Synthesis of Zinc Oxide Nanopyramids

Rebecca Raymond, Timothy J. Boyle, Nelson S. Bell, Bernadette A. Hernandez-Sanchez, Luke N. Brewer, Thomas J. Headley

Sandia National Laboratories, Advanced Materials Laboratory, 1001 University Boulevard SE, Albuquerque, NM 87106

Email: rraymon@sandia.gov

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Introduction

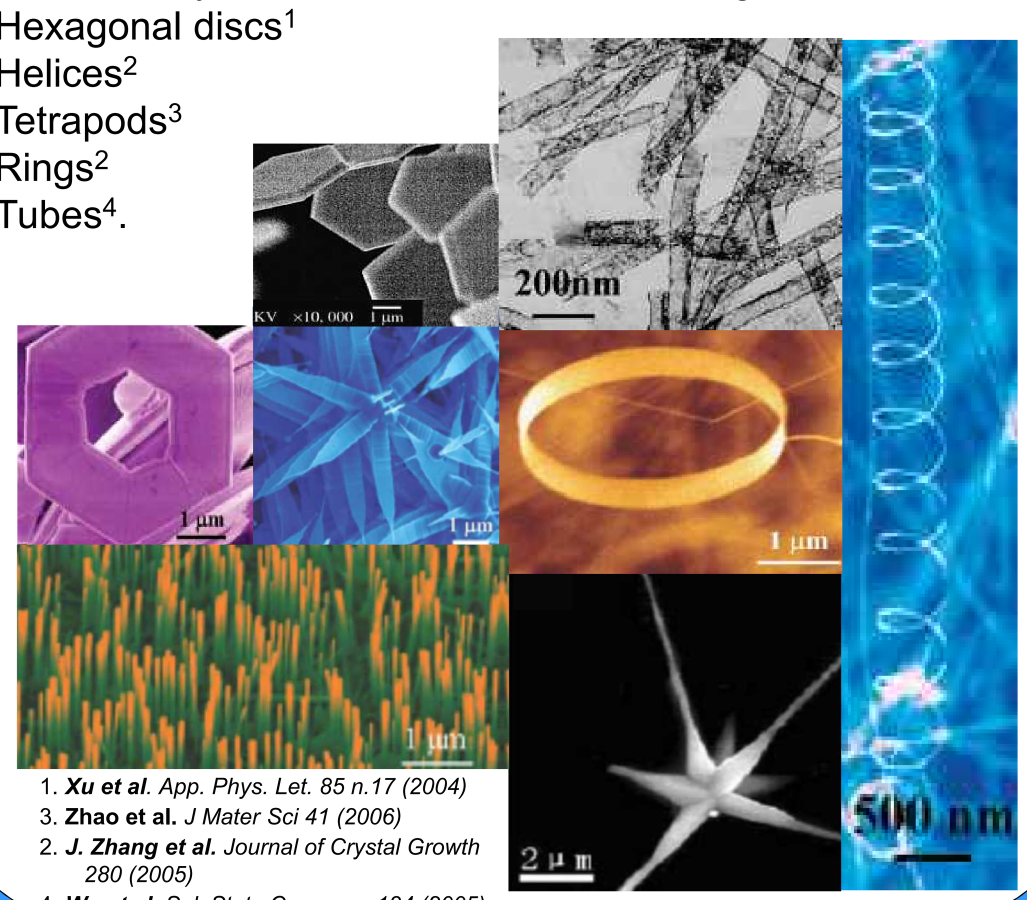
Nanomaterials are of recent interest due to the properties noted in their size regime. We have focused our research on the production of nanoceramic particles with an emphasis on controlling the morphology of zinc oxide (ZnO) zincite nanoparticles. We are interested in this material for its semiconducting capabilities, biocompatibility and electronic properties. All of these characteristics can be drastically altered by the morphological properties of the final nanoparticle so control over this particle growth is critical in generating tailored materials. Recently we discovered a solution precipitation route that yielded ZnO nanopyramids.

Several variables are being investigated to determine the underlying parameters that control and favor the production of nanopyramidal zincite.

Zinc Oxide Nanomaterials

Numerous morphologies of the ZnO wurtzite nanoparticles have been synthesized in literature including:

- Hexagonal discs[1]
- Helices[2]
- Tetrapods[3]
- Rings[2]
- Tubes[4].

