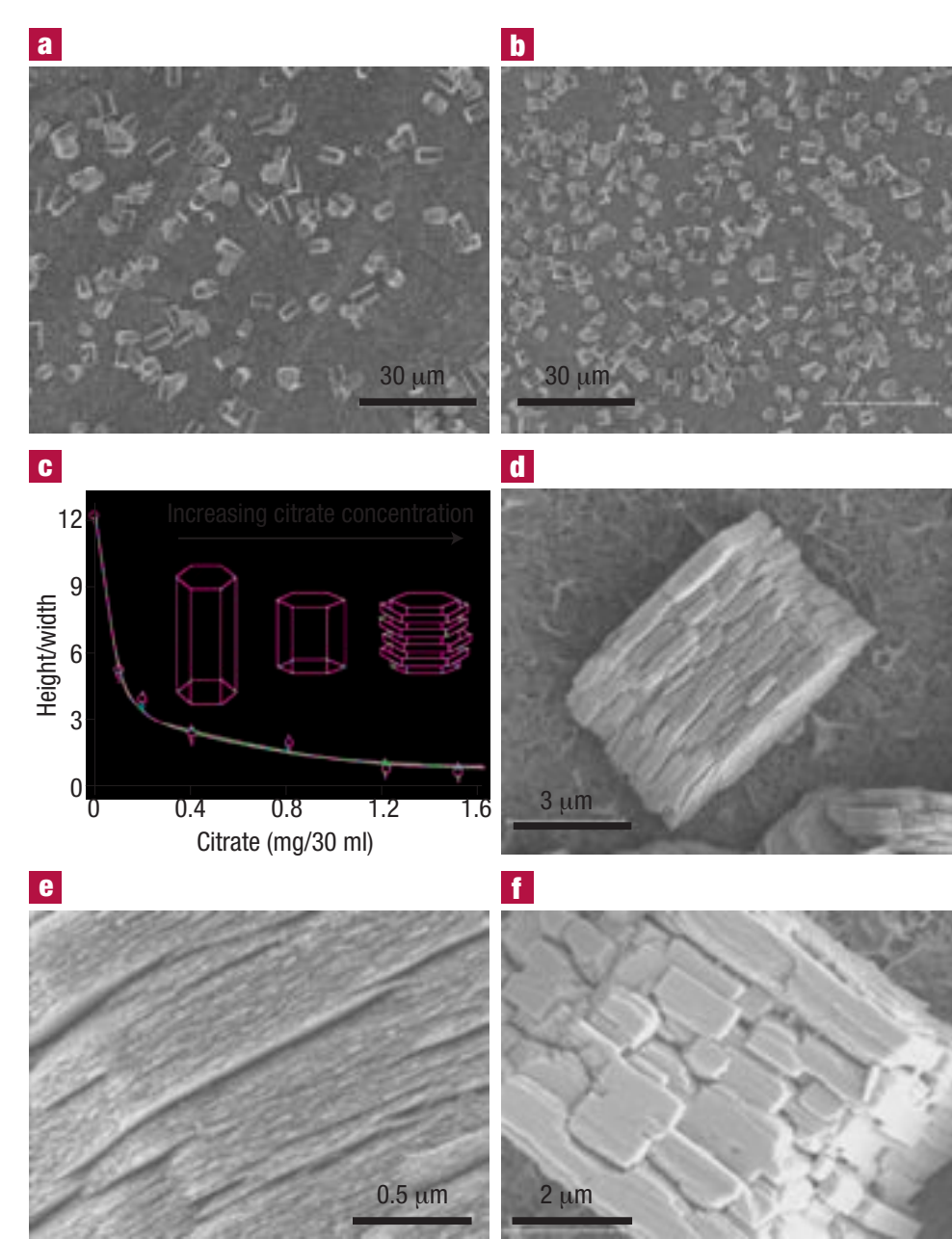
**Our objective:** to study how one might influence the crystal growth and morphology of this complex nanocrystalline material system.

