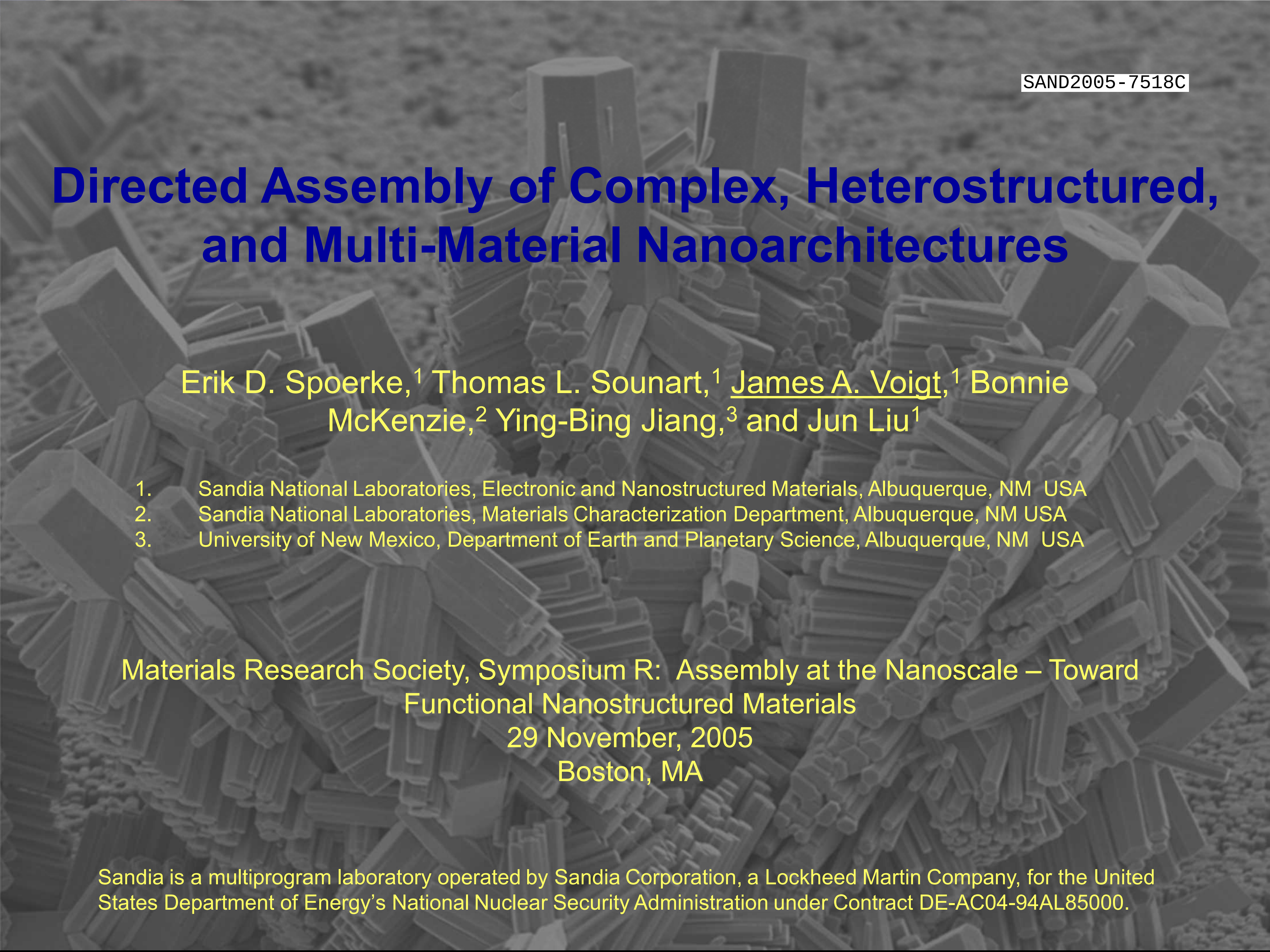

SAND2005-7518C

Directed Assembly of Complex, Heterostructured, and Multi-Material Nanoarchitectures

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Materials Research Society, Symposium R: Assembly at the Nanoscale – Toward Functional Nanostructured Materials
29 November, 2005
Boston, MA

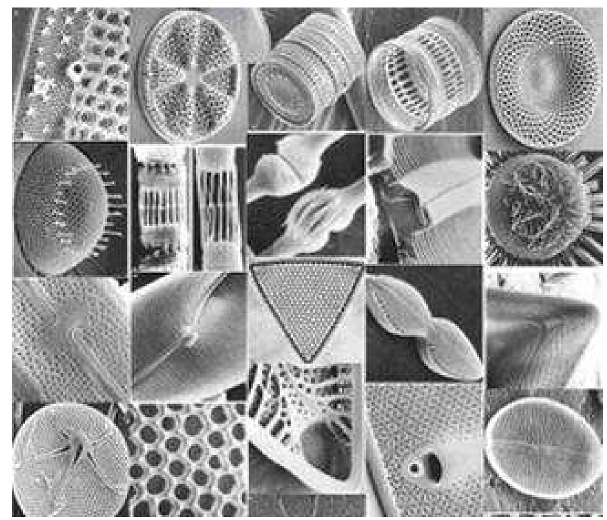
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Complex Nanocrystalline Films: Motivation

- **Potential Applications in energy conversion/storage, chemical/biological detection, optics, catalysis, separations, etc.**
- **Chemical properties of nanocrystals depend on the morphology, crystalline surfaces, and interfaces.**
- **Develop scalable, cost-effective, environmentally friendly synthetic approaches for making complex nanomaterials.**

Biominerals as a source of inspiration – technologically important materials

Shells made of $CaCO_3$



Diatoms made of silica

Round, Crawford, Mann, "The Diatoms: Biology and Morphology of the Genera", 1990

Mimicking Natural Order with Technological Materials

Key Concepts:

