Nanoscience in Adolescence

George M. Whitesides

Department of Chemistry and Chemical Biology

Harvard University

gwhitesides@gmwgroup.harvard.edu

Change: Where does it come from? What Is Invention? Innovation?

- The "tea-kettle problem:" Why is the water hot?

Where does change come from?

•The "tea-kettle problem:" Why is the water hot?

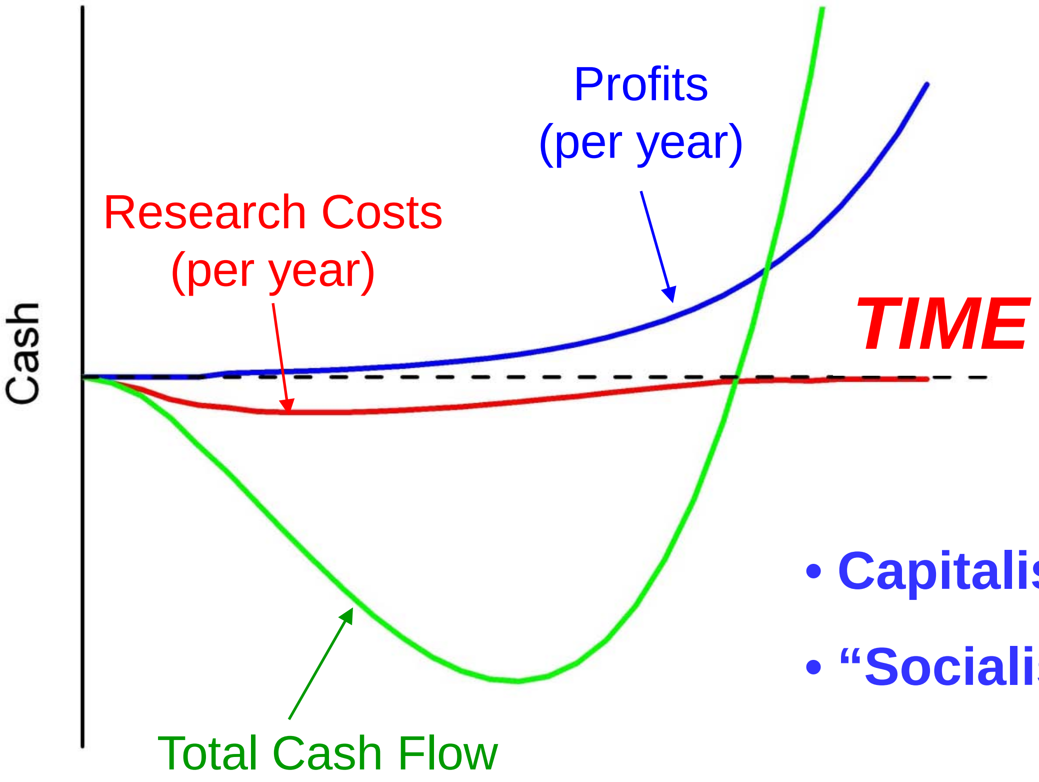
- The kinetic energy of the water molecules is high (scientific)
- The kettle was on the stove (historical)
- Because I wanted tea (intentional)

"What *is* innovation?"

How does a business exploit a new idea?

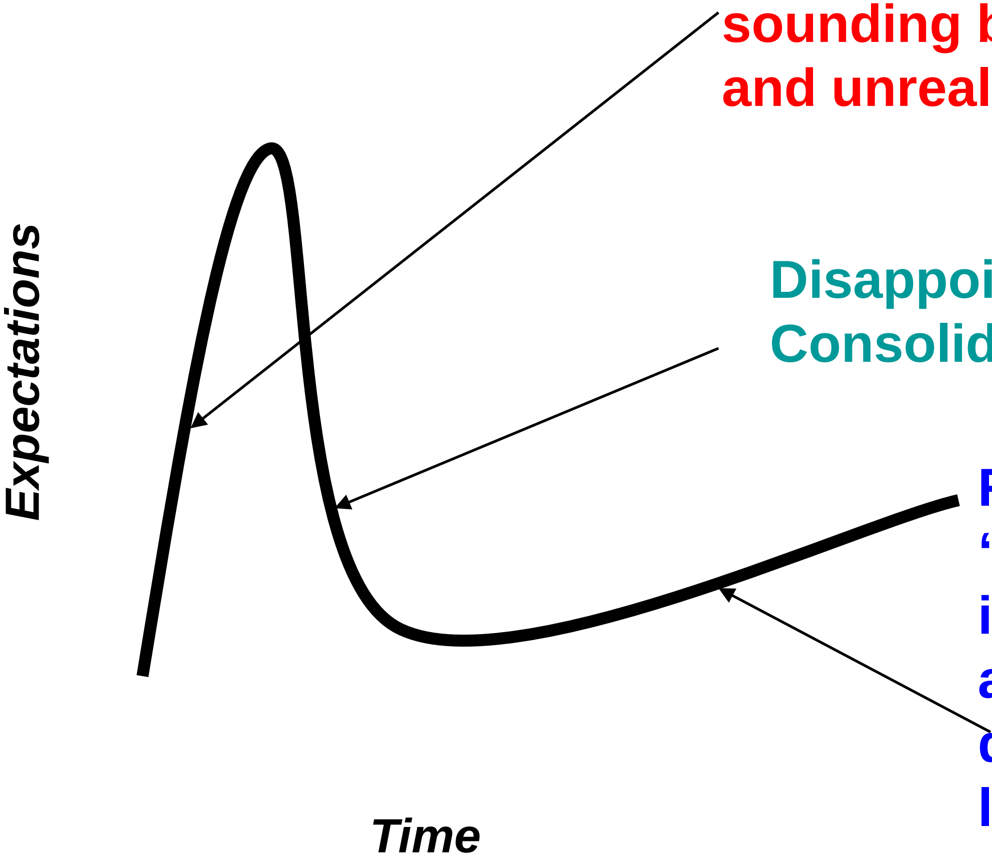
- **Inventing fundamentally new products (U.S.)**
- **Developing *better* products, and engineering *better* ways of making them (Europe, Korea, Japan)**
- **Using inexpensive labor and low-cost capital to make lowest-cost products (China, India)**