### Synthetic Approach

Consider citric acid:



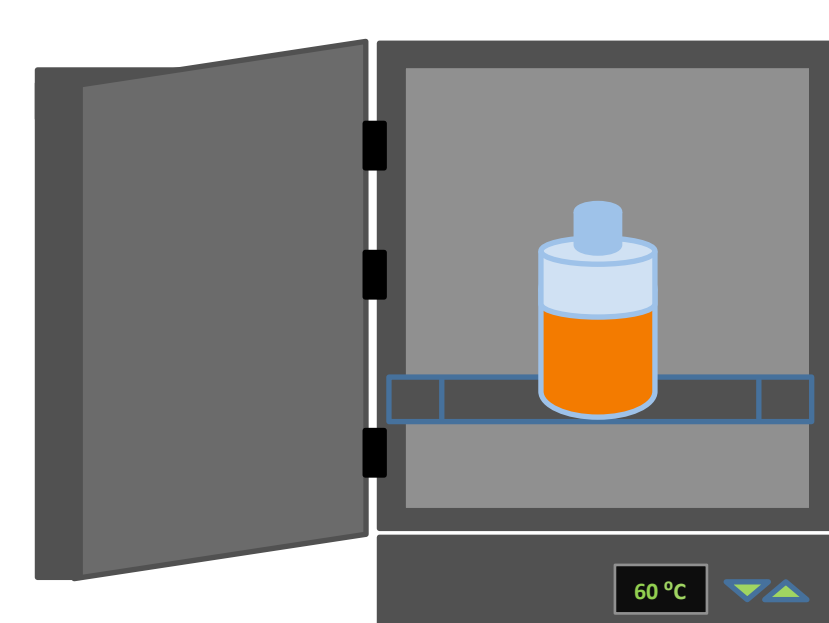
Citric acid and other citrate salts have been used to modify crystal growth in a variety of materials systems.



Z.R. Tian, et al., Nature Mater. (2003) 2, p 821.

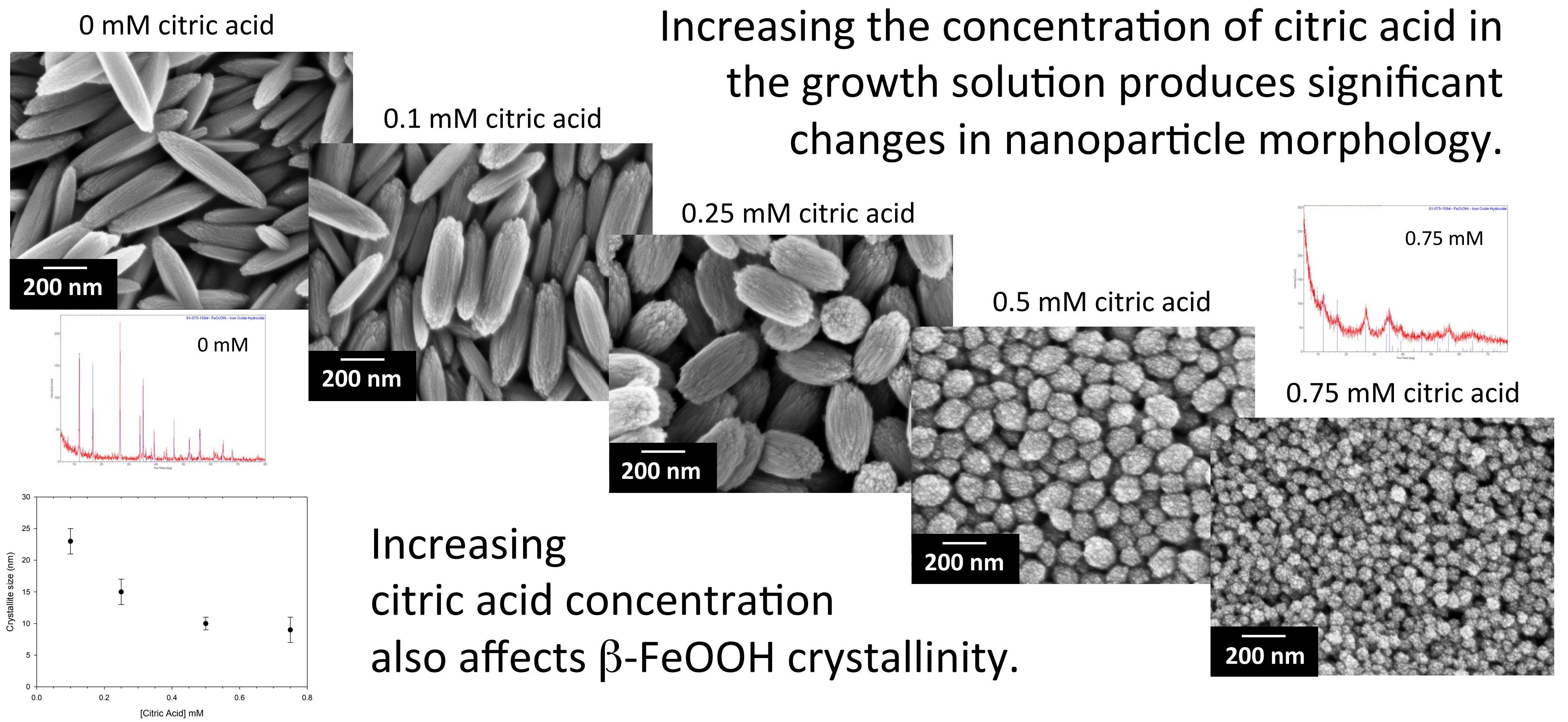
**Standard  $\beta$ -FeOOH:** 100 mM aqueous ferric chloride ( $\text{FeCl}_3$ ) incubated at 60°C overnight.

