Synthesis of Nanostructures

Opportunities for Scattering Methods

Teri W. Odom
Northwestern University

16 July 2005

Overview

- Nanocrystal growth and characterization
  - Solution methods
  - High temperature methods
- Prototypical systems
  - CdSe quantum dots
  - Semiconducting nanowires
  - Carbon nanotubes
- New, specific challenges
  - Other chemical systems
  - Nanostructures on surfaces
  - Assemblies of nanostructures
  - A different kind of nanostructure
- The “so-what” question

What do we know so far?

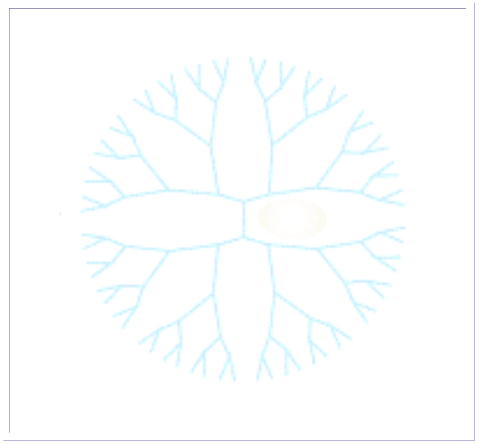
What do we want to know?

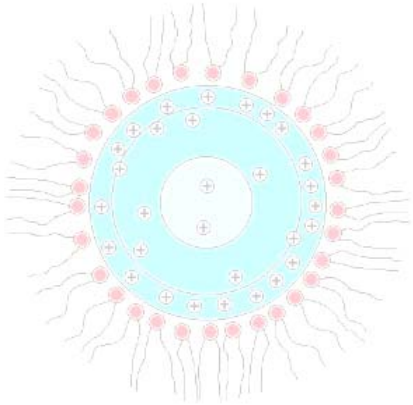
Prototypical Systems

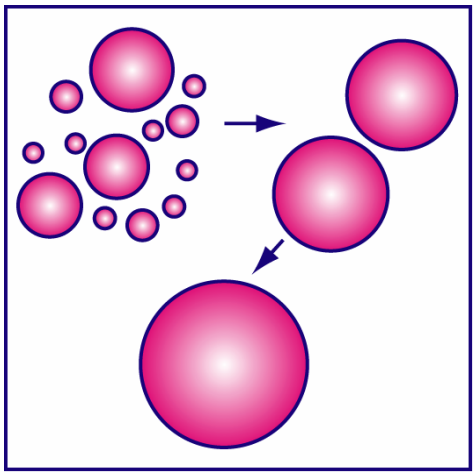
- CdSe quantum dots
- Semiconducting nanowires
- Carbon nanotubes

- Advantages of scattering methods
  - Crystalline facets and edges
  - Defect characterization
  - In-situ growth kinetics

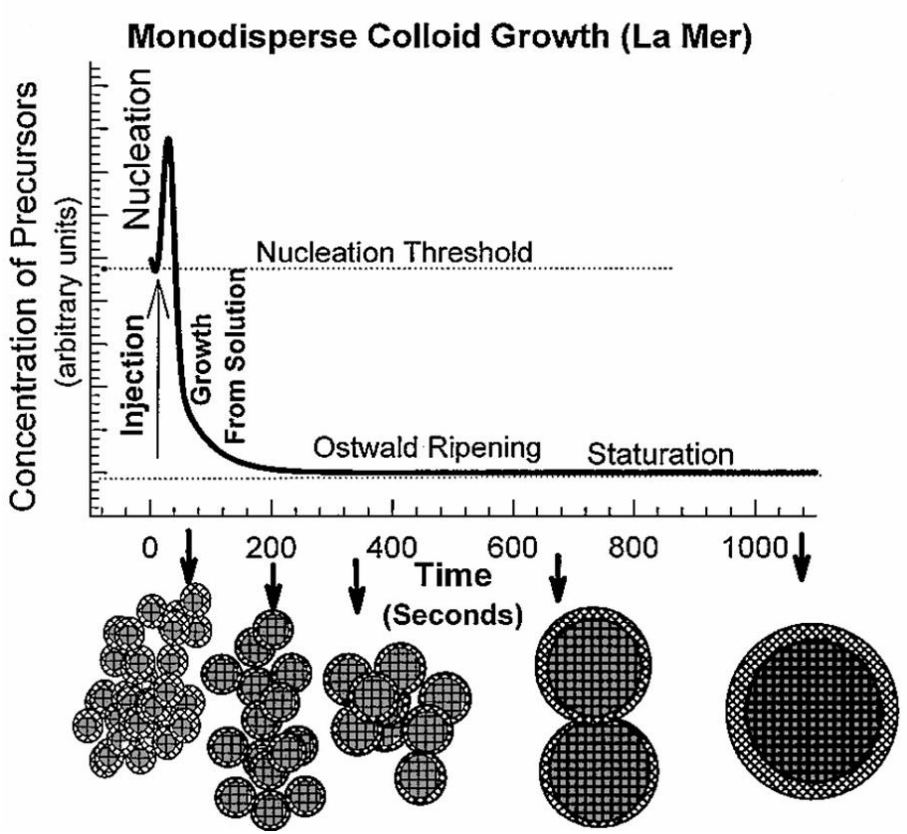
Zero Dimensional (0D) Growth

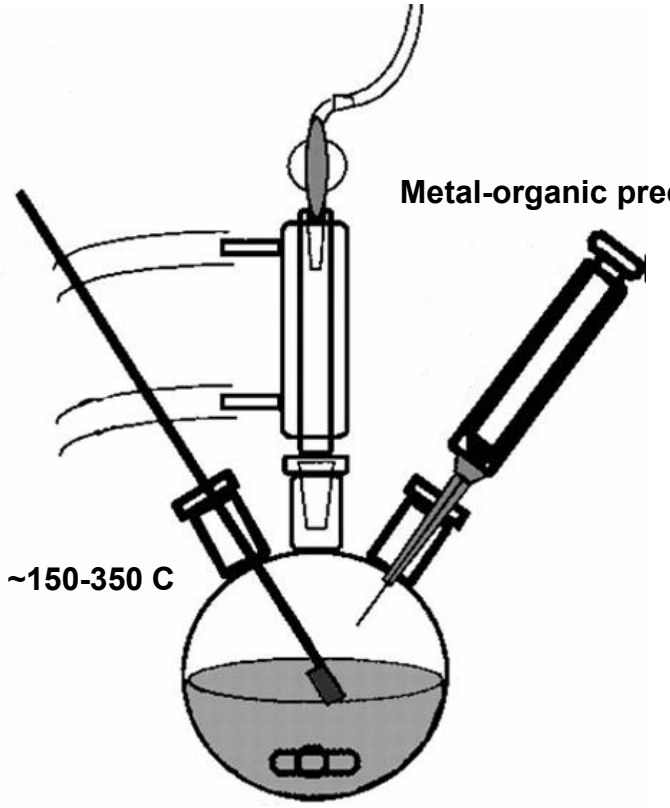






Nucleation and Growth



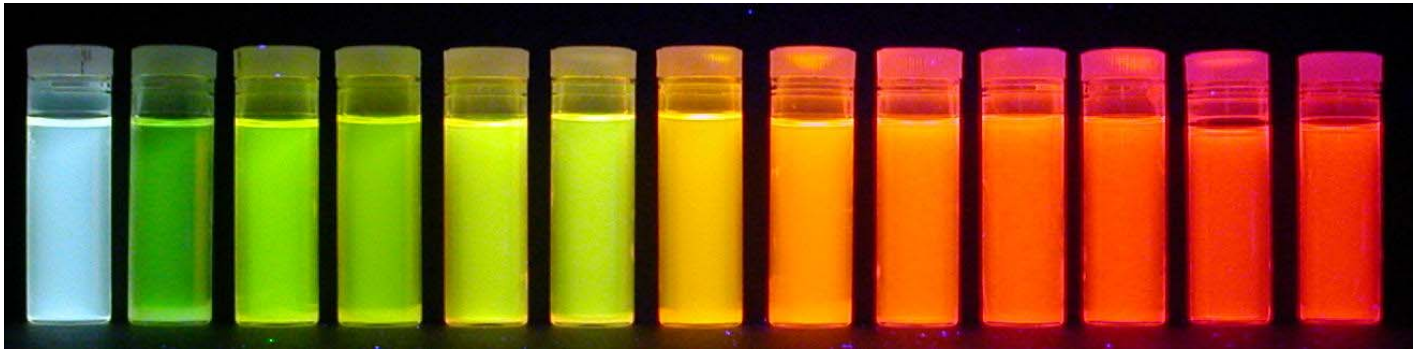


Hot coordinating solvent (mixture of Tri-n-octylphosphine (TOP)/TOPO)

C.B. Murray, *Annu. Rev. Mater. Sci.* 30, 545 (2000)