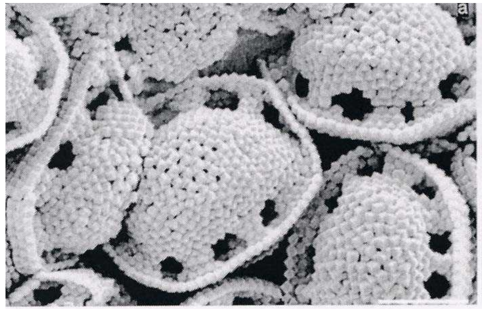
•Solution-phase crystal growth

•Multi-step sequential growth processes

•Application of organic crystal growth modifiers

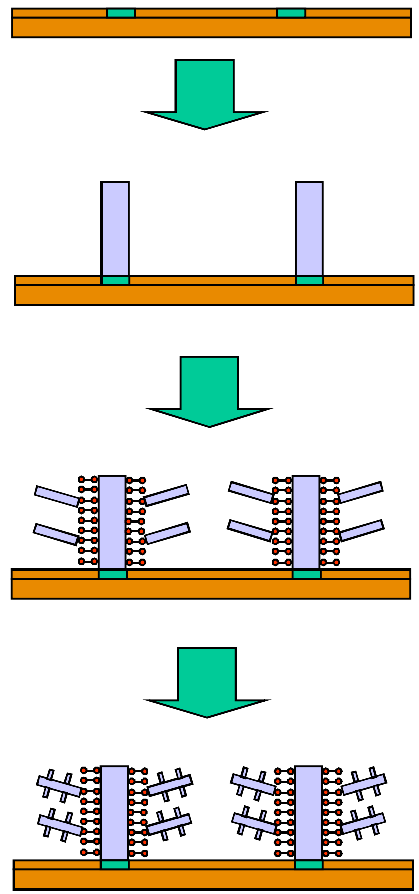
•Controlled nucleation and growth

Higher-Order Structures: Sequential Nucleation and Growth



Diatoms – SiO_2 **Coccolith - $CaCO_3$**

Young et al, J. *Structural Biology*, 1999



Primary Growth

Secondary Growth

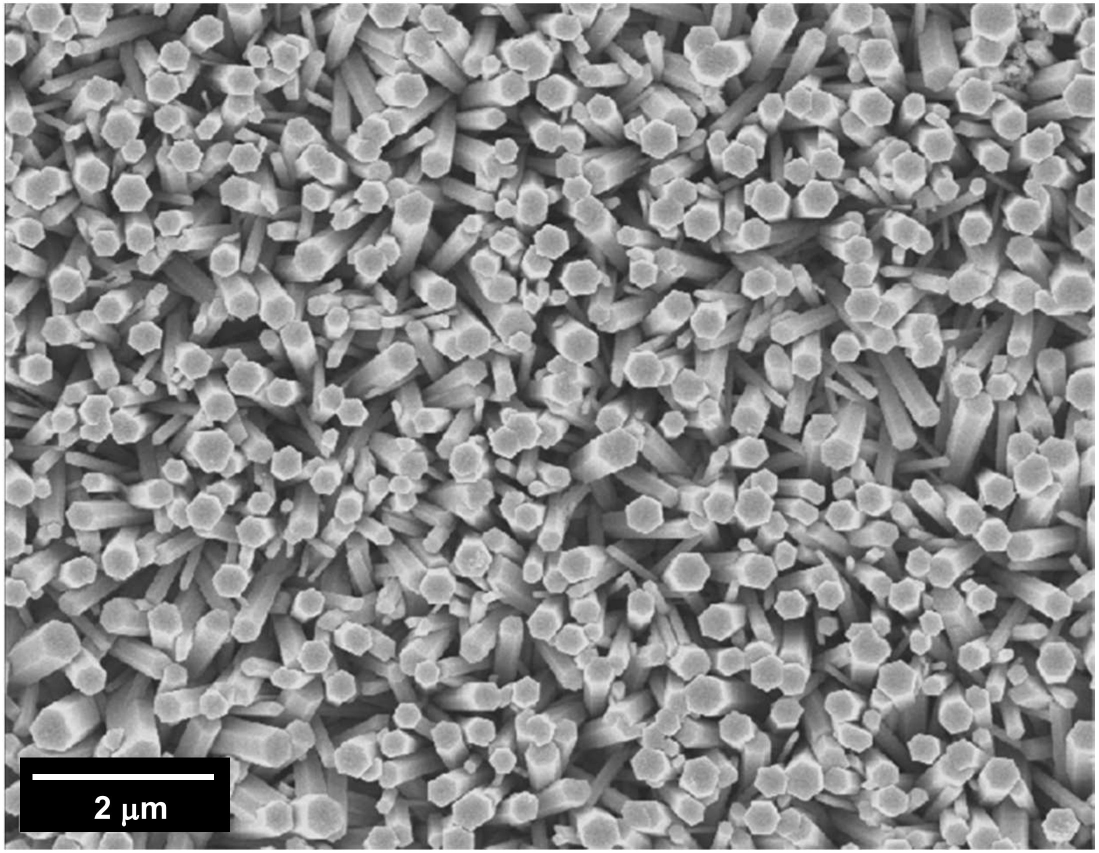
Tertiary Growth

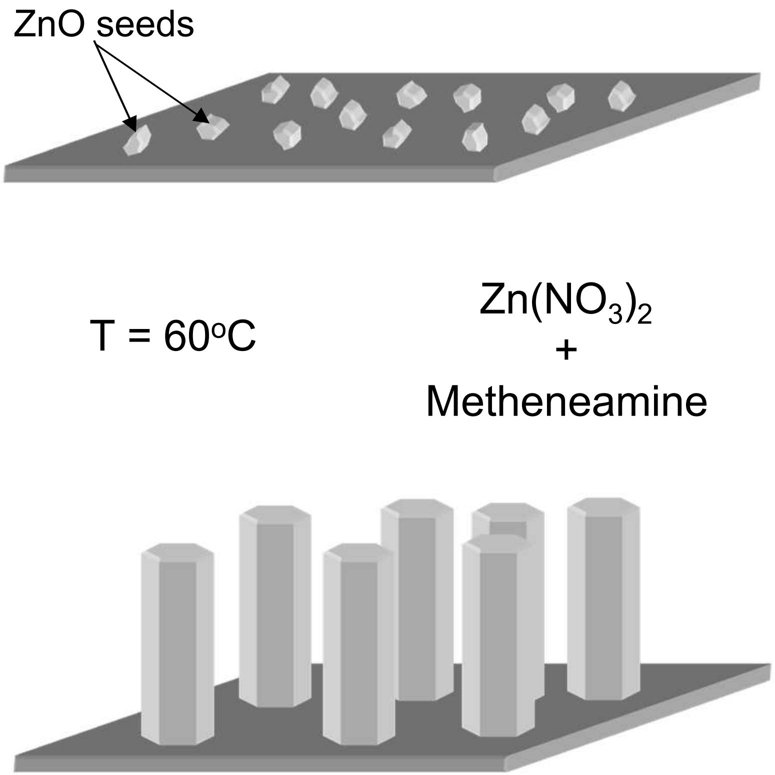
Large scale ordering in biominerals:

- **Complex, multilevel architectures**
- **Good structural control**
- **Organization over large distance**

Solution Phase Synthesis of ZnO Nanorod Arrays: Primary Structures

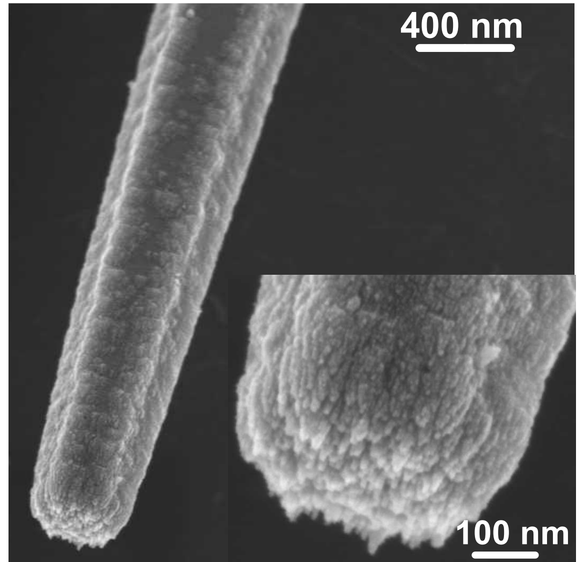
Controlling crystal "seeds" facilitates control of nanorod arrays

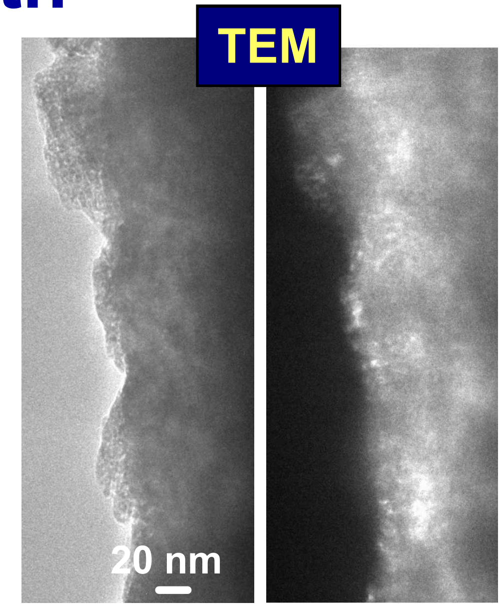




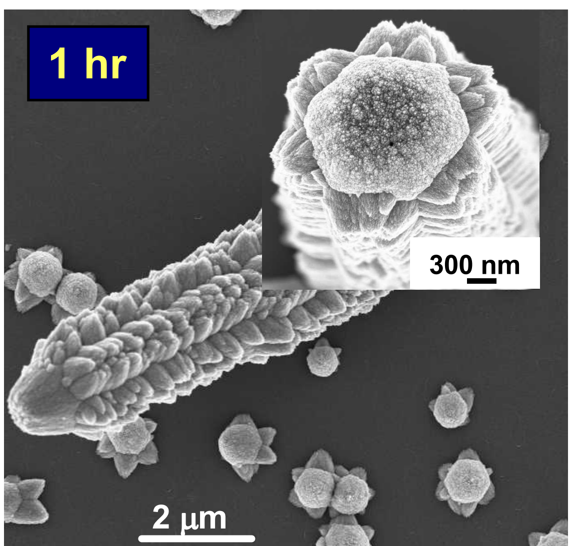
Organically-Mediated Secondary Nucleation and Growth

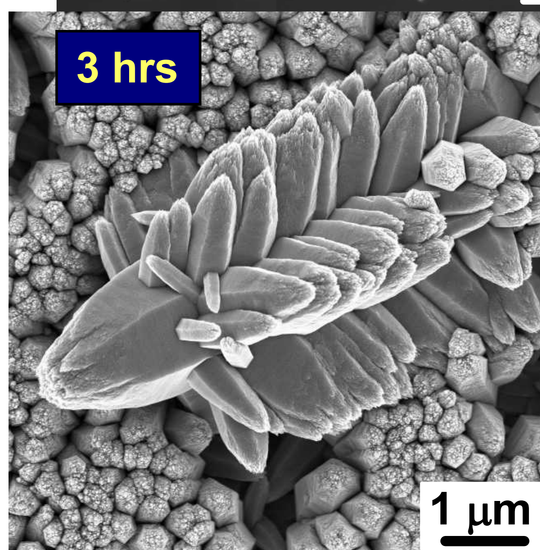
30 min:
Polycrystalline nanoparticle layer has nucleated on ZnO rod surface