The Capitalist Window on Change: Time and Risk-Discounted Cash Flow



- Capitalist?: Financial Return
- “Socialist”?: Social Return

All New Technologies: *A Short, Qualitative History*



Exaggerated expectations: exciting-sounding but irreproducible results and unrealistic claims.

Disappointment and (Over) reaction; Consolidation

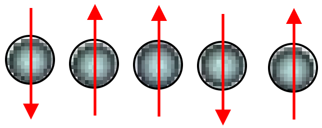
Return to fundamentals; “discovery” and “science” in addition to technology and applications; development of new tools; large applications and real commercial investment.

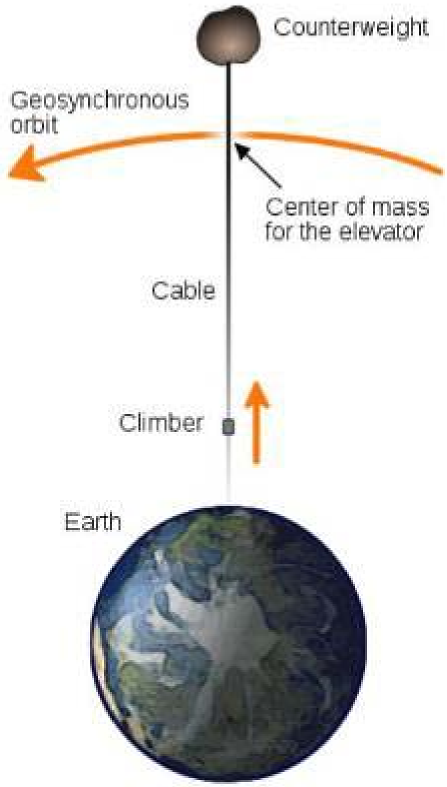
Take-home (*my* opinion) for Nanoscience and -technology*:* Past History, Future Opportunity

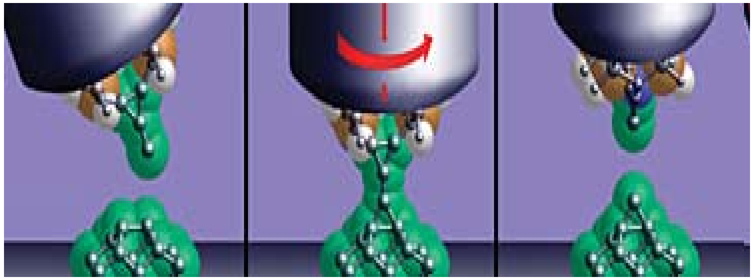
- **Past: Structure**
- **Future: Function (*aka:* jobs and competitiveness)**
  - **Support for nanoelectronics and information tech.**
  - **Commodity Infrastructure: energy, water,**
  - **Heterogeneous Catalysis**
  - **Environment: CO_2, albedo management, …**
  - **Biomedicine: fundamentals of functional structures, imaging, plants**
  - **Bioanalysis; nanotoxicology**

At the Beginning: Expectations for Nano

- **Applied Quantum Phenomena**
  - **- Quantum computing**
- **Futurist Speculations**
  - **- Nanobots; The Assembler**
- **Revolutionary Materials**
  - **- Buckytubes and the space elevator**
  - **- Quantum Dots**
- **Revolutionary electronics**
  - **- Single-molecule transistors**
  - **- Ultradense computers**
- **Biomedicine**
  - **- "Nanotherapeutics"**
- **Risks:**
  - **- Nanobots, etc**
  - **- Nanoparticle Toxicology**