Semiconducting and Metallic NCs

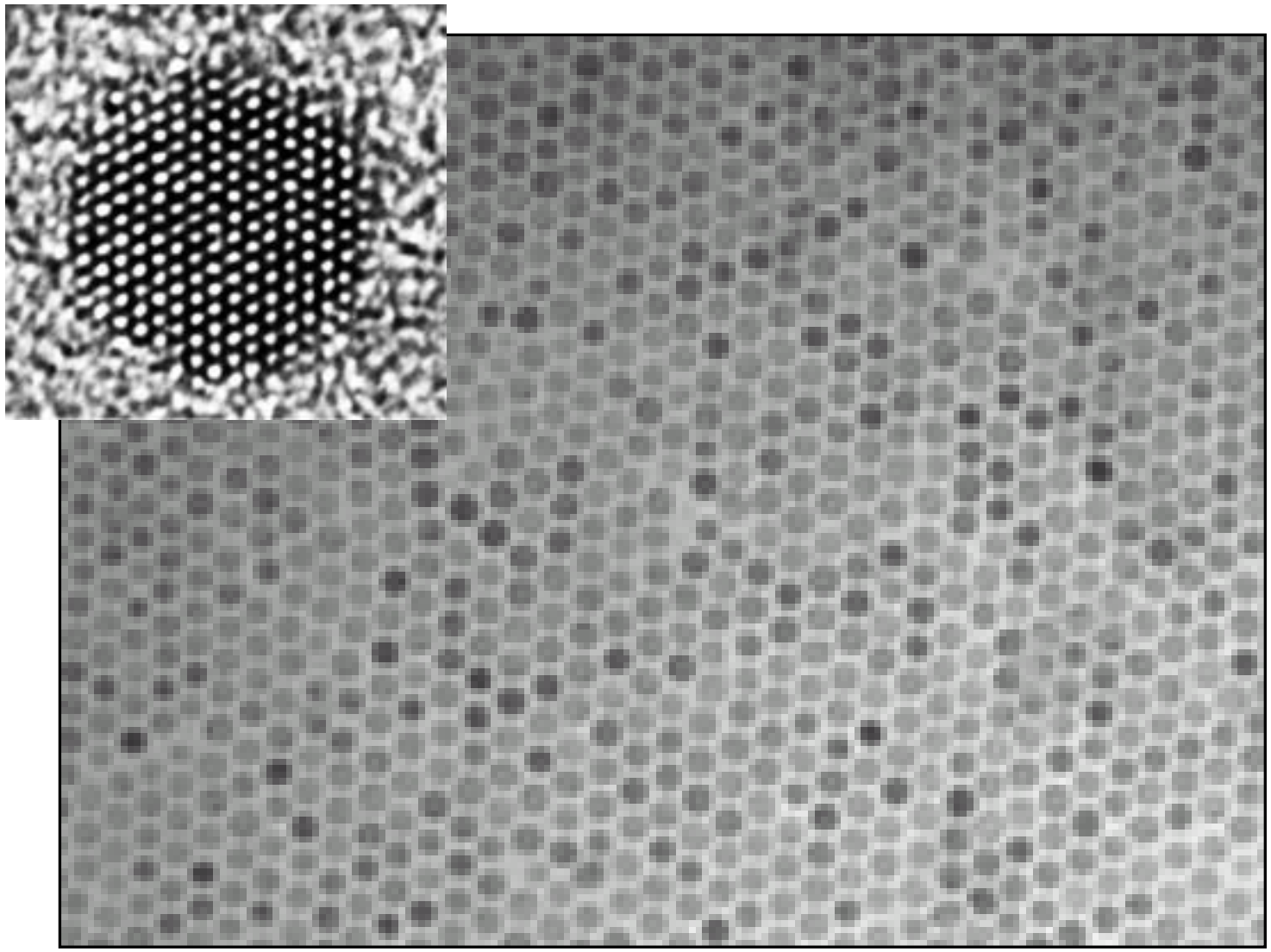
CdSe/ZnS Semiconducting Nanocrystals



Ag Metallic Prisms and Nanoparticles

Y. Babayan and T.W. Odom; C.A. Mirkin

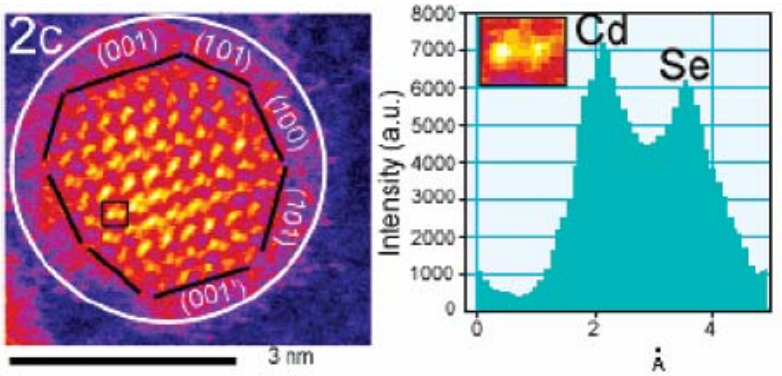
TEM of CdSe Quantum Dots

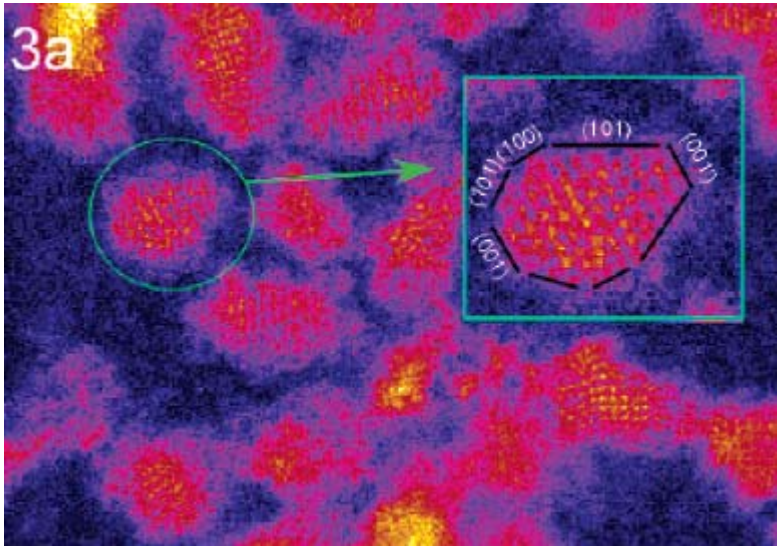


A.P. Alivisatos and NanoSys

Determination of CdSe Facets

Z-contrast Scanning Transmission Electron Microscopy (STEM)

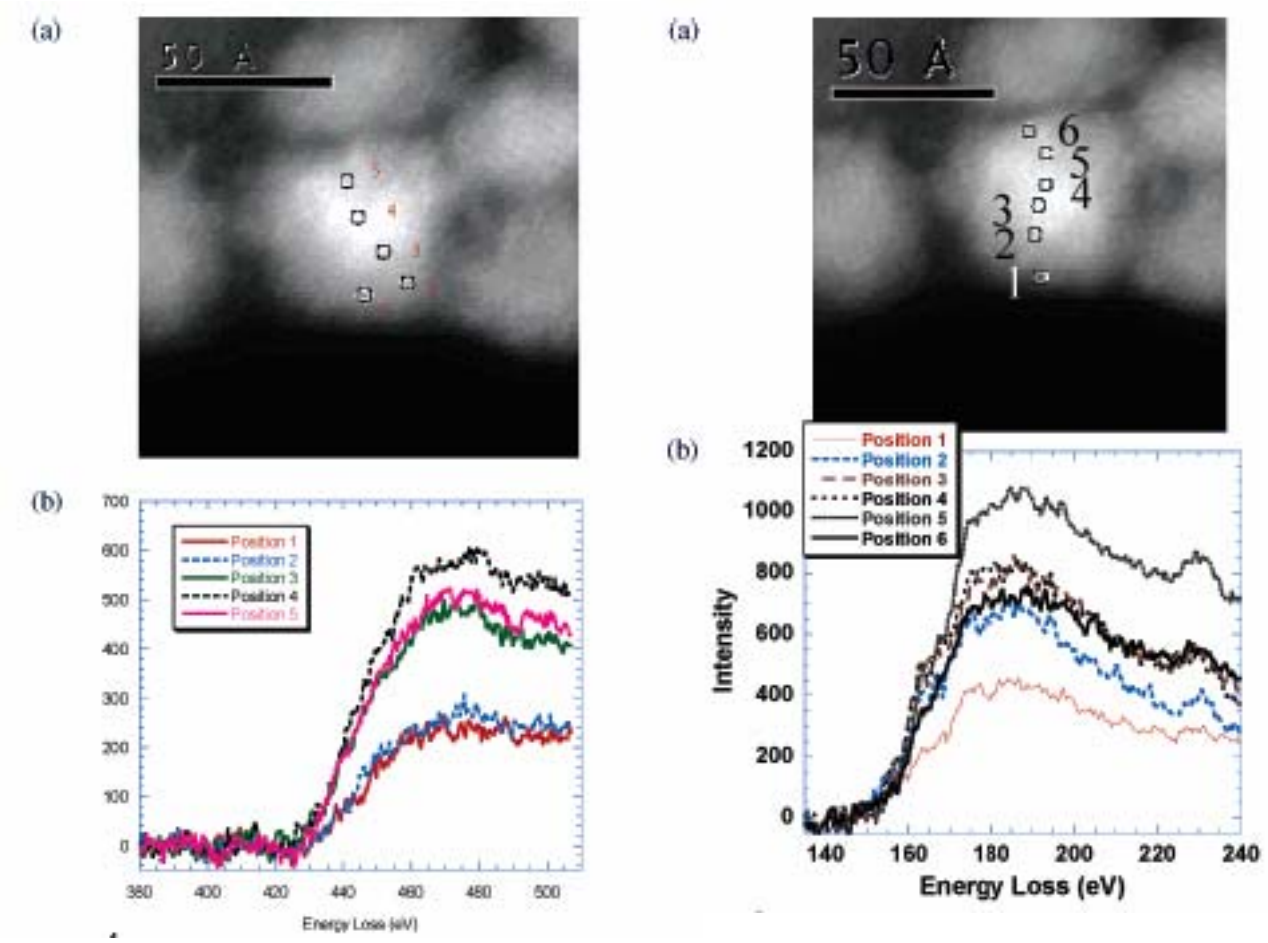




J.R. McBride, T.C. Kippeny, S.J. Pennycook, and S.J. Rosenthal, *Nano Letters* 4, 1279 (2004).

Outer Shell Determination of CdSe/ZnS

STEM and Electron energy loss spectroscopy (EELS)

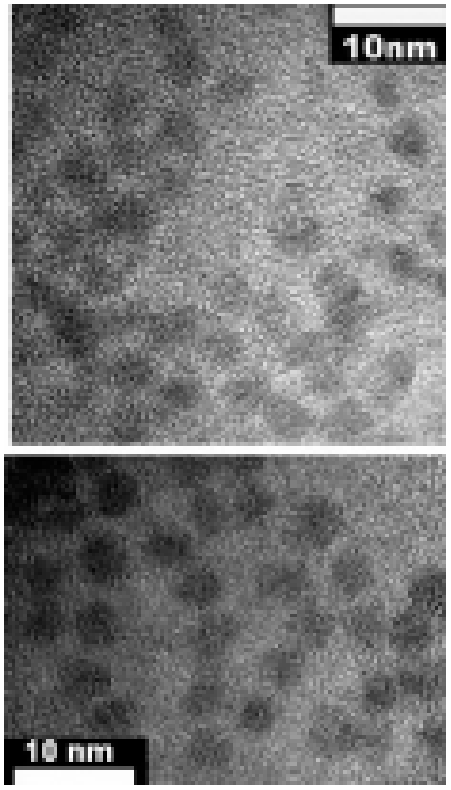


Z. Yu, L. Guo, H. Du, T. Krauss, J. Silcox, *Nano Letters* 5, 565 (2005)

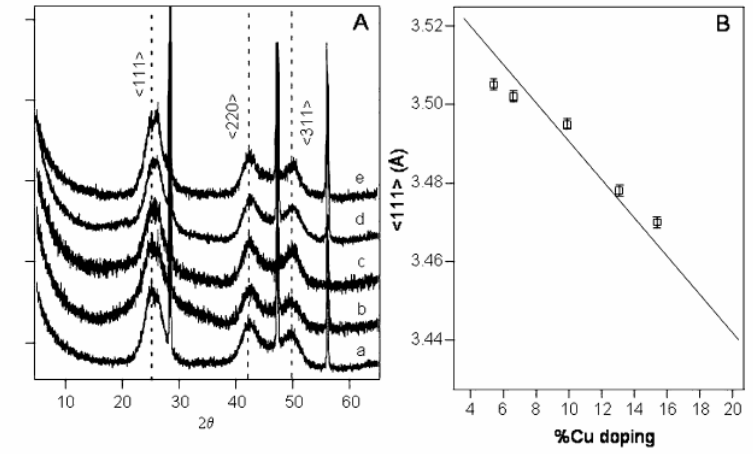
Cu-doped CdSe Quantum Dots

Powder XRD and Soft X-ray Absorption Near Edge Spectroscopy

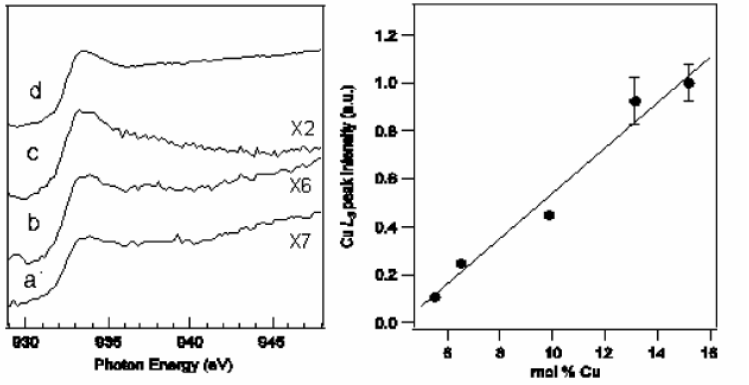
- **Oxidation state of Cu: Cu(I)**
- **Chemical environment of Cu**