Precipitate collected and washed by centrifugation.



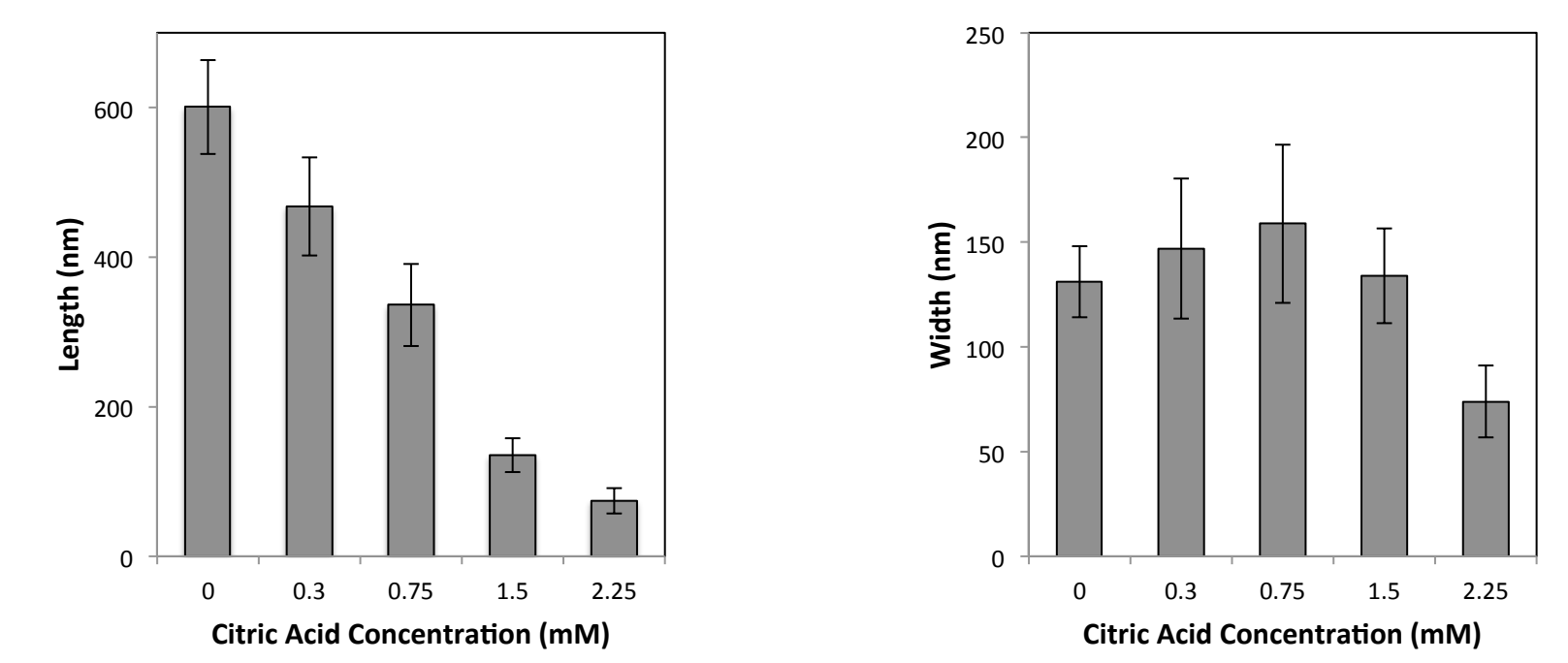
**Modified  $\beta$ -FeOOH:** citric acid (or other growth modifier) is co-dissolved with ferric chloride prior to heating.