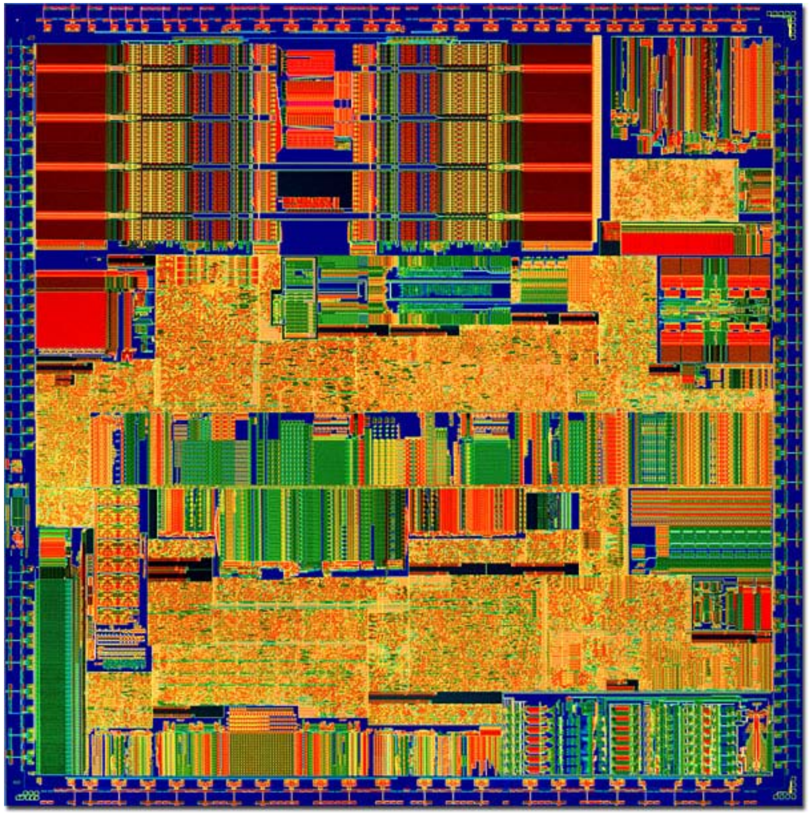


Drexler *C&EN* **2003**

What *is* “nanoscience/technology”?

- ***No universal definition***
- **Dimensions are “small” (< 50 nm? < 20 nm?). In popular terms “too small to see” (< 10 µm)**
- **“Between molecules and macroscopic matter”**
- **New properties, especially room-temperature quantum behavior (quantum dots)**
- **Classical technology, but smaller than current technology**
- **“What I do” (whatever that is)**

Nano*technology* is *here and highly developed:* Integrated circuits, memory, . . .



Current best commercial CMOS technology has 22- to 40-nm design rules

“End of Moore’s Law” may be as small as < 10 nm

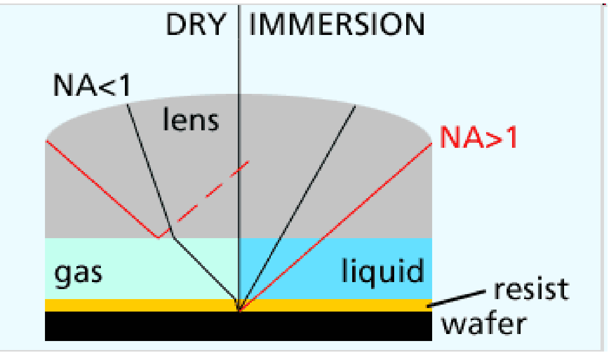
(“Small” is no longer the problem: heat dissipation, power management is. Leakage, etc soon will be.)

New properties of materials (e.g., phase change, electron polarization) may be more interesting than “small”

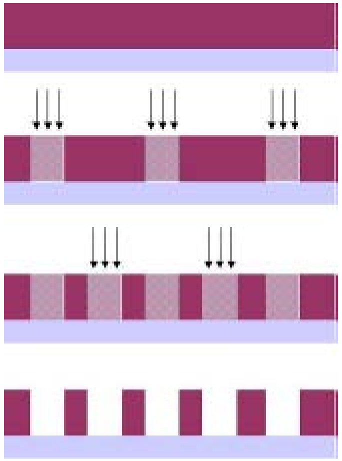
Reality: *Evolutionary* nanoelectronics will extend to 8 – 40 nm (expensively) using light