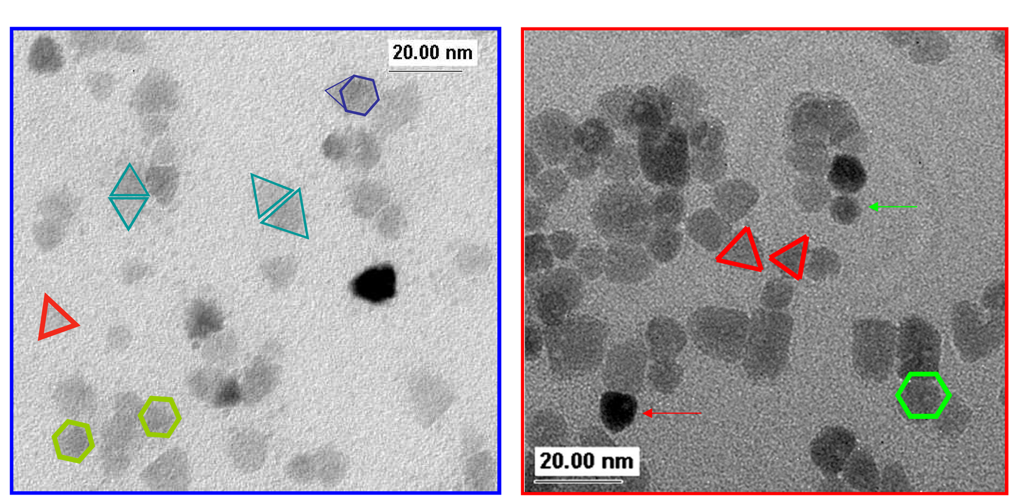


1. **Xu et al.** App. Phys. Let. 85 n.17 (2004)
3. **Zhao et al.** J Mater Sci 41 (2006)
2. **J. Zhang et al.** Journal of Crystal Growth 280 (2005)
4. **Wu et al.** Sol. State Commun. 134 (2005)

Zinc Oxide Pyramids

The nanopyramid procedure involves the reaction of zinc acetate dihydrate ($Zn(OAc)_2(H_2O)_2$) in butanediol with tetramethyl ammonium hydroxide pentahydrate (TMAOH).

$$Zn(OAc)_2(H_2O)_2 + 2\ TMAOH \rightarrow ZnO\ particles$$

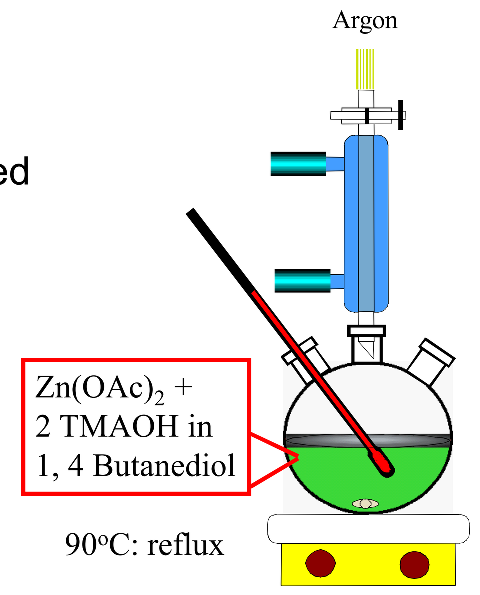


Original ZnO Pyramids — ZnO Pyramids prepared by Boyle group

Problem:
Synthetic pathway was not successfully producing desired morphologies.

The procedure was then varied at specific points in order to gain control over particle growth.