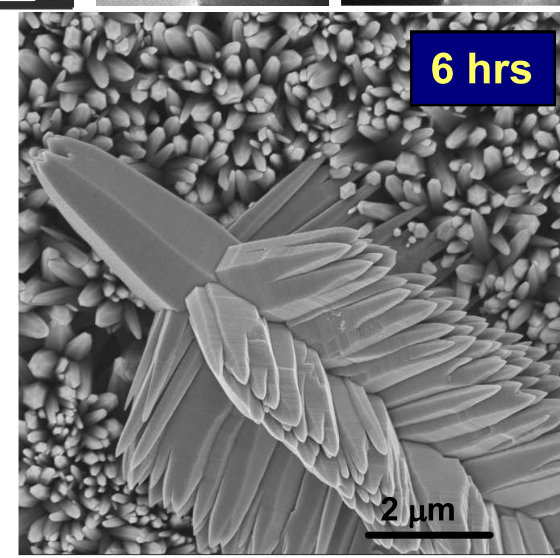




Coalescence:



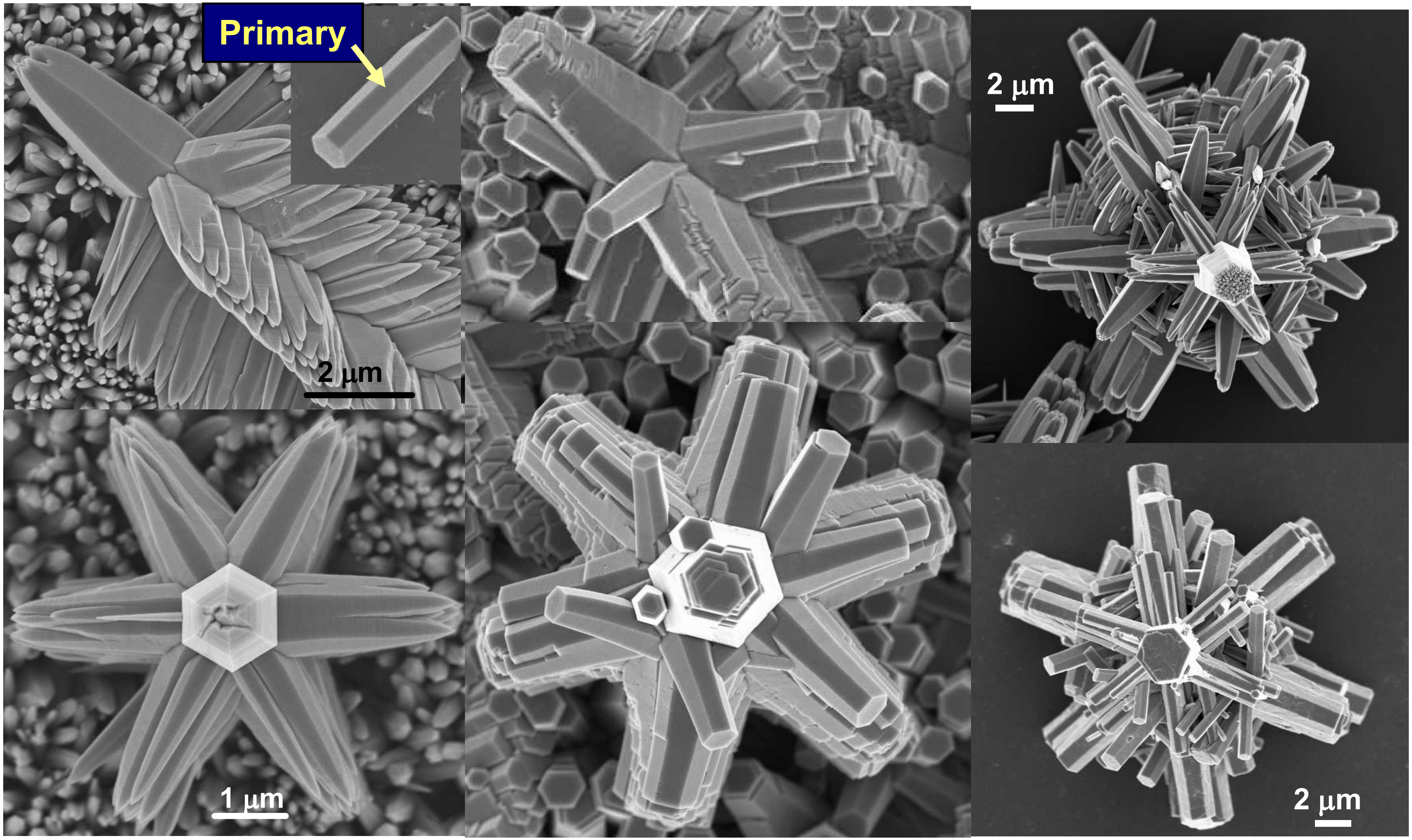




Reaction time

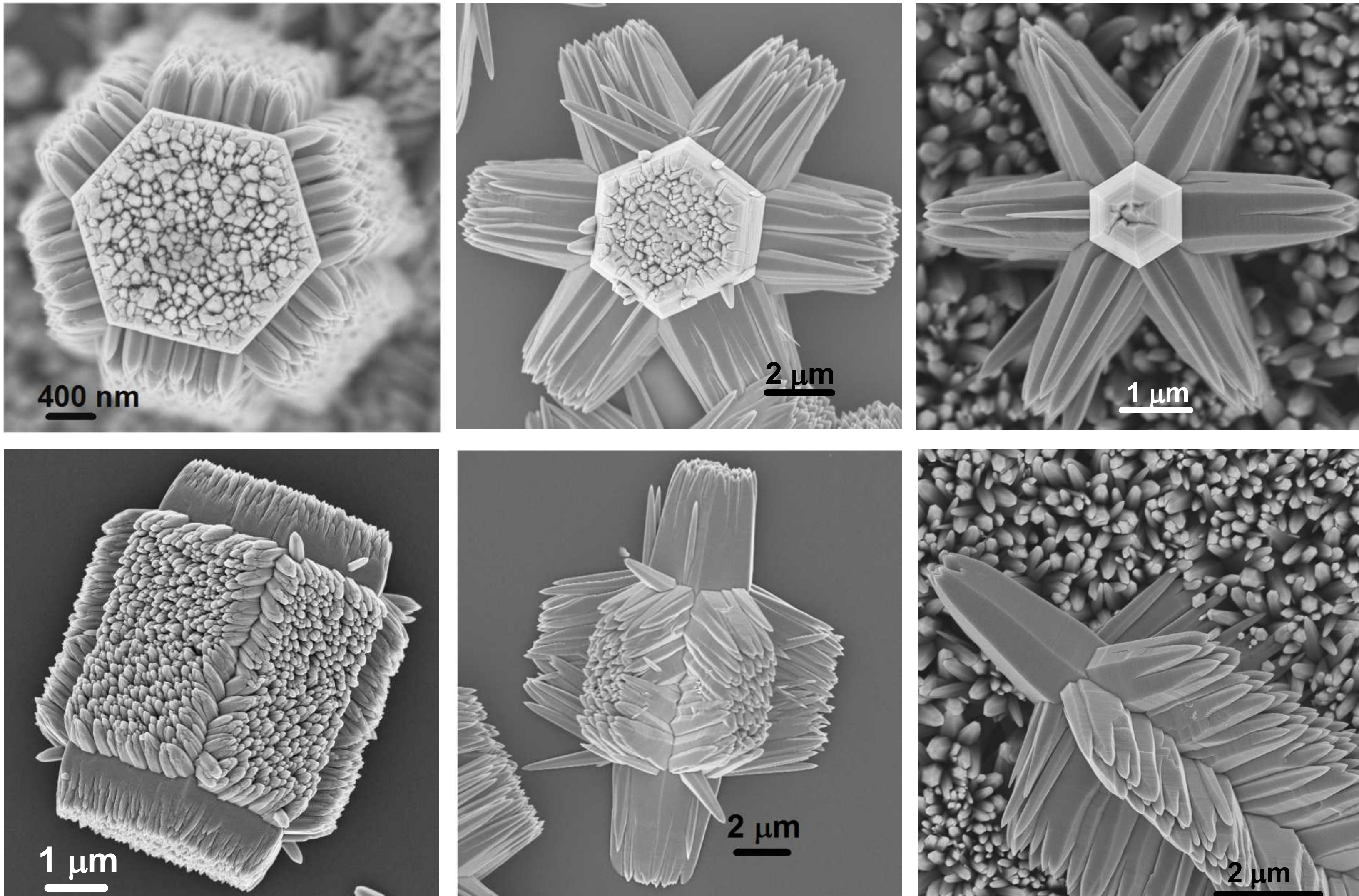
Higher-Order Structures: Sequential Nucleation and Growth