- **Reality is almost unbelievable technological development**

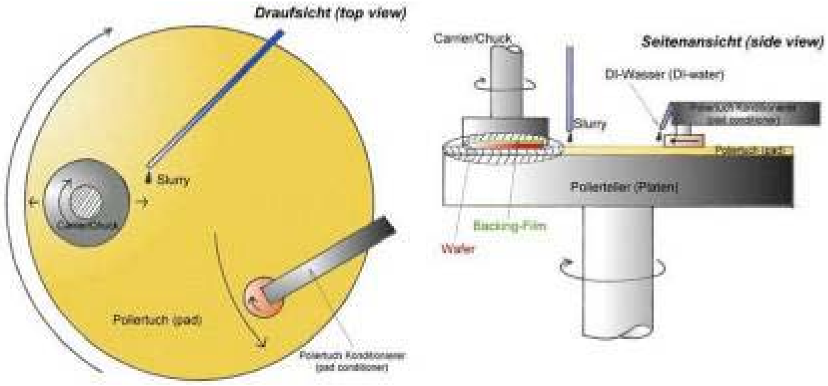
Phase-shifting masks



Fluid immersion



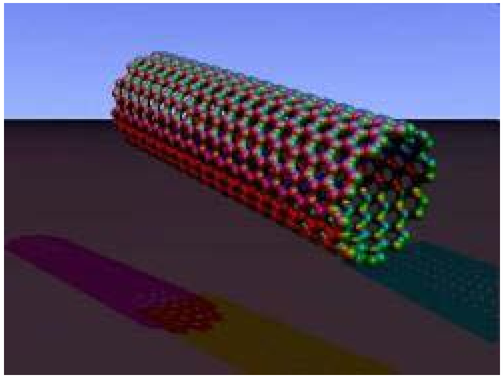
Dual exposure



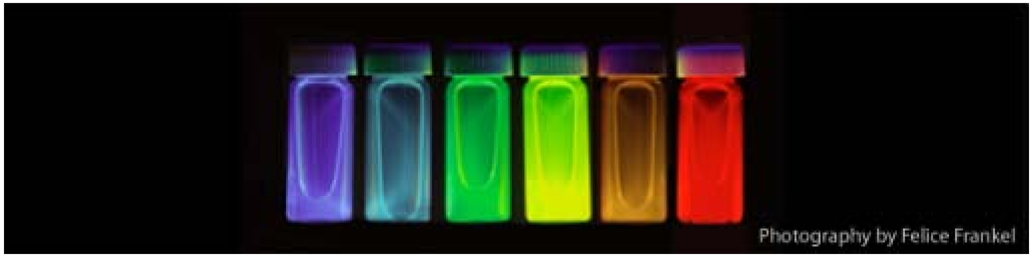
Chemical mechanical polishing

Reality: New materials, but slow development of applications

- Buckytubes and maybe Graphene

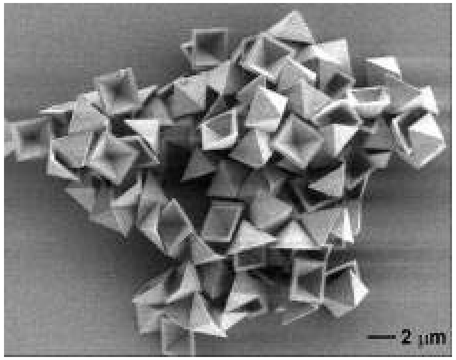


- Quantum dots



M. Bawendi

- Other small particles



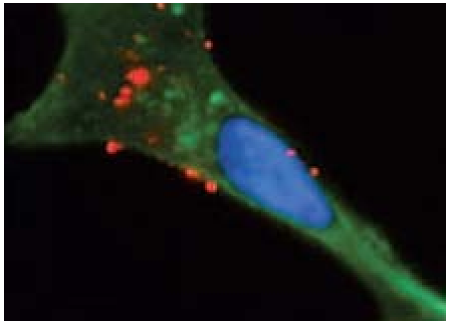
Xu et. al. *Nano Lett.* **2004**

- (Nanoscale matter: grains, Interfaces, Debye layer, etc.)

Reality: Biomedical--Progress, but focused on conventional "high-technology" model