### Crystal Growth Results



Quantifying the change in crystal size shows that increasing citric acid:

- Decreases particle length
- Increases, then decreases particle width

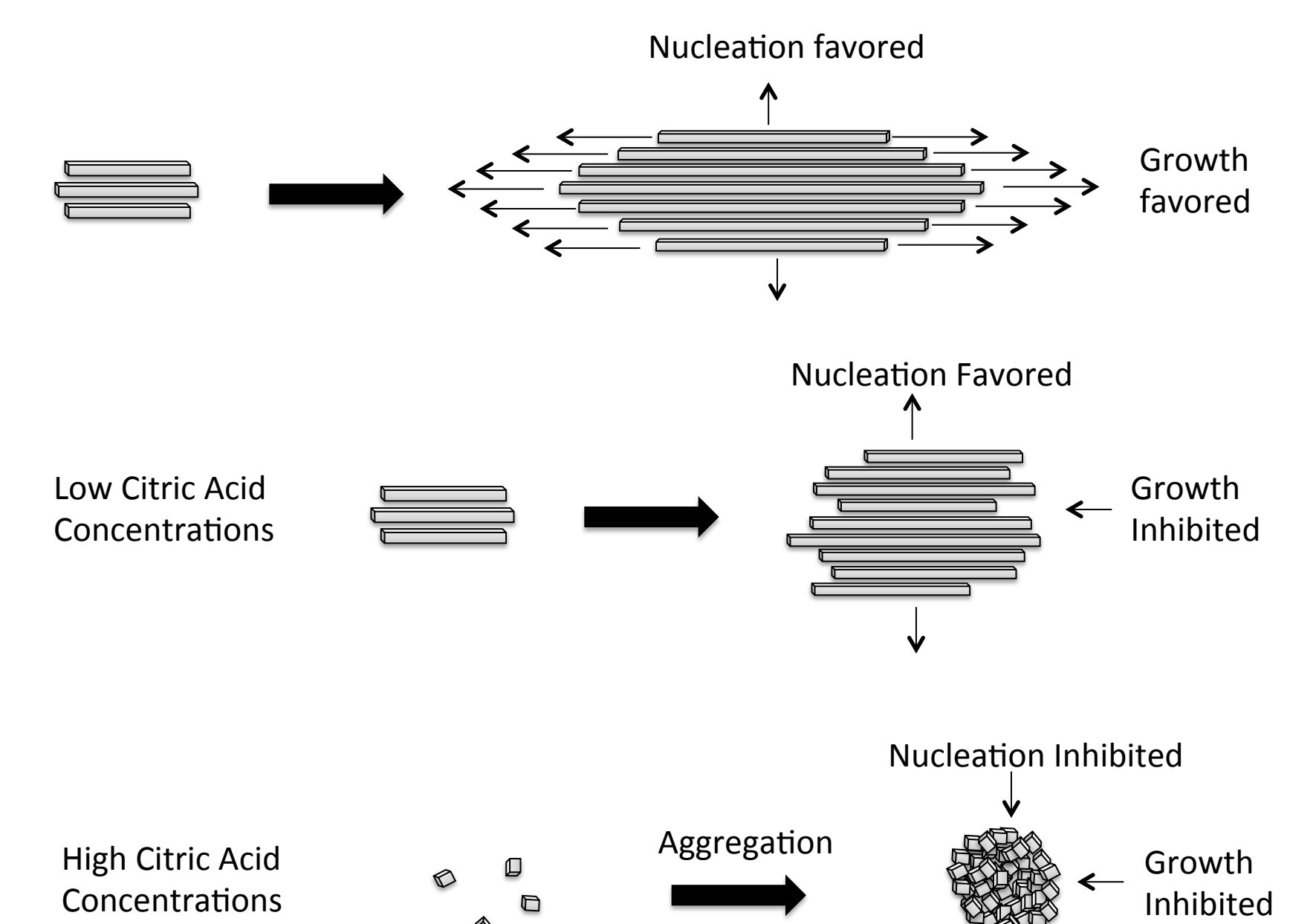