Secondary Structure | **Healed Secondary** | **Tertiary Structure**



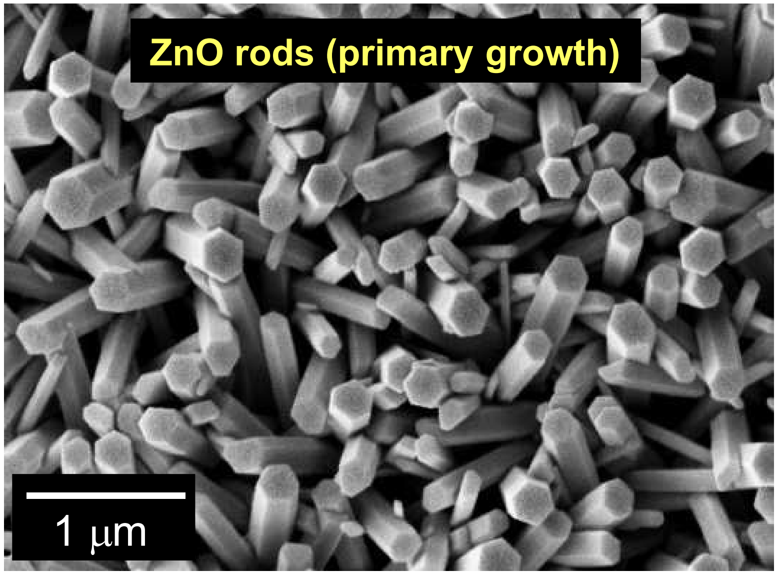
Diaminoalkanes (e.g. ethylene diamine, diaminopropane, diaminobutane)

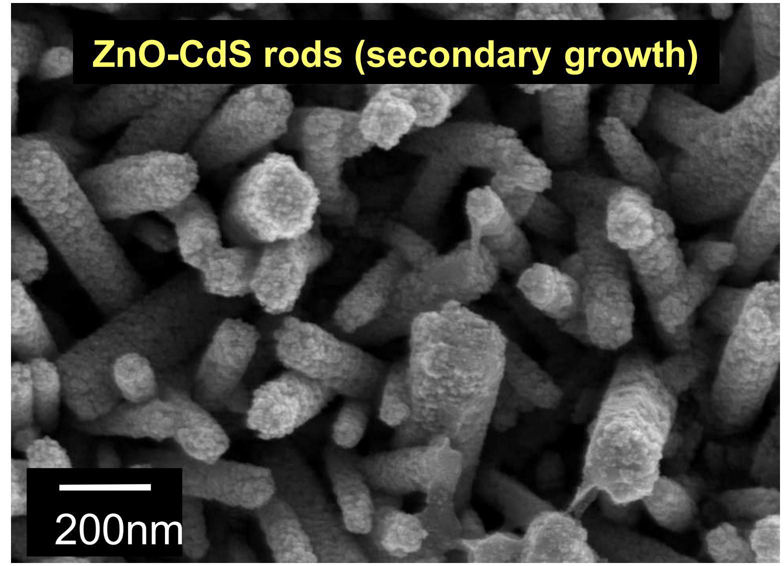
Organic Modifiers:
Effect of Diamine Concentration