Characteristics to control:
- Size
- Morphology
- Contrast

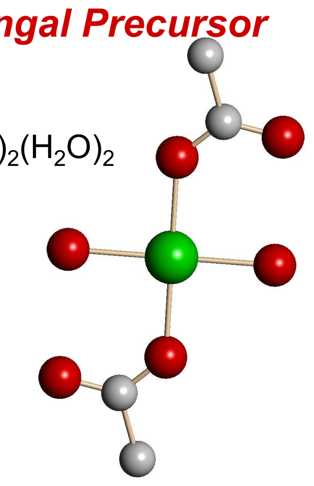


Synthesis of Precursors

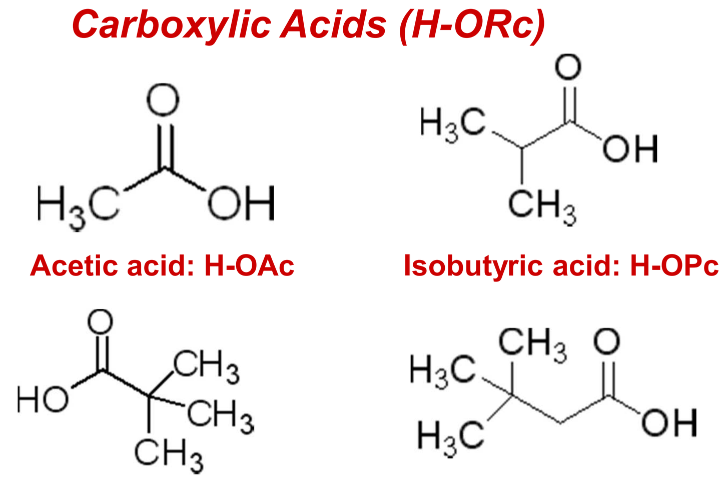
The solution route explained requires the use of zinc acetate dihydrate. However, for our purposes in mapping the reaction, we wanted to explore the effect of the precursor. This lead us to synthesize several novel zinc carboxylates. Also, because we wanted to explore the effect of water content on the system, we also synthesized anhydrous zinc carboxylates

$$Zn(Et)_2 + 2\ H\text{-}ORc \rightarrow Zn(ORc)_2 + 2\ H(Et)$$

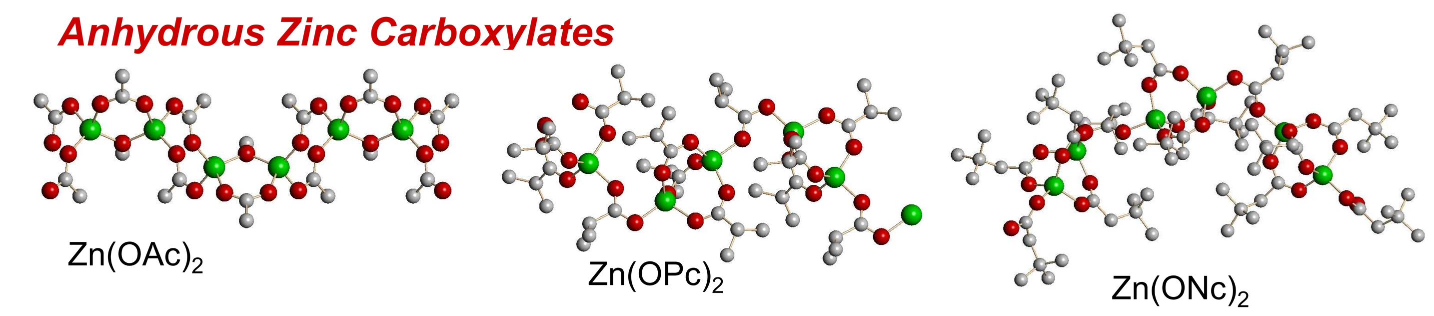
Oringal Precursor



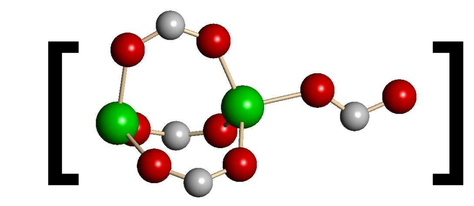
Carboxylic Acids (H-ORc)