### What does that tell us about citric acid-modified crystal growth?

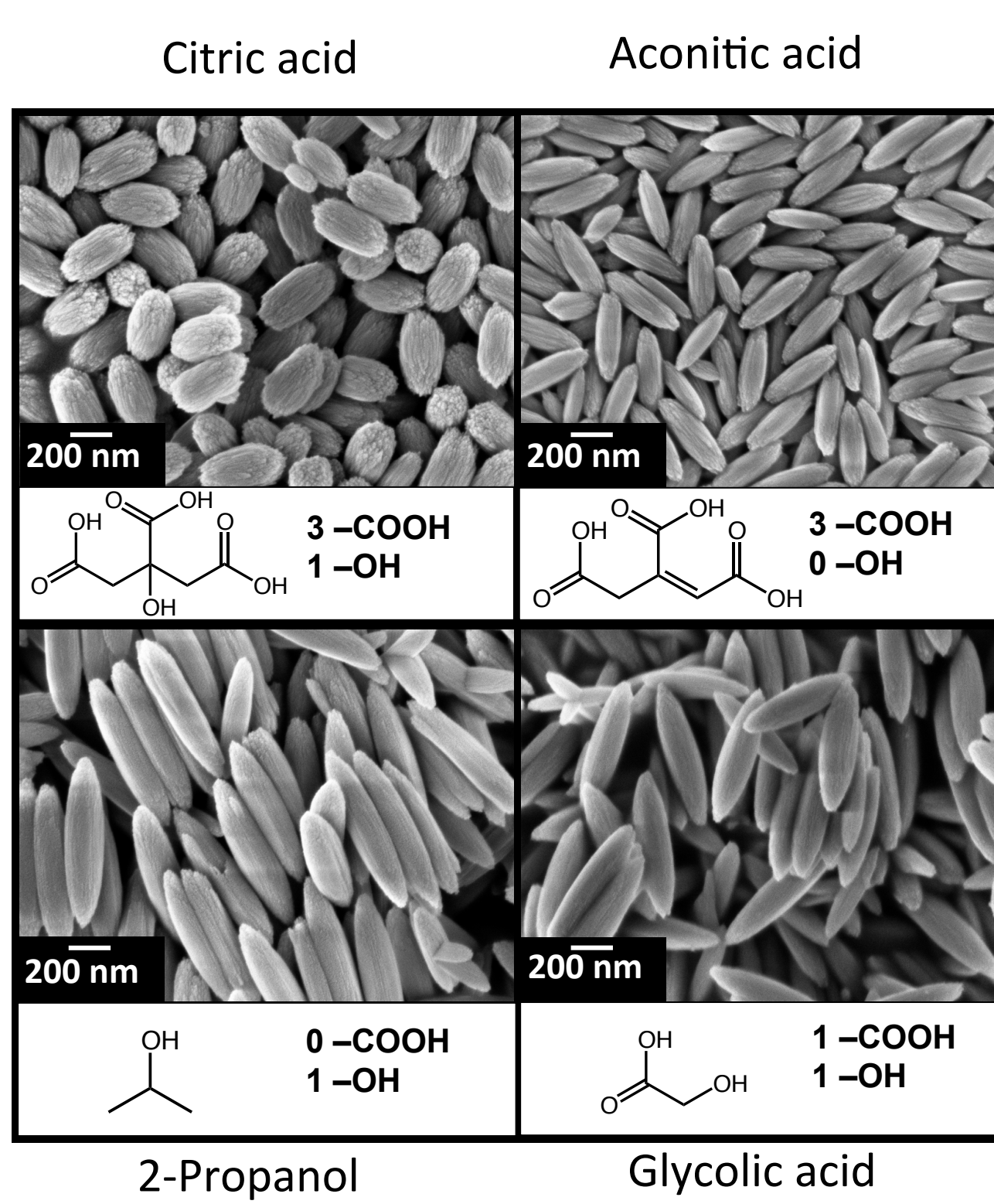
Akaganeite particle growth is a combination of nanotube growth (elongation) and nucleation of secondary crystals (bundle growth).