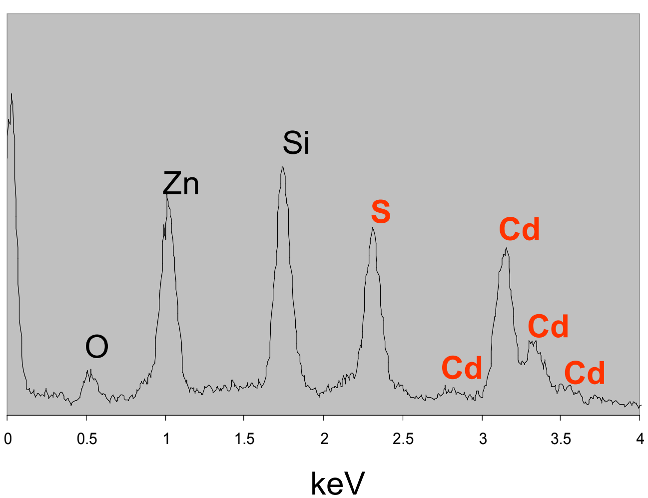
Increasing Diamine Concentration

Secondary Growth in a Multimaterial System: ZnO-CdS

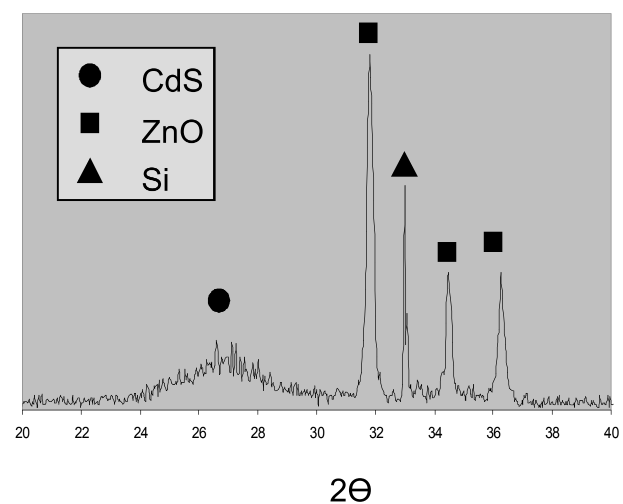




Energy Dispersive X-ray Analysis of ZnO-CdS

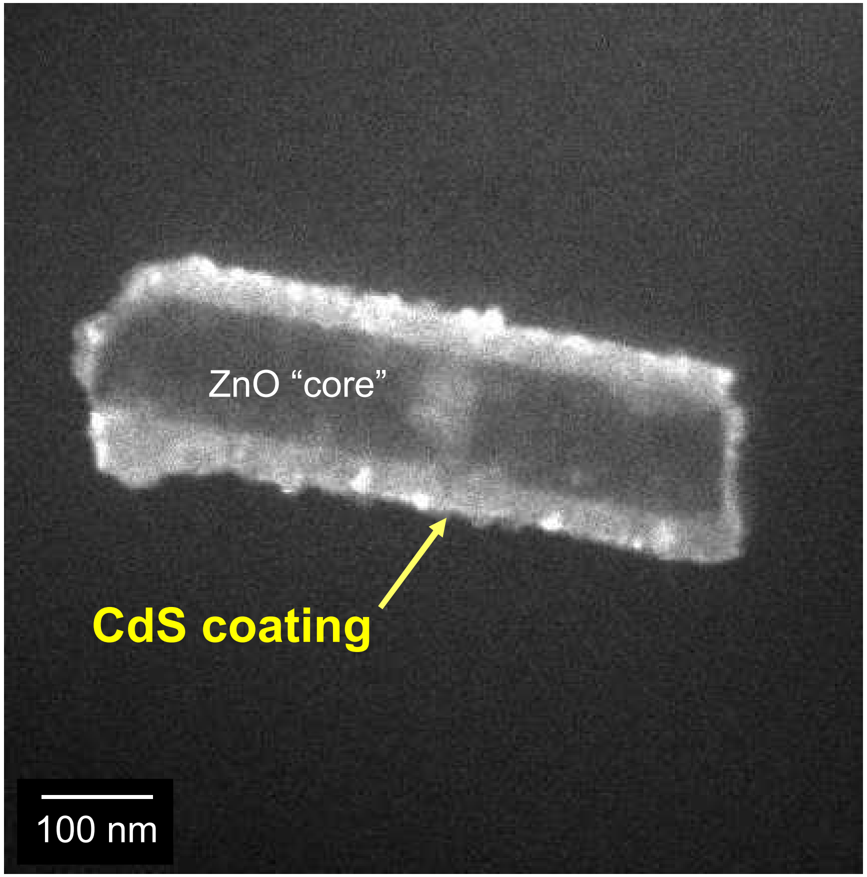


X-ray Diffraction of ZnO-CdS

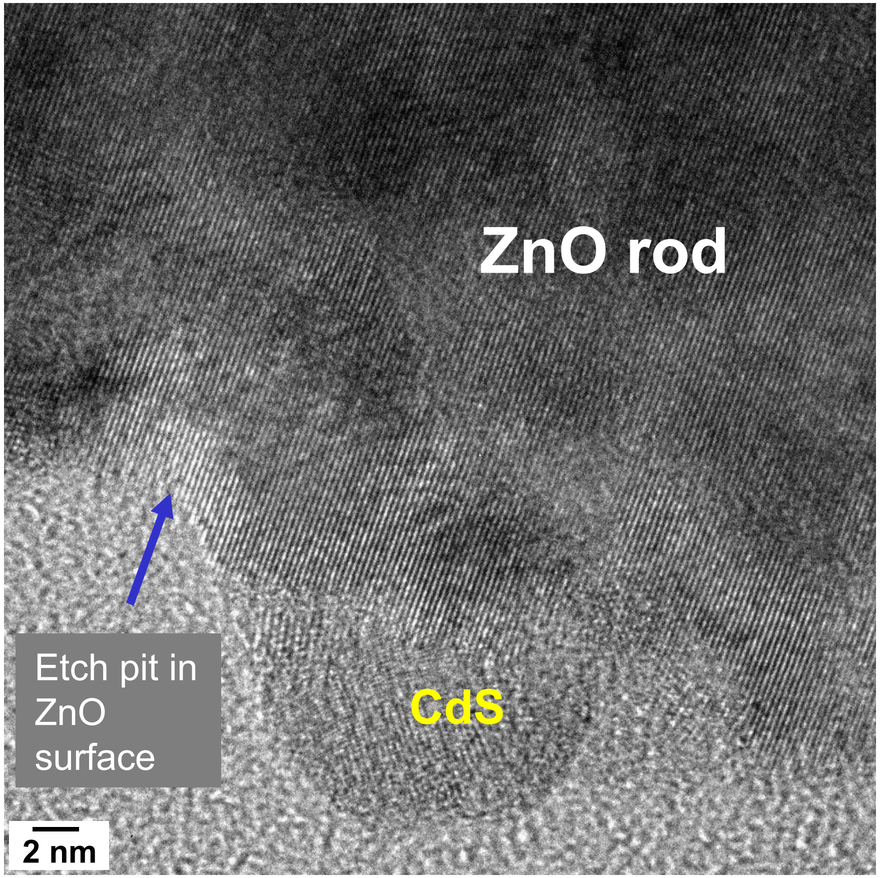


TEM Images of CdS-ZnO Heterostructures

Dark-field image of CdS coating on ZnO rod "core"



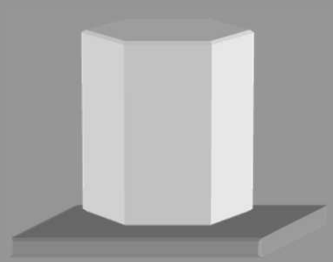
High resolution image of CdS nanoparticle nucleated on ZnO rod