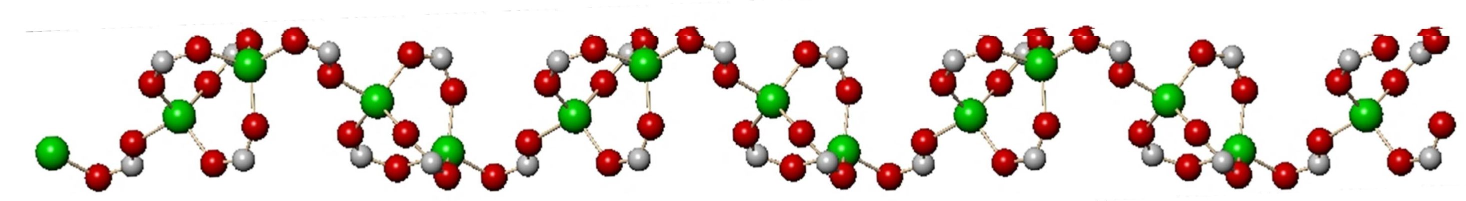


Anhydrous Zinc Carboxylates



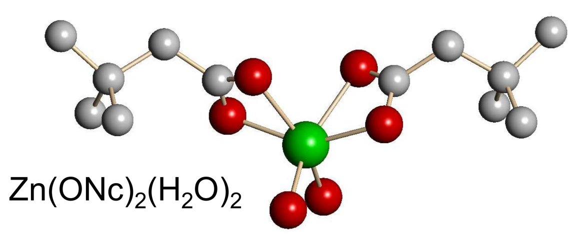
Anhydrous carboxylates, grown from toluene all resulted in:
- Long polymer chains
- Consistent with literature, spiral chain shown below:





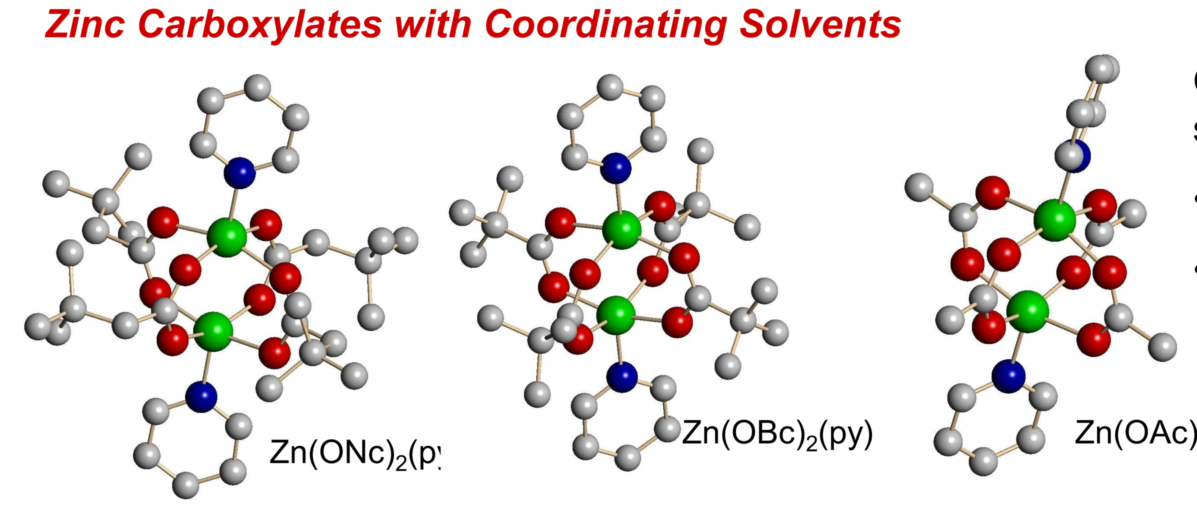
Clegg et. al. Inorg. Chem Acta. 186 (1991)

Zinc Carboxylates from Water



Hydrate versions of carboxylates:
- Consistently monomers
- Highly crystalline
- Other hydrates found to be polycrystalline

Zinc Carboxylates with Coordinating Solvents



Crystallization out of coordinating solvents resulted in:
- "Capping" of molecule
- Consistently results in dimer molecule

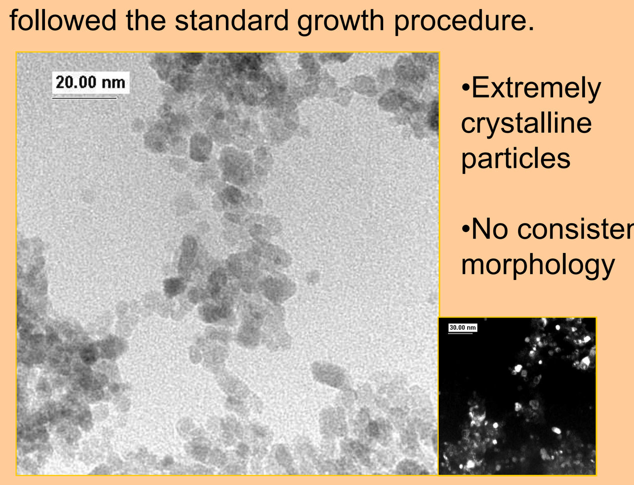
Control of Experimental Procedure

Several factors were identified to be the most likely to change the morphology of the nanopyramids.