<111> shifts to smaller *d* as Cu level is increased

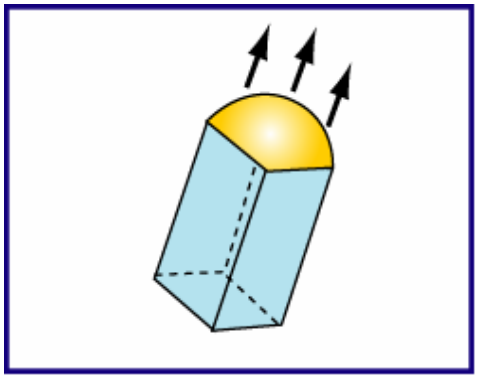


Cu *L*- edge p*eak* intensity prop to molar % Cu



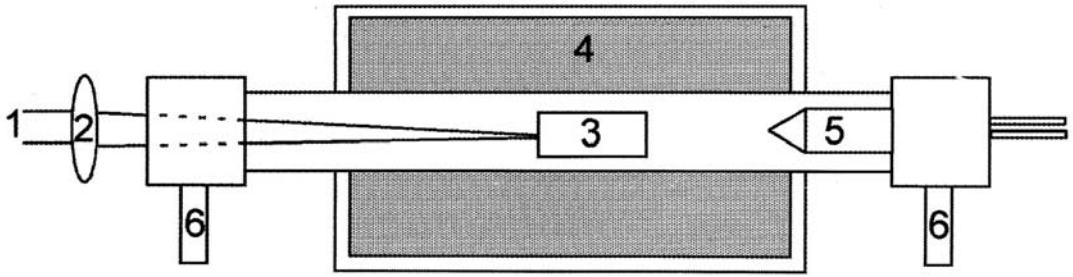
R.W. Meulenberg, T.V. Buuren, K.M. Hanif, T.M. Willey, G.F. Strousse, L.J. Terminello, *Nano Letters* 4, 2277 (2004)

One Dimensional (1D) Growth

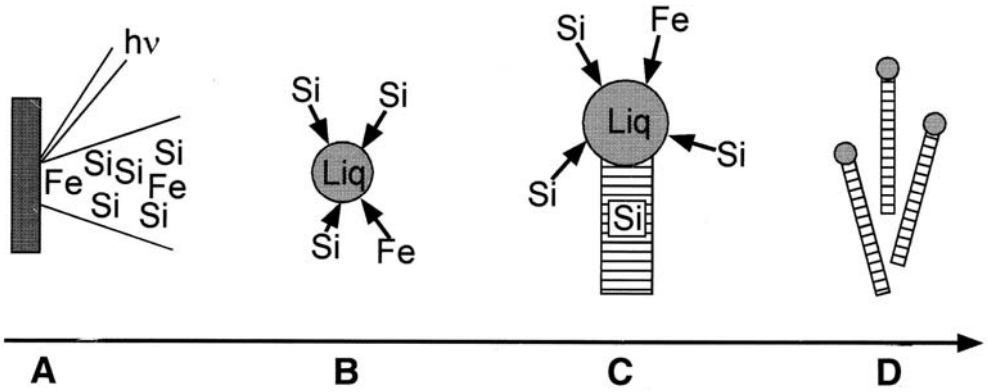


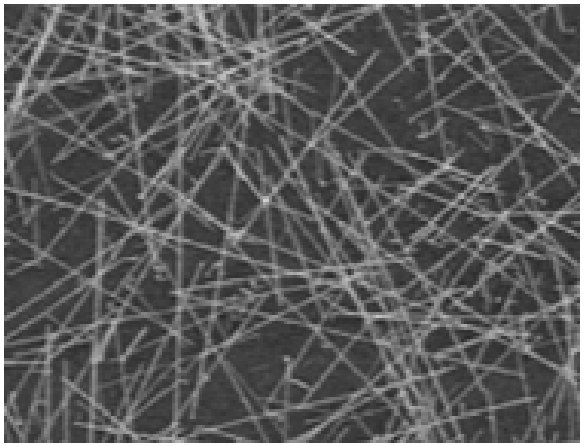
Adapted after Y. Xia et al., *Adv. Mat.* 15, 353 (2003)

Laser-assisted Catalytic Growth



(1) Pulsed laser; (2) Focusing lens; (3) Composite target; (4) Furnace; (5) Cold finger; (6) Pump system

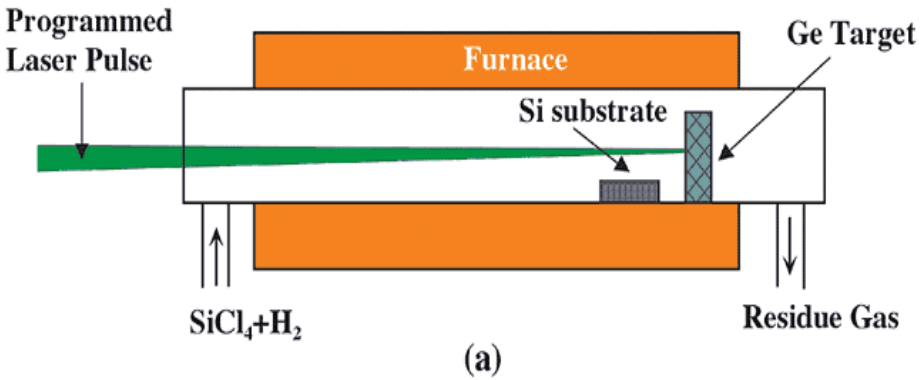


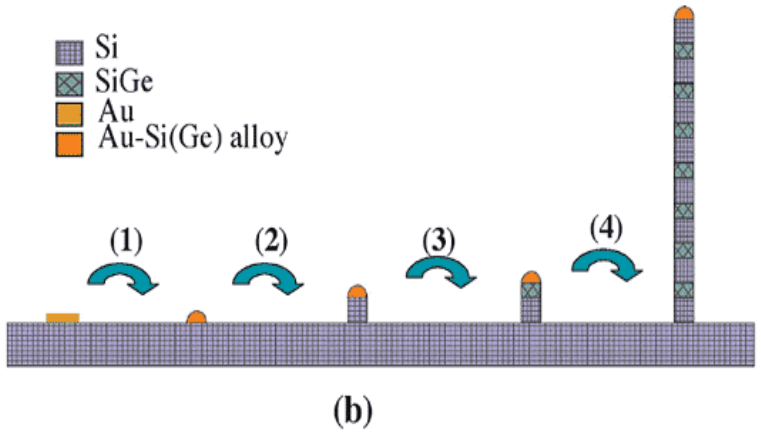


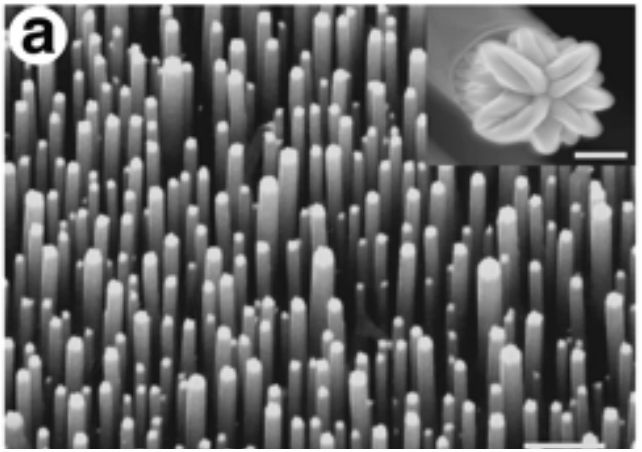
Examples: InP, GaAs, InAs (Au colloids); GaN (Fe colloids)

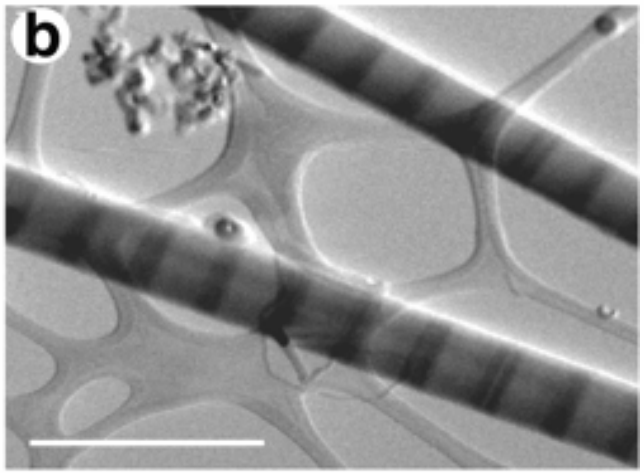
A. Morales, et al., *Science* 279, 208 (1998)