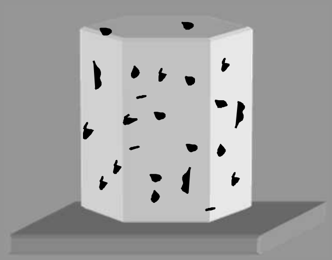
images courtesy of Y-B Jiang, University of New Mexico

Mechanism for CdS Growth on ZnO

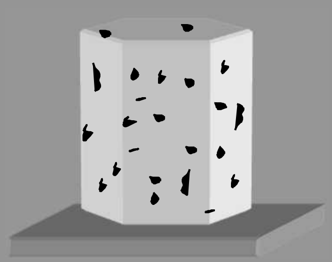
$$CH_3CSNH \xrightarrow{Cd^{2+}} CH_3CN + H_2S(\leftrightarrow CH_3CN + H^+ + HS^-)$$



pH 5.5 → pH 3.5



$$Cd^{2+} + HS^- \xleftrightarrow{ZnO} CdS + H^+$$



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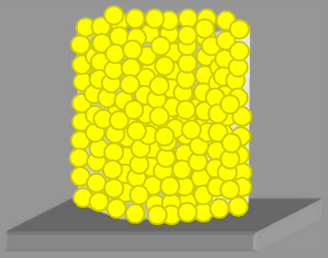
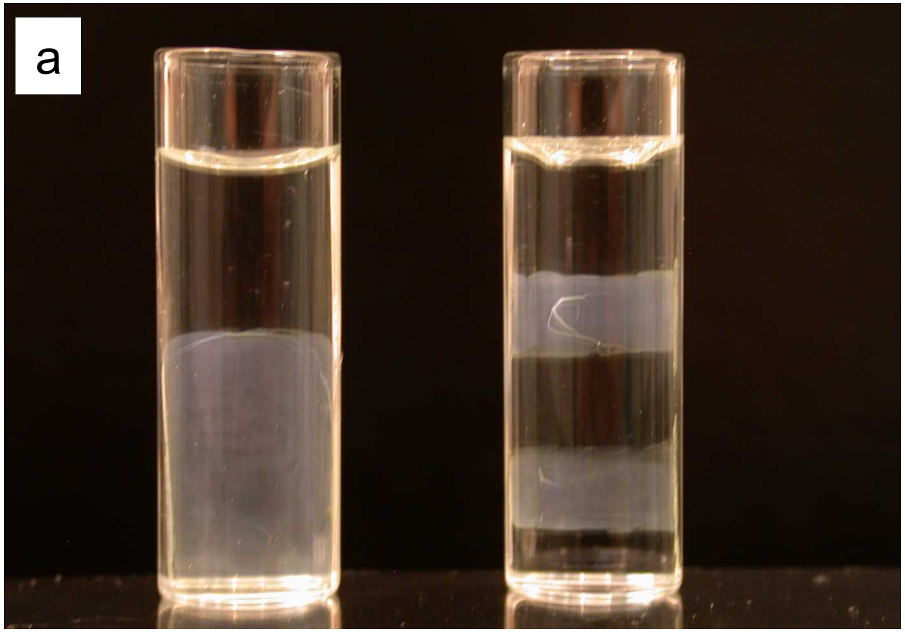
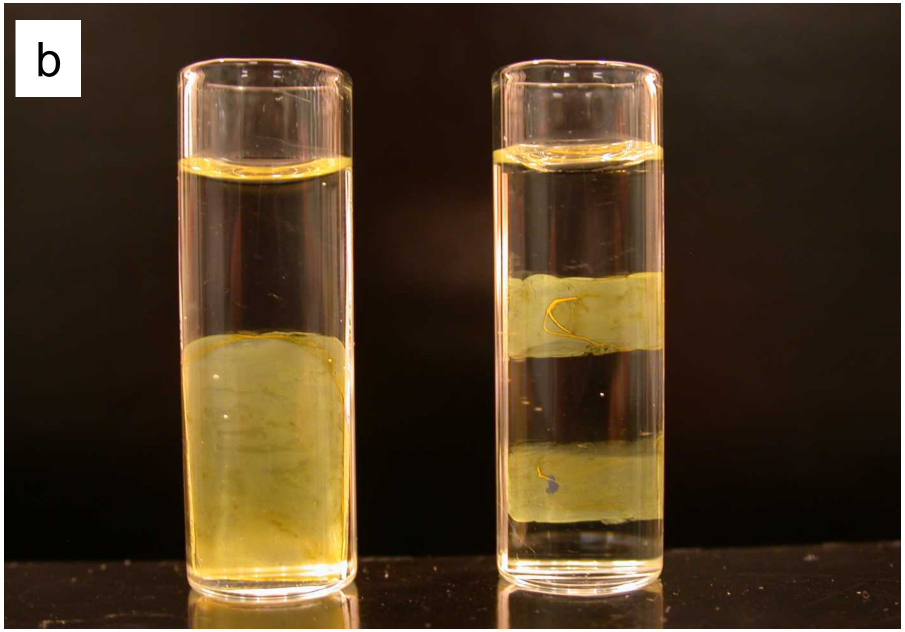