Variations:
1. Precursor utilized
2. Water content of the system by using anhydrous reactants
3. Water content of the system by introducing excess water into the system
4. Pressure experienced by the particles while undergoing "ripening" process
5. Time the solution was allowed to "ripen"

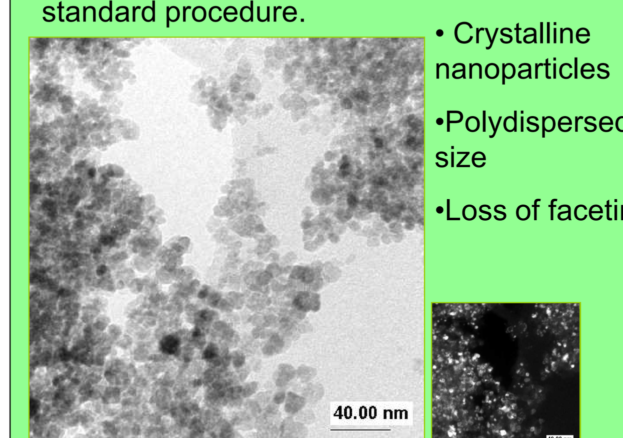
$Zn(OAc)_2(H_2O)_2$ is heated in 1,4 butanediol to 90 °C — $Zn(OAc)_2(H_2O)_2$ is cooled to 30 ºC — TMAOH is added dropwise to the $Zn(OAc)_2(H_2O)_2$ solution — Reaction is stirred at room temperature for 24 hours — Reaction is heated to 90ºC and ripened under vacuum atmosphere for 24 hours

Reaction A: Zinc *tert*-butyl acetate ($Zn(ONc)_2$) was reacted with the TMAOH in butanediol and followed the standard growth procedure.



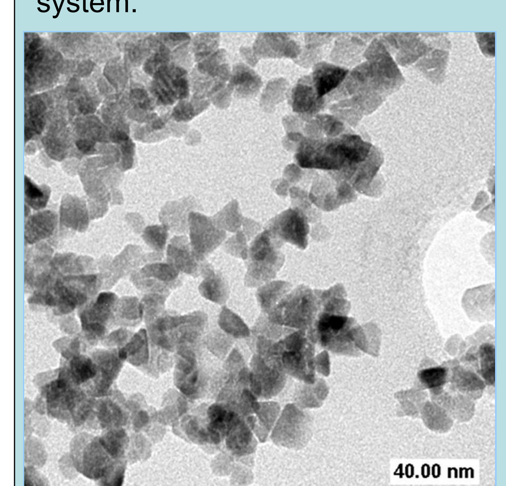
- Extremely crystalline particles
- No consistent morphology

Reaction B: Anhydrous zinc acetate was utilized. Zinc acetate was reacted with the TMAOH in butanediol and grown in the standard procedure.



- Crystalline nanoparticles
- Polydispersed in size
- Loss of faceting

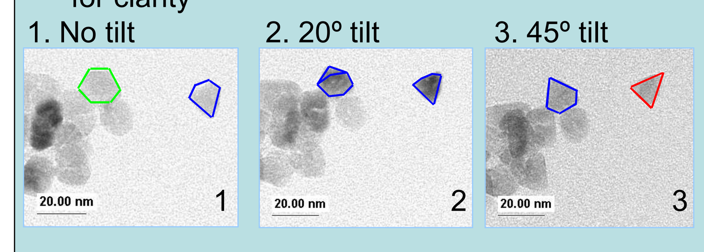
Reaction C: Reaction of $Zn(OAc)_2{\cdot}2H_2O$ with TMAOH was allowed to occur; however, immediately before ripening process, 10 equivalents of water were added to the reaction system.



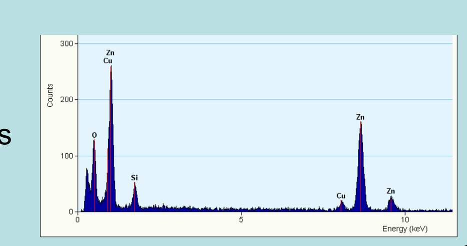
- Desired faceting achieved
- Consistent triangular morphology visible.