Laser-assisted catalytic growth + CVD



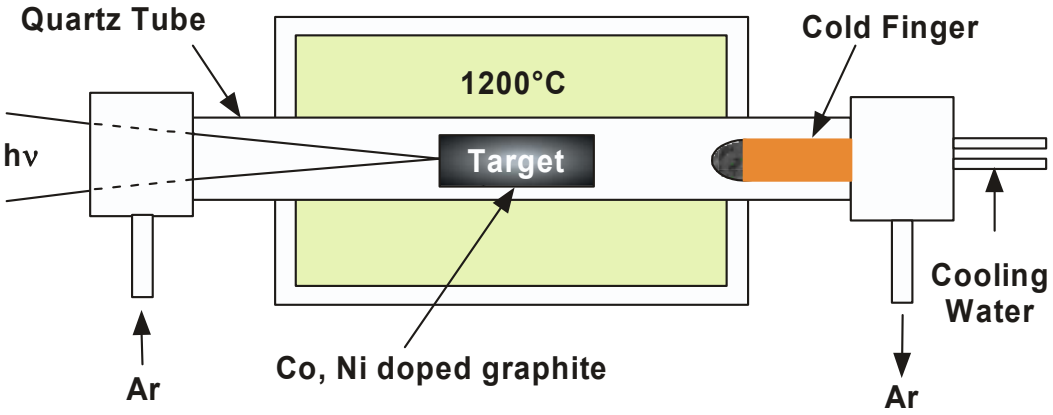


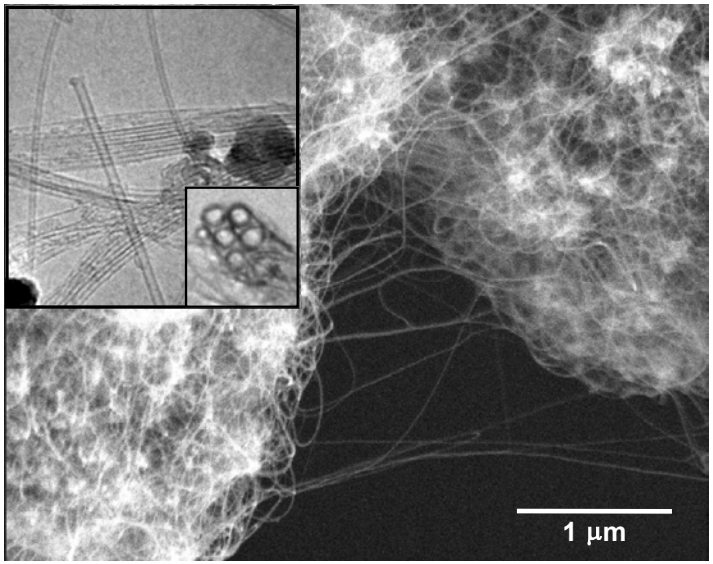




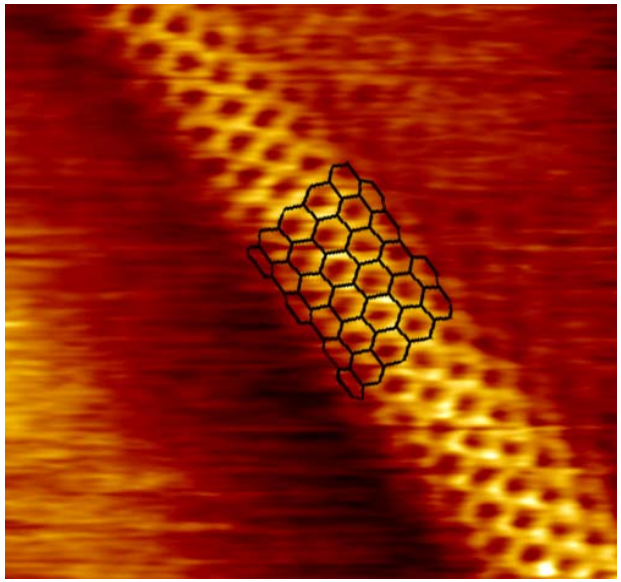
P. Yang, *Nano Lett.* 2, 83 (2002)

Laser Ablation of a Graphitic Target



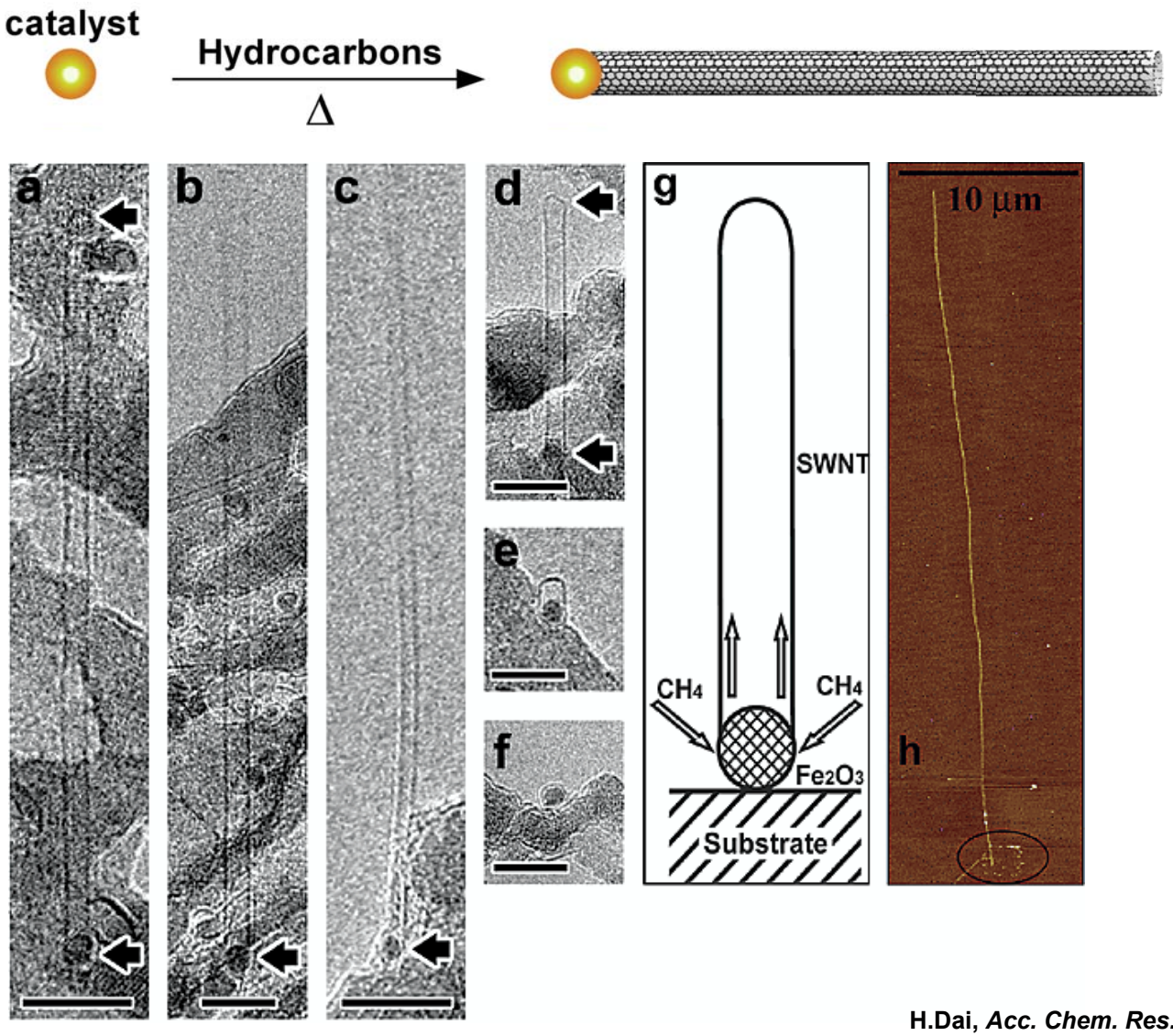


J. Hafner et al. *Chem Phys. Lett.* 296, 195 (1998).



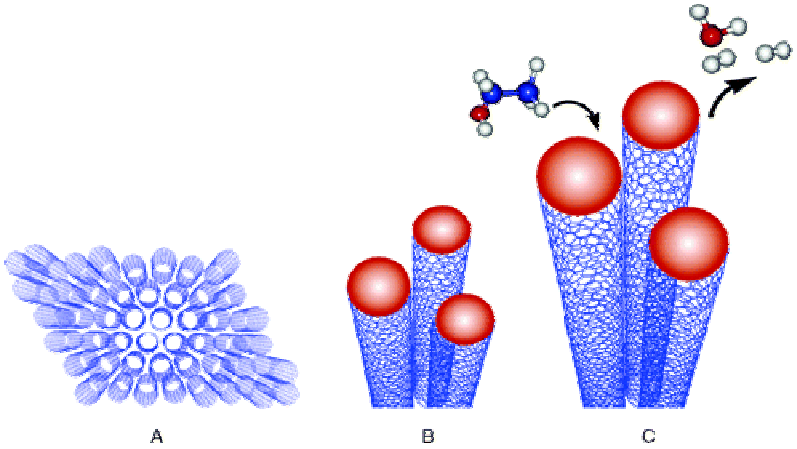
T.W. Odom, et al., *Nature* 391, 62 (1998)

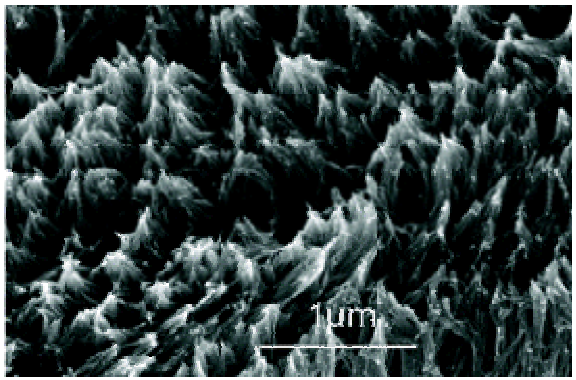
Chemical Vapor Deposition (CVD)



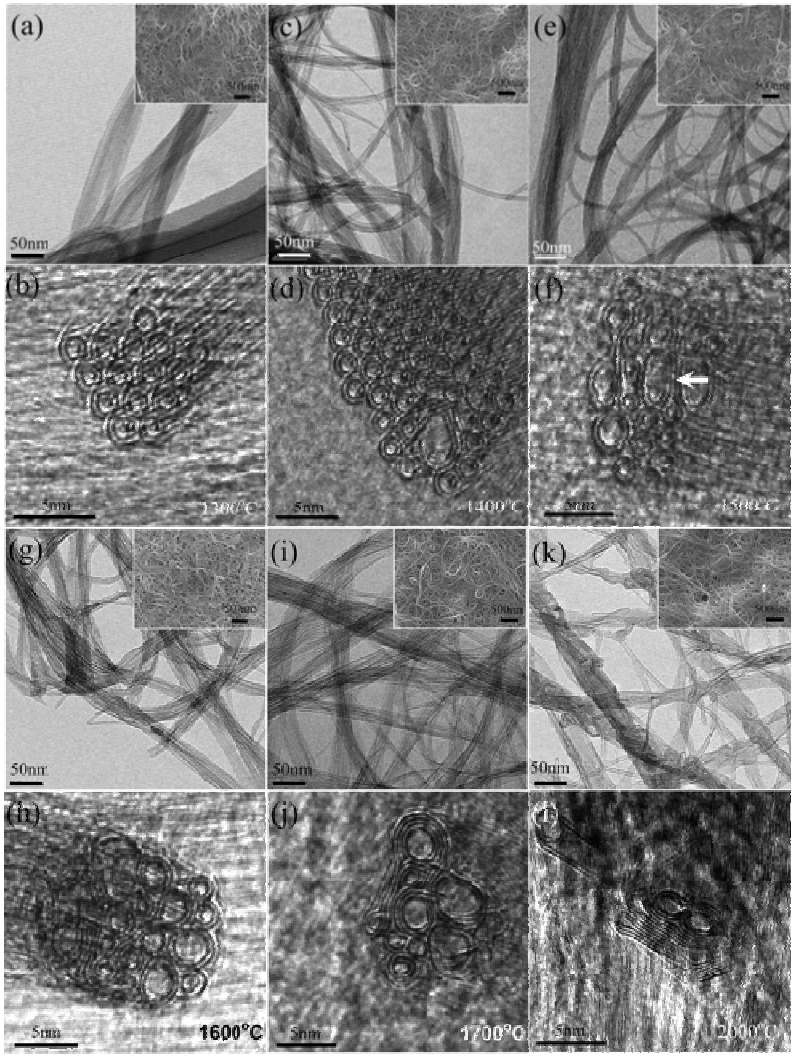
H.Dai, *Acc. Chem. Res.* 35, 1035 (2002)

Carbon Nanotube Growth and Defects





In-situ growth kinetics could enable chirality determination



Nano Lett., 5 (6), 997 -1002, 2005 *Nano Lett.*, 5 (6), 1099 -1105, 2005

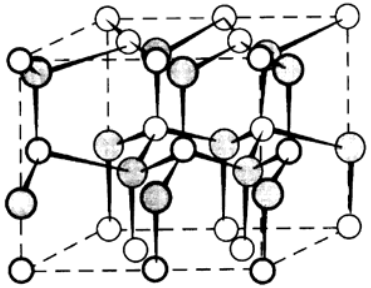
Nanocrystals Different from Bulk?