Selective CdS Growth on ZnO

ZnO rods grown in spatially-selective regions on glass at t_0 in CdS reaction solution



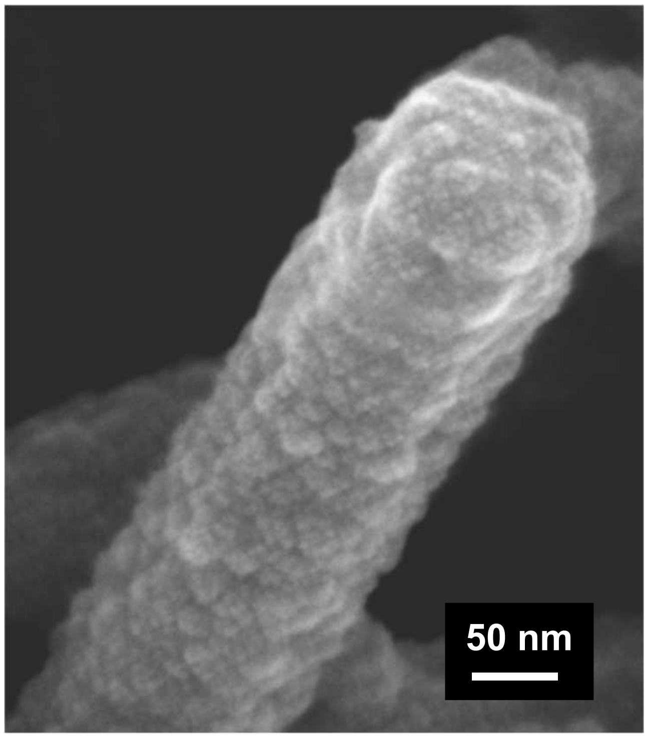
CdS (yellow) selectively deposited on ZnO-covered regions after 10 minutes at 60°C in reaction solution.



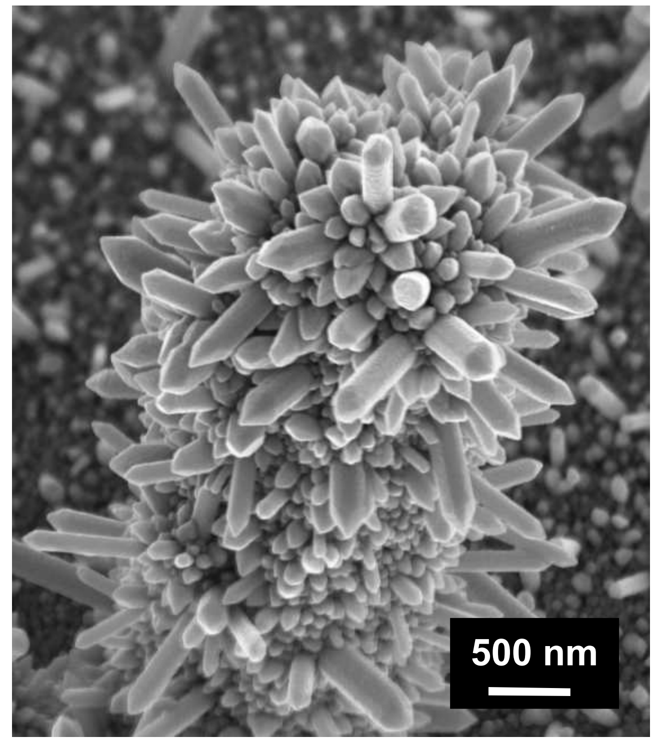
Tertiary Heterostructures:

CdS rod growth on ZnO Rods

CdS Nanoparticles Coated on a ZnO Nanorod



CdS Nanorods on ZnO (EDA, thiourea, $Cd(NO_3)_2$, 180°C)



Secondary CdS growth protects the primary ZnO rod from the harsh reaction environment needed for tertiary growth

Conclusions

- **Aqueous-phase nucleation & growth is a powerful, low-cost, environmentally friendly approach for controlling nanostructures in semiconductor films**
  - Applicable to various technologically important materials
  - Rational design and control of crystal morphology
  - A wide range of oriented nanostructures accessible using similar methods
- **Stepwise nucleation & growth can generate complex and hierarchical structures difficult to access with other methods**
- **Combing bottom-up and top-down approaches has great potential for producing large arrays of hierarchical nanostructures**


Thank you!