Below: Pictures of TEM tilted in order to see the 3D morphology of the particles. Shapes are outlined for clarity

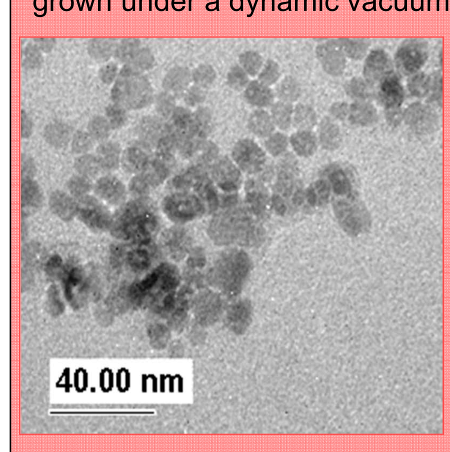
1. No tilt 2. 20º tilt 3. 45º tilt



EDS spectra showing peaks for ZnO nanoparticles:

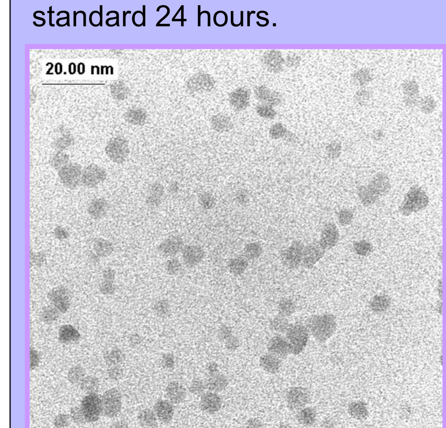


Reaction D: Standard reaction was maintained. During the ripening step, the particles were grown under a dynamic vacuum.



- Increased faceting
- Increased desired morphologies
- Increased contrast

Reaction E: Standard reaction was maintained. But during the ripening step, the particles were allowed to ripen for 60 hours rather than the standard 24 hours.



- Increase in faceting
- Distinctive shapes arise
- Improved contrast

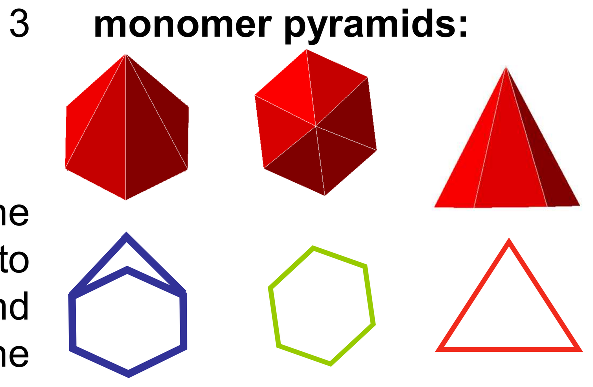
Interpreting the TEM Images

TEM images are a 2 dimensional representation of 3 dimensional objects.

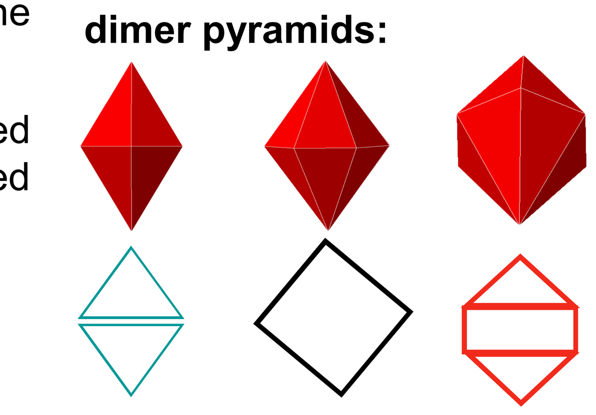
Consequently, when viewing the TEM images, we had to consider both the dimer and monomer shapes as well as the orientations that either shape may have been in when the TEM was taken.

To the left we have illustrated the most commonly viewed orientations of the pyramids.

Possible orientations of monomer pyramids:



Possible orientations of dimer pyramids:



Summary and Conclusions

Throughout our investigation of the growth patterns of the zinc oxide pyramids, several factors have presented themselves as critical for the production of pyramids rather than polydispersed morphologies.
- Precursor
- Factors during the ripening process
  - Time allowed for Ostwald ripening
  - Pressure experienced by the particles (dynamic vacuum)
- Water content

Optimized Synthetic Route:
- Use of hydrous precursor
- Dynamic vacuum environment for growth
- Use of long periods of time for growth
- Addition of excess water to the system

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