- Shape control of nanoparticles
- Surface coordination
- Different dimensionality

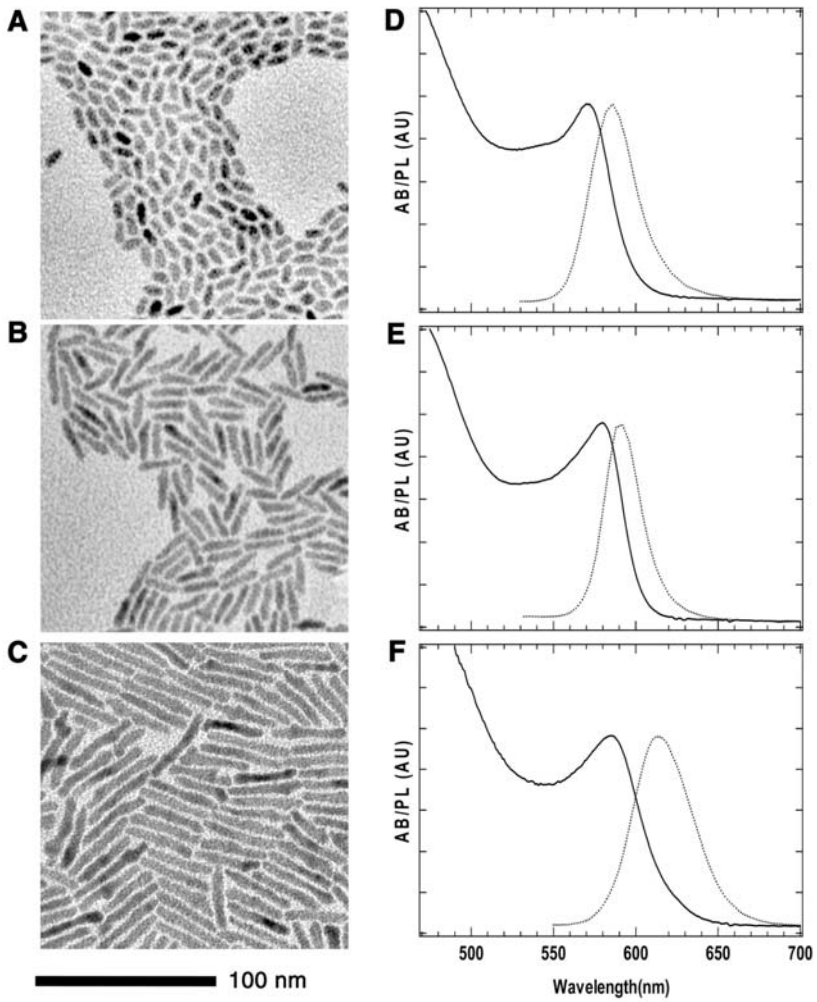
- Benefits of scattering methods
  - Surface chemistry (coordination)
  - Symmetry and dimensionality
    - Bond lengths
    - Bond angles
    - Degree of disorder

Shape Control of CdSe NCs

- Control of shape of CdSe using mixed surfactants (phosphonic acids with longer alkyl chains)
- Rapid growth of CdSe along the *c*-axis of wurtzite structure initially
- Strong Cd ligand necessary to maintain a high precursor concentration



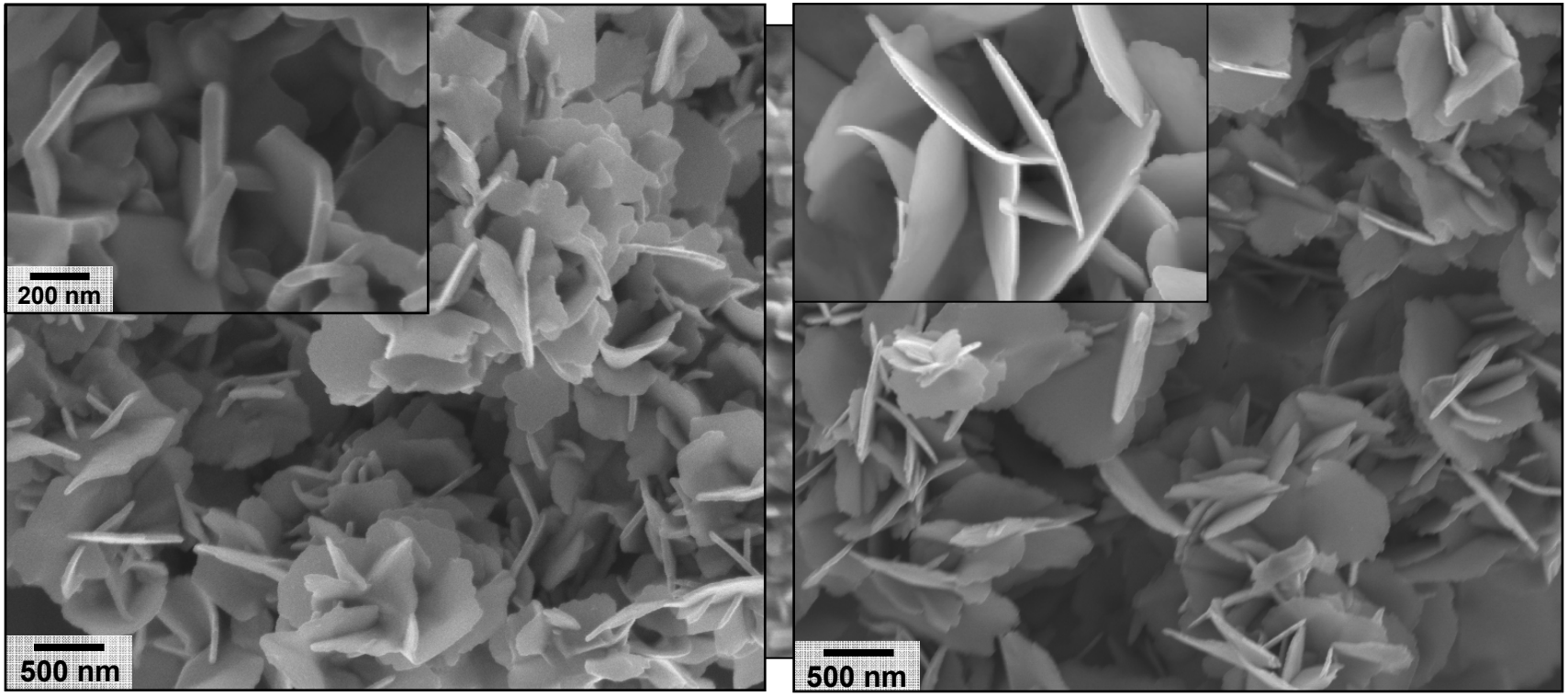
○ Cd ● Se



X. Peng, et al., *Nature* 404, 59 (2000)

Nanoscale $NbSe_2$ Materials

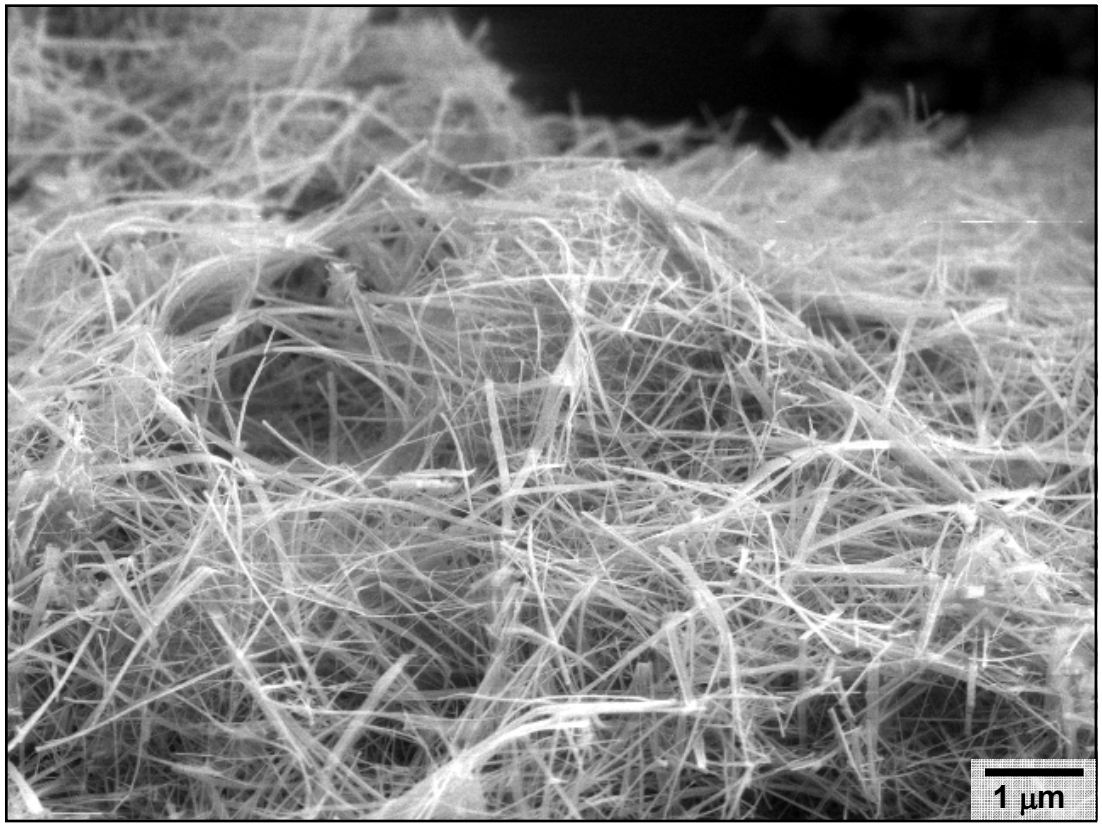
$NbCl_5$ + Se —(dodecylamine, 250 C)→ black solution —(extract)→ solid —(N_2, 450 C)→ $NbSe_2$