Medical Diagnostics

- Labeling
- Imaging
- Analyzing



Therapy

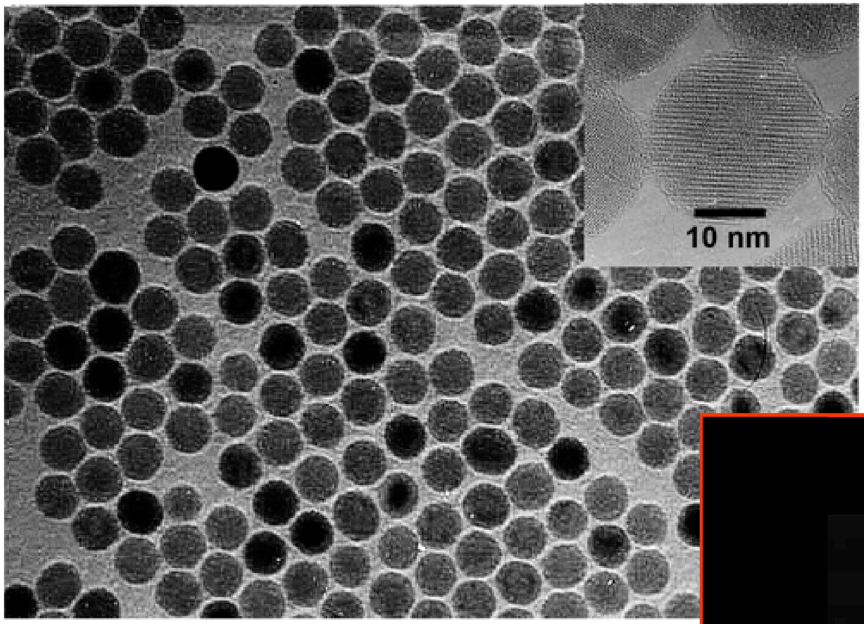
- Hydrophobic Nanoparticles
- Transportation
- Controlled Release

Carbon nanotubes
Quantum dots
Magnetic nanoparticles
Metal nanoparticles

Challenges

- Volume-, tissue-, or cell-specific targeting
- Remote guidance and activation
- Safety Issues - biocompatibility and toxicity

Nano*particles*: MRI Contrast Agents



MRI = magnetic resonance imaging

Magnetite
T. Hyeon
Seoul National Univ.

A number of areas are approaching reality

- Buckytubes; graphene for electrically conductive plastics, perhaps electrochemical storage
- Low-cost methods of nanofabrication: printing, molding, others for consumer electronics, photovoltaics
- Optical systems for new optical effects, solid-state lighting, displays
- Nanoparticles/rods/cups/whatever with defined shapes for barcoding/tracking; delivery of hydrophobic drugs
- Nanometrology for industrial processing

Some Current Areas of Research: Examples in Fabrication

- Printing/molding
- Phase-shifting lithography
- 3D structures and Self-assembly
- Nanoskiving
- Holes
- Optics

Nanofabrication: Unconventional Approaches

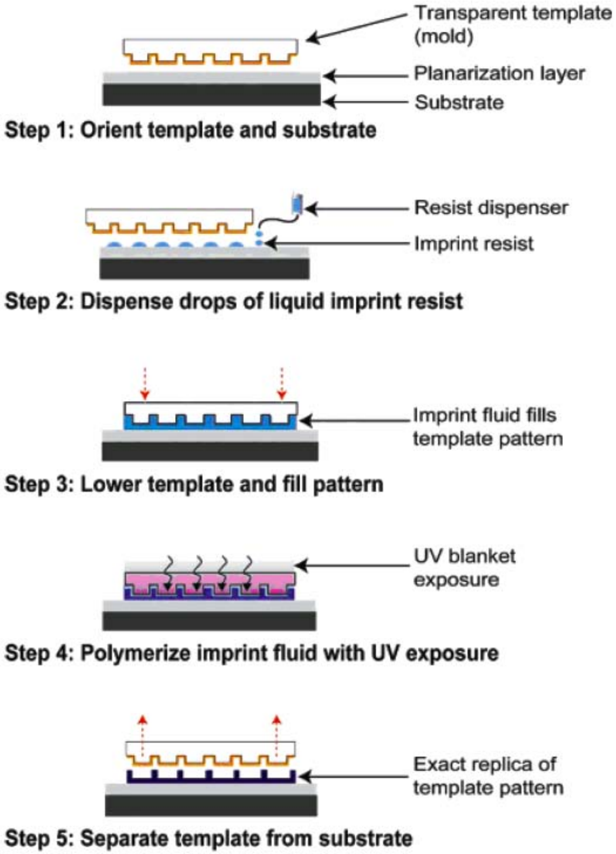
- **Many applications require methods alternative to e-beam and photolithography: Lower cost and different attributes**

  - Circumventing diffraction limits in photolithography
  - Nontraditional materials & substrates
  - Reducing cost (capital and operating)
  - Increasing access (e.g., “dirty cleanroom” technology)
  - 3D, curved surface, flexible etc structures

Molding & Printing

- Replace "mask" with "stamp" ("proximity" → "contact")