Low concentrations of citric acid preferentially inhibits crystal growth, but favors secondary nucleation.

At high citric acid concentrations, both crystal growth and secondary nucleation are inhibited, producing disorganized aggregates.

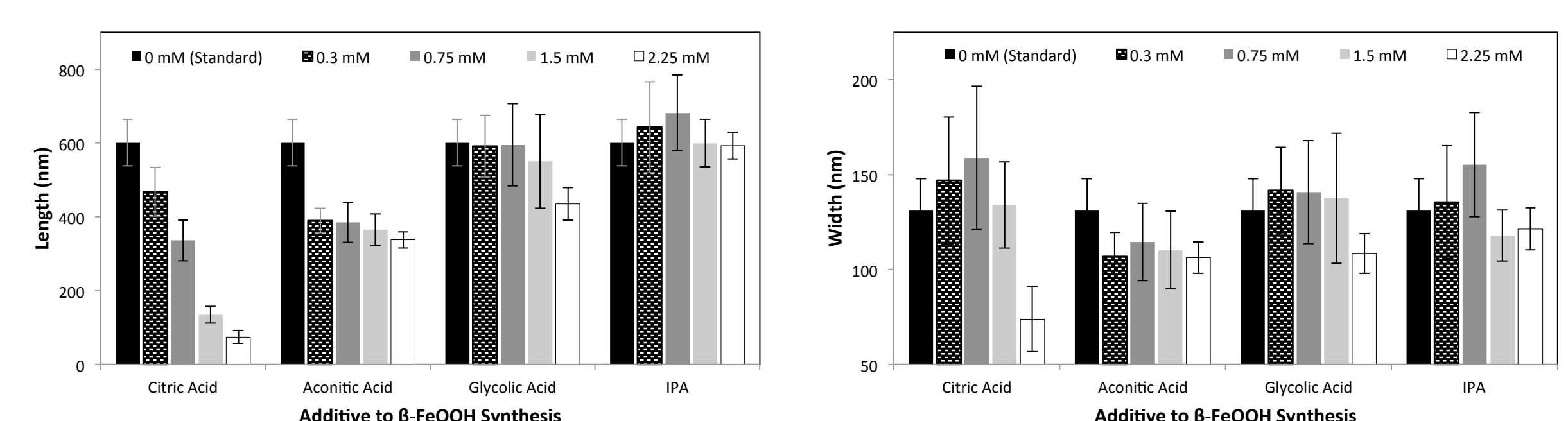


### What is behind the crystal growth modification?



Control experiments with other molecules containing acids and hydroxyls suggest growth modification may arise from cooperation between acids and hydroxyls on citric acid:

- Crystal length is most affected by multiple carboxylic acid groups
- Secondary nucleation (particle width) may be enhanced by the hydroxyl groups



### Conclusions

- Citric acid is an effective crystal growth modifier for  $\beta$ -FeOOH, affecting both crystallinity and particle morphology.
- Growth modification occurs through both crystal growth inhibition and secondary crystal nucleation inhibition.
- Multiple carboxylic acid groups on citric acid likely affect crystal elongation, while the hydroxyl group may affect secondary crystal nucleation.