P. Sekar, E.C. Greyson, J.E. Barton, and T.W. Odom, *JACS* 127, 2054 (2005)

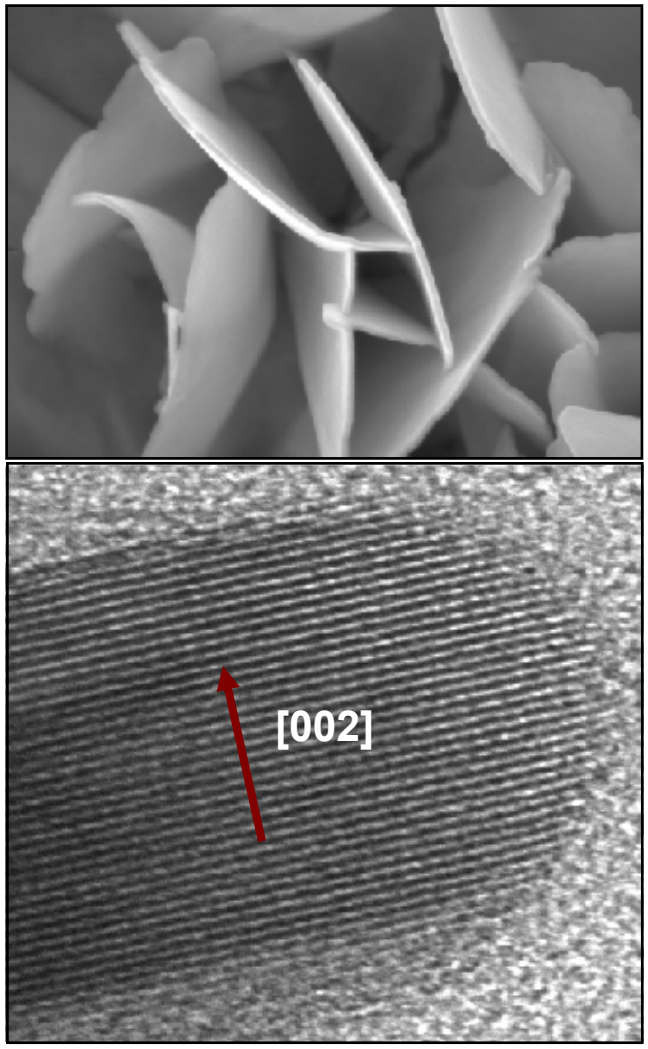
1D $NbSe_2$ Nanostructures

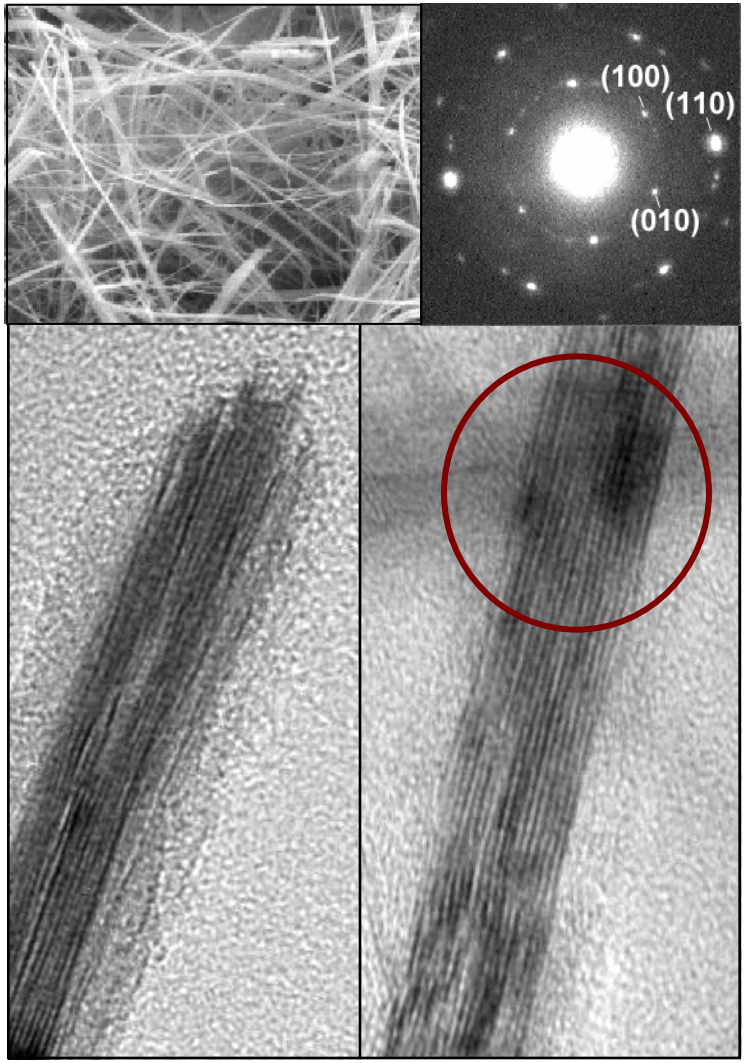
$NbCl_5$ + Se —(oleylamine, 280 C)→ black solution —(*quench at RT*)→ solid —(N_2, 450 C)→ $NbSe_2$



P. Sekar, E.C. Greyson, J.E. Barton, and T.W. Odom, *JACS* 127, 2054 (2005)

Crystalline $NbSe_2$ Nanostructures





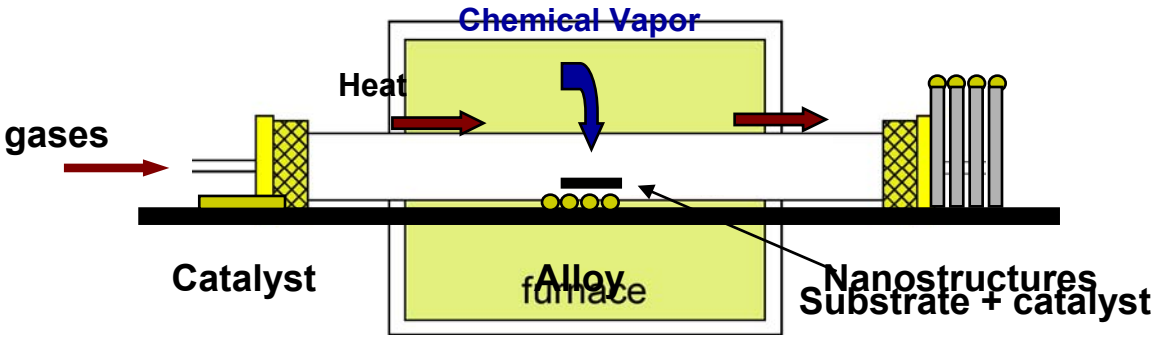
P. Sekar, E.C. Greyson, J.E. Barton, and T.W. Odom, *JACS* 127, 2054 (2005)

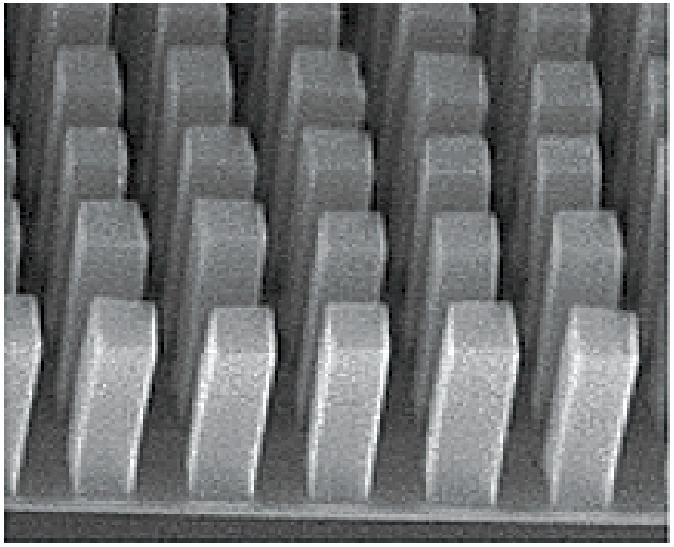
Nanostructures on Surfaces

- Directed growth methods
- Nanoscale patterning
- Scanning probe lithography
- Solution assembly of nanocrystals

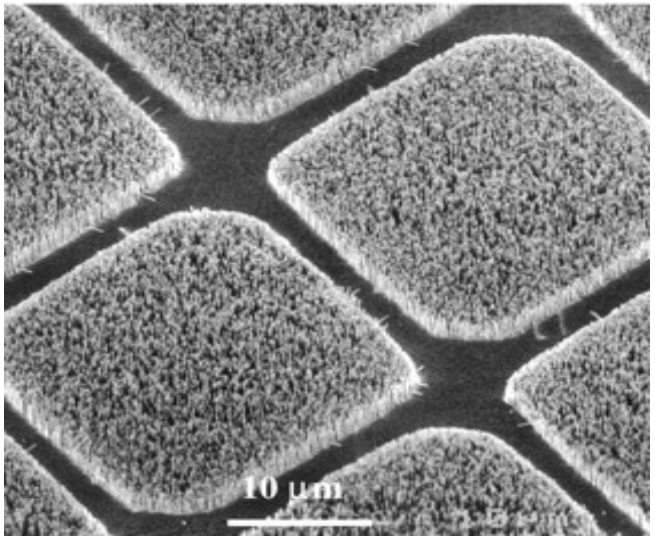
- Advantages of scattering methods
  - Particle distribution
  - Particle size
  - Interfaces
  - Local environment and packing