Step-and-flash nanoimprinting

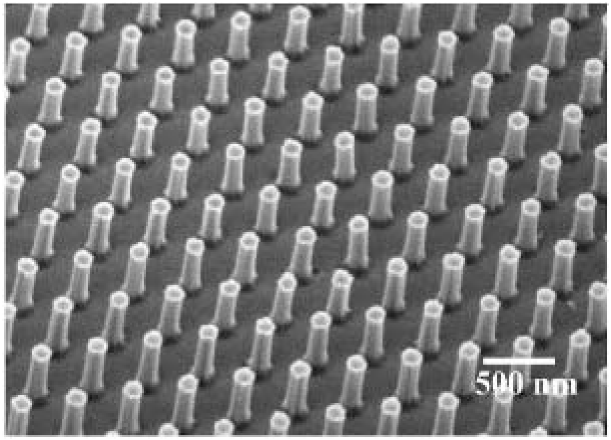


Willson & coworkers *Macromolecules* **2008**

Isolated particles w/ low-γ_{SL} stamp

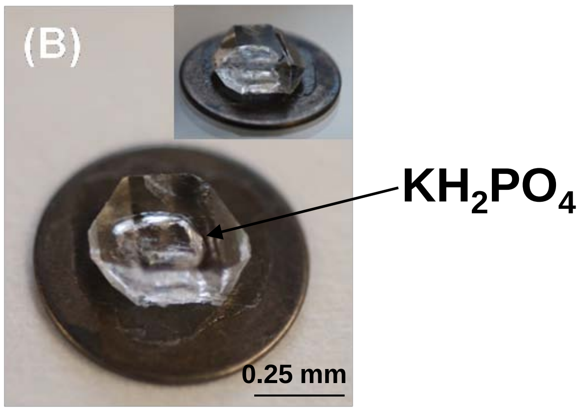
DeSimone & coworkers *JACS* **2005**

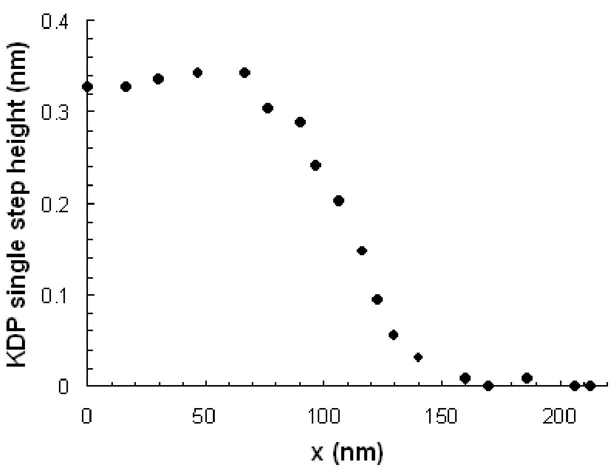
Discrete TiO_2 pillars

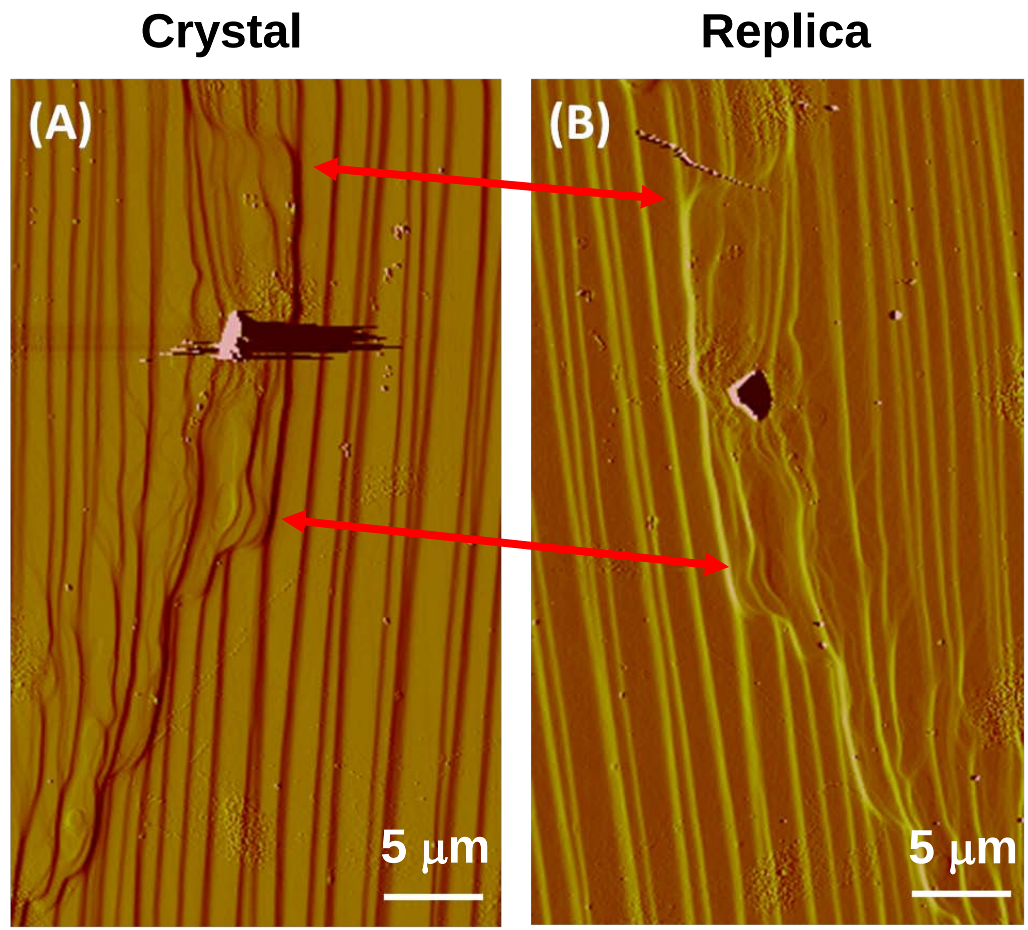


DeSimone & coworkers *Adv. Mater.* **2008**

KDP Crystal Replica Molding: Replication of Single Layers of Ions. Metrology?