Directed Growth of Nanostructures



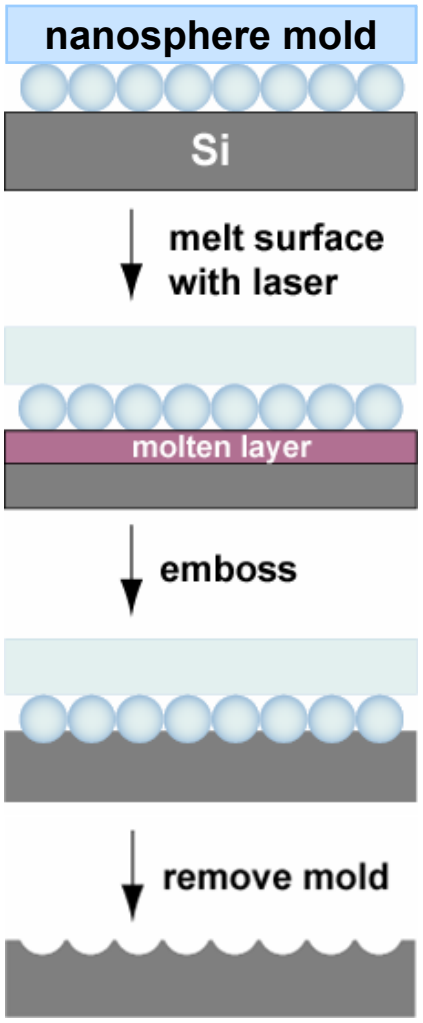


H. Dai (Stanford), *Acc. Chem. Res.* 35, 1035 (2002)

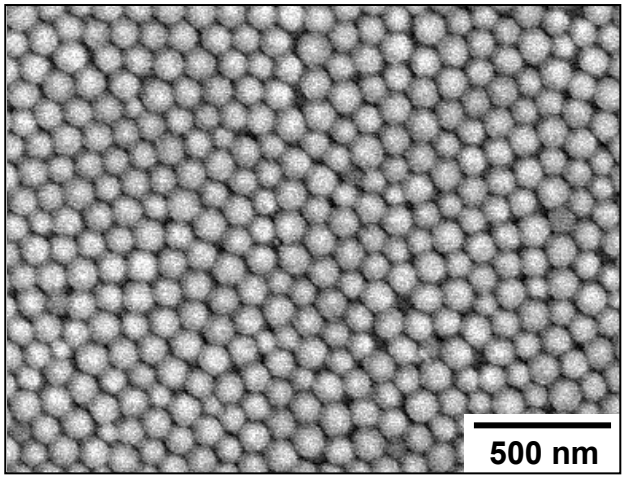


P. Yang (U.C. Berkley), *Science* 292, 1897 (2001)

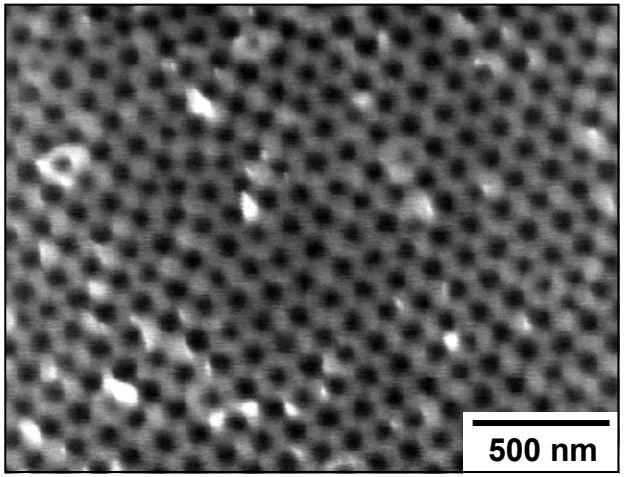
Laser-assisted Embossing



100-nm sphere mold

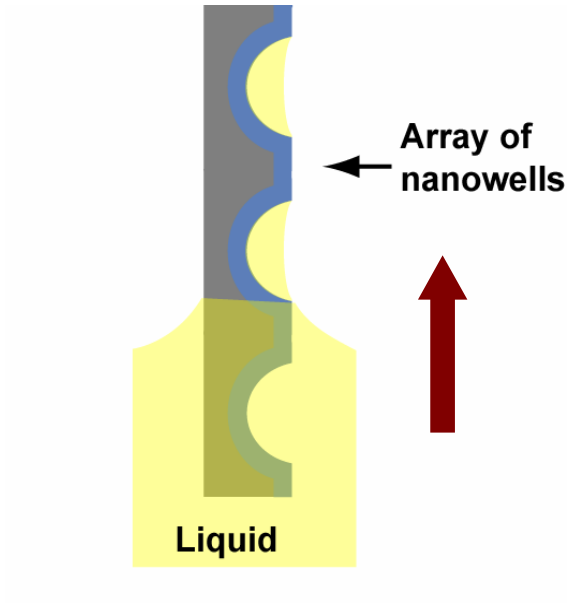


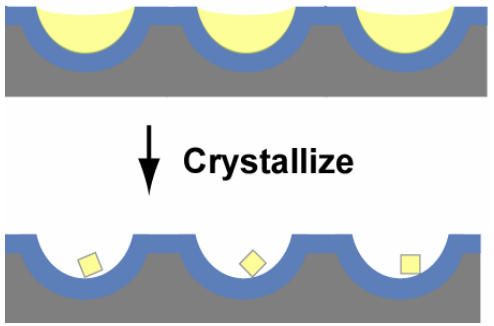
Silicon nanowells

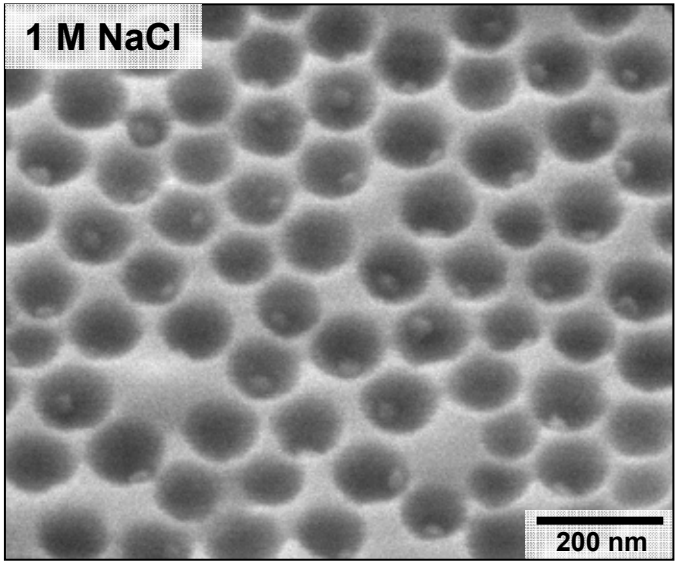


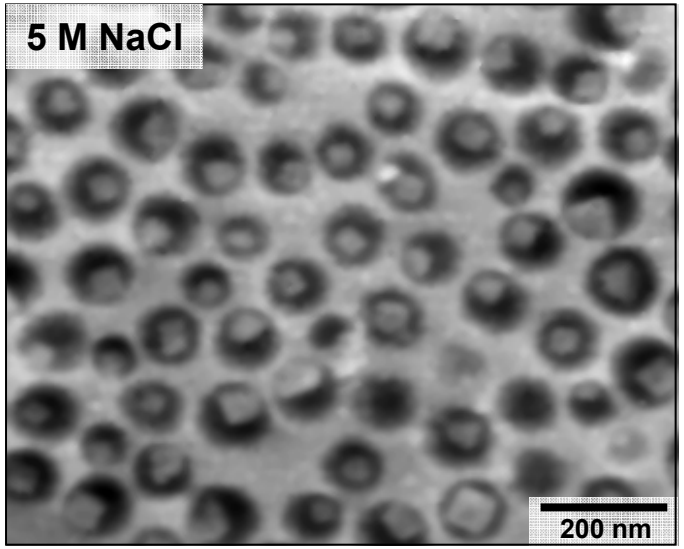
J.E. Barton and T.W. Odom, *Nano Letters* 4, 1525 (2004)

Size-selected Growth of Crystals



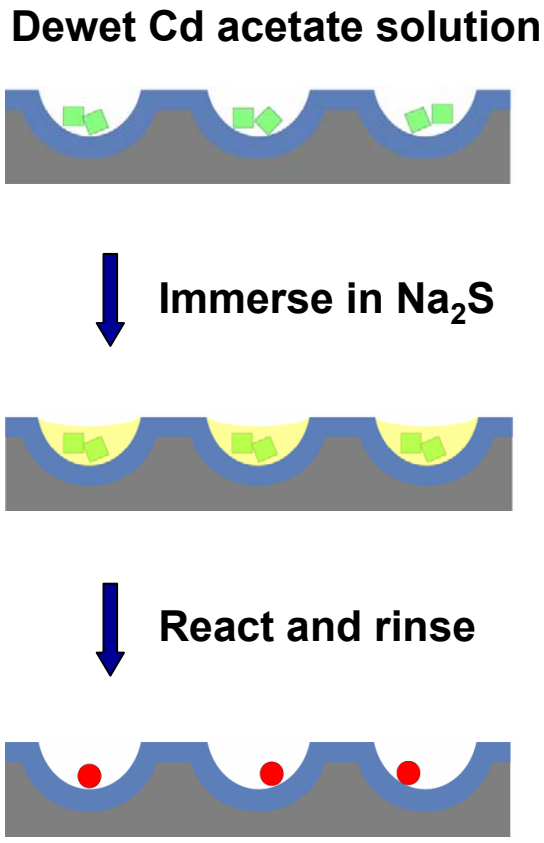


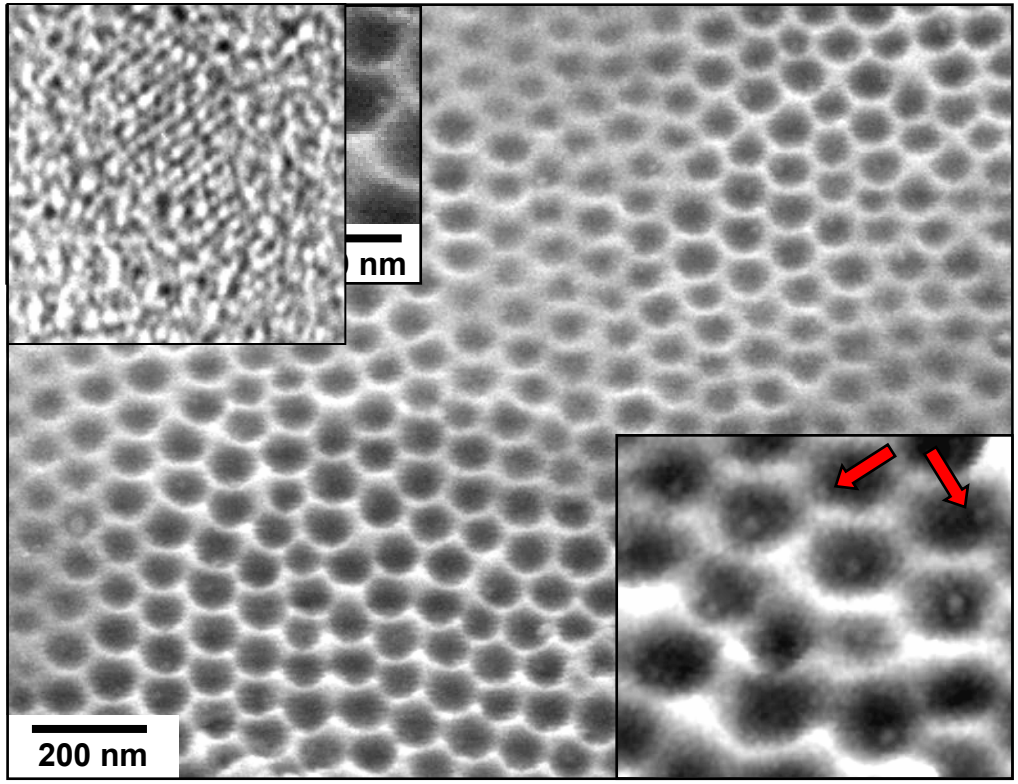




J.E. Barton and T.W. Odom, *Nano Letters* 4, 1525 (2004)