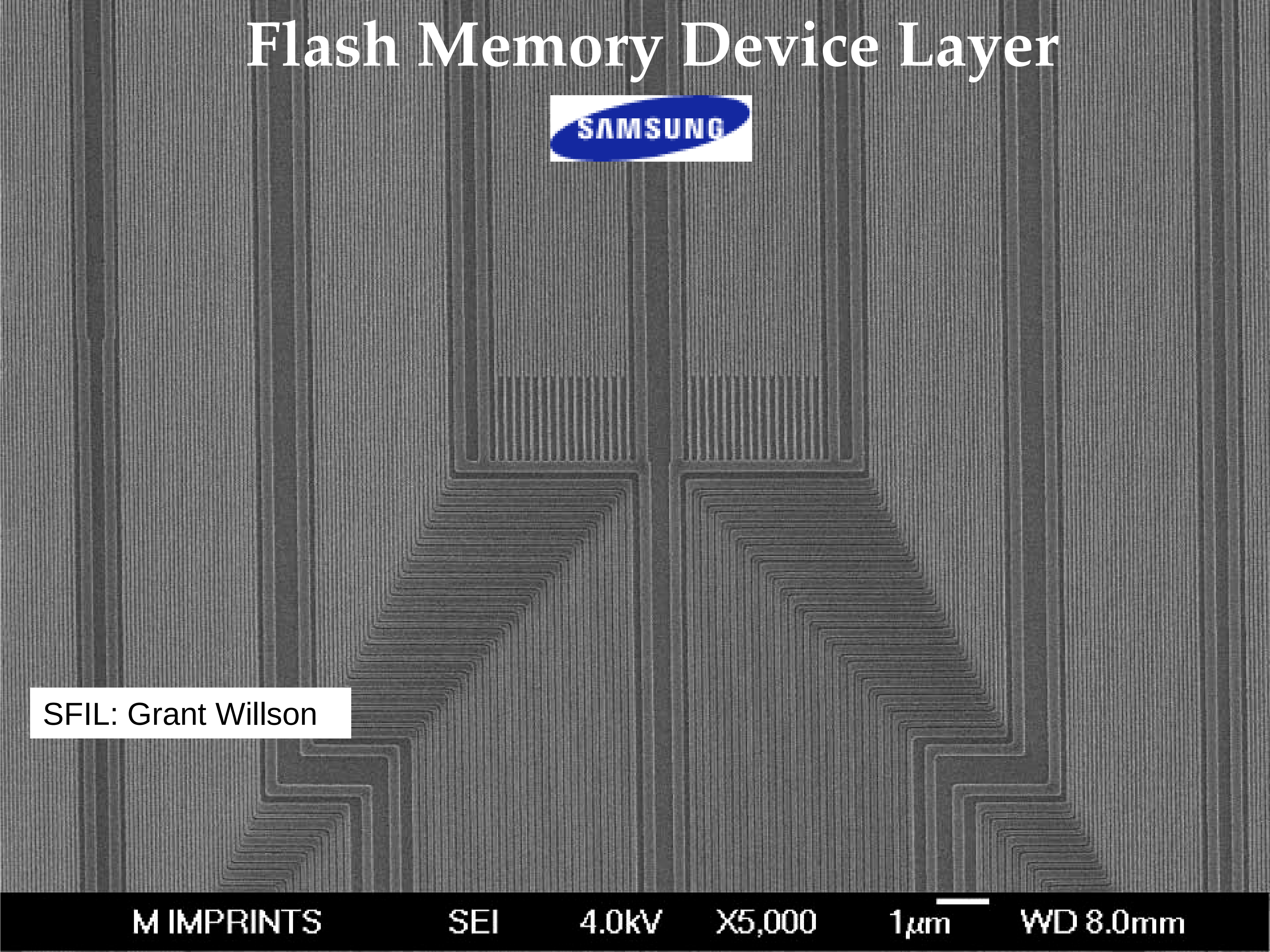






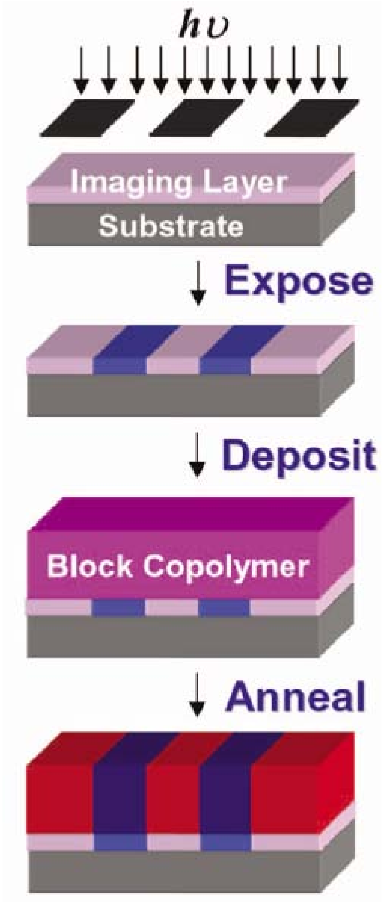
"Macro steps" 5-15 nm in height,
from the bunching of ~10-40 atomic steps

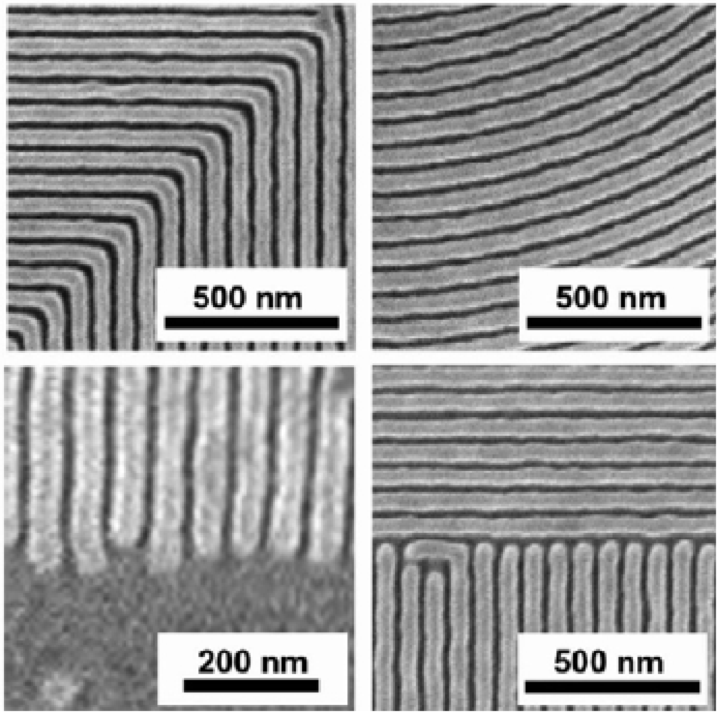
Flash Memory Device Layer



Phase-Separated Copolymers

- Use photo-generated chemical patterns to direct block copolymer morphology