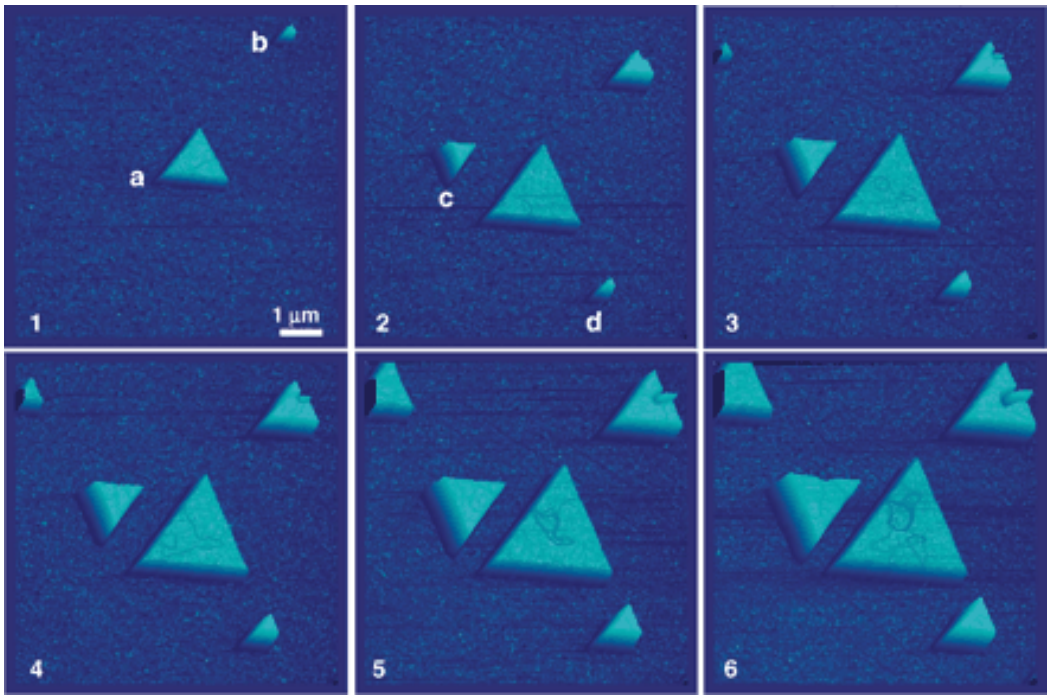
CdS Nanocrystal Growth in Nanowells

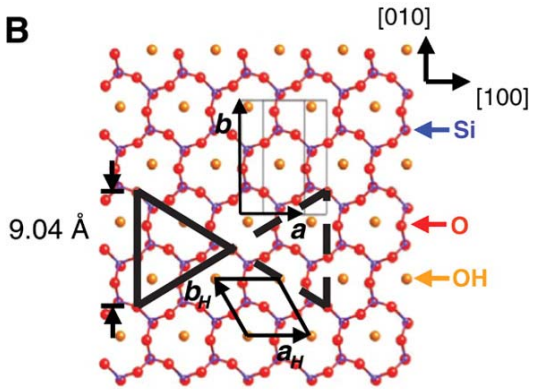


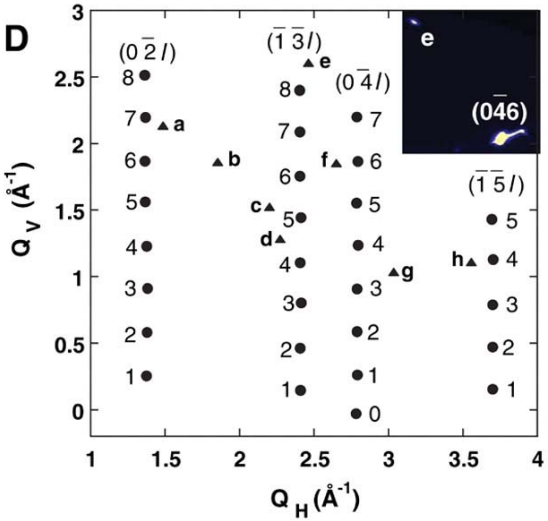


J.E. Barton and T.W. Odom, *Nano Letters* 4, 1525 (2004)

Poly-lysine Hydrobromide Microcrystals





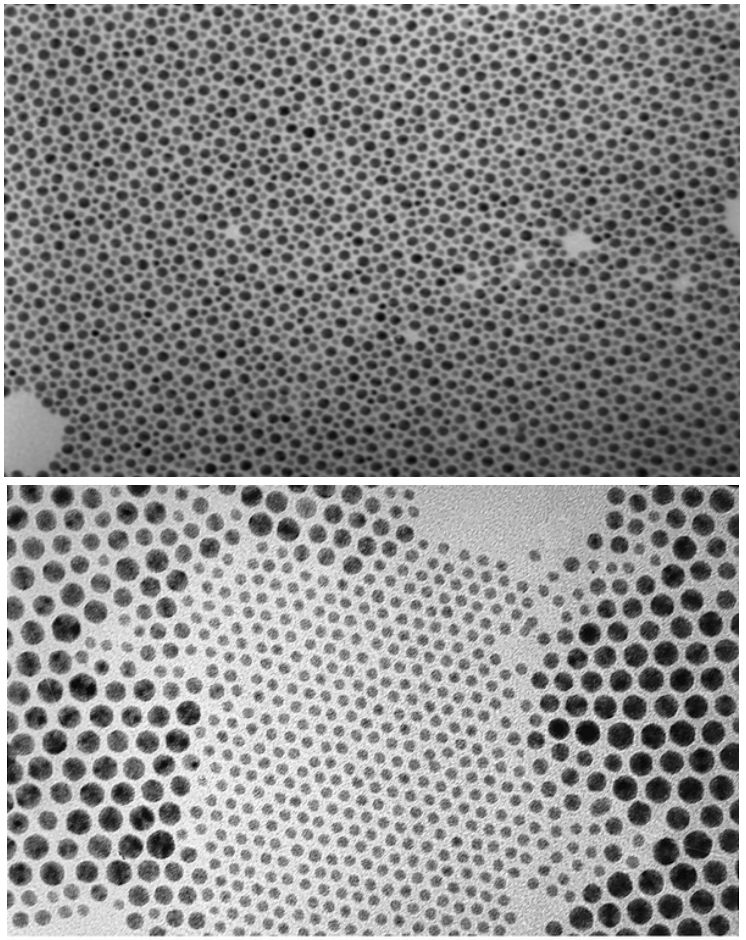


- Single crystal XRD ~ 100 μm^3
- Signal averaged over large area

C.A. Mirkin and M. Bedzyk, *Science* 307, 1763-1766 (2005)

Assembly of Binary Nanocrystals

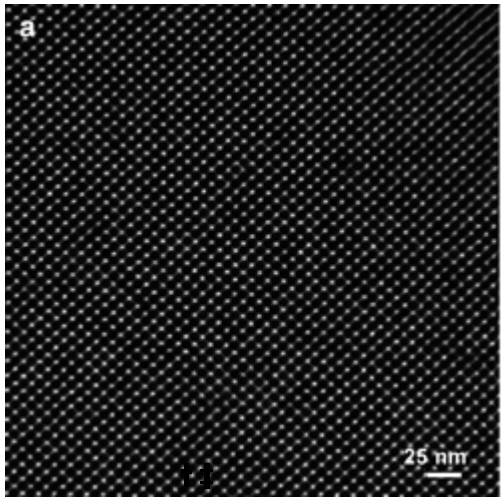
- **Thiol-stabilized Au NCs**
  - AB_2 phase forms with radius ratios ~0.58
  - 4.5 and 7.8 nm Au NCs
  - Phase-segregation with larger radius difference
- **CdSe NCs**
  - Solvent mixture (low-boiling point alkane and high-boiling alcohol)
  - Repulsive interaction between NCs remains until mixture evaporates



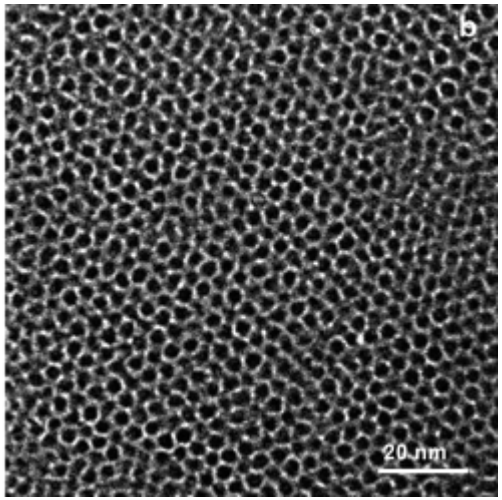
C.J. Kiely, et al., *Nature* 396, 444 (1998)

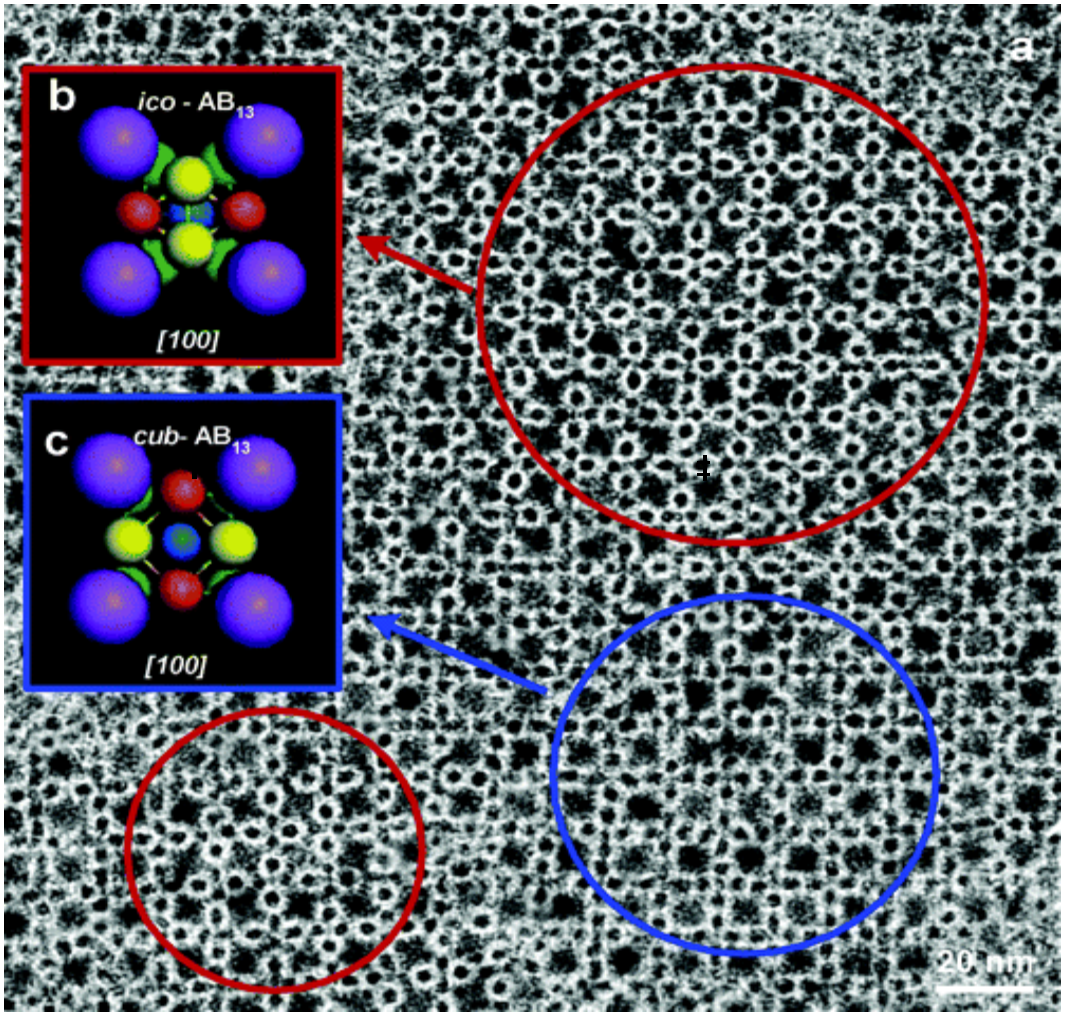
Polymorphism in AB_{13} NC Superlattices

5.8-nm PbSe



3.0-nm Pd





E.V. Shevchenko, D.V. Talapin, S. O'Brien, C. B. Murray, *JACS* ASAP (2005)

Summary and Outlook

Common Tools

- Electrons as probes
  - SEM
  - TEM
  - EELS
- X-rays as probes
  - PXRD
  - XPS
  - XANES
- Results
  - Size, shape
  - Elemental analysis
  - Coordination
  - Crystallinity

Wish List

- STEM with x-rays
- Reduced beam size
- Important NS problems
  - NS distribution and size
  - In-situ growth kinetics and energetics
  - Individual nanocrystals
  - Assemblies of NSs
  - Crystallinity of interfaces and surfaces
  - Bond angles and lengths
  - Imbedded defects

The "So What" Question

- **If these challenges are overcome …**
  - **Controlled structure and properties**
  - **Increased control over design**
  - **Improved monodispersity of product**

- **Move beyond "passive nanostructures"**
  - **Active nanostructures with tailorable soft and hard components**
  - **Control of packing and functional assemblies of nanostructures**
  - **3D architectures and formation of *systems***

Odom Group Members

FUNDING

Start-up Funds, NSF NSEC, NSF NUE, NASA, IBNAM, ACS PRF-G, Research Corporation, Packard Foundation, NSF CAREER,
Sloan Foundation, DuPont Young Investigator Award, Cottrell Scholar Award