Stoykovich & Nealey *Mater. Today* **2006**

• Circumvents diffraction limits: physics limit < 0.01 nm; chemistry limit (granularity of matter) not understood

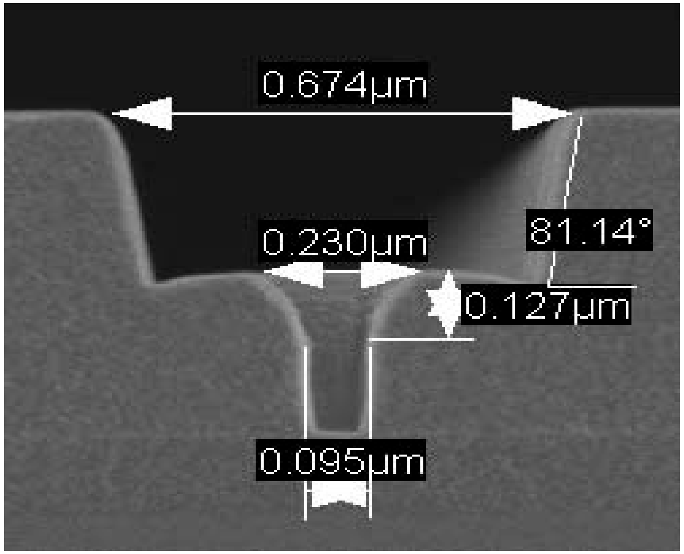
• Anomalously *high* resolution (<0.5 nm on open benchtop)

• 3D; eliminate process steps

• potential for roll-to-roll manufacturing: *radical* reduction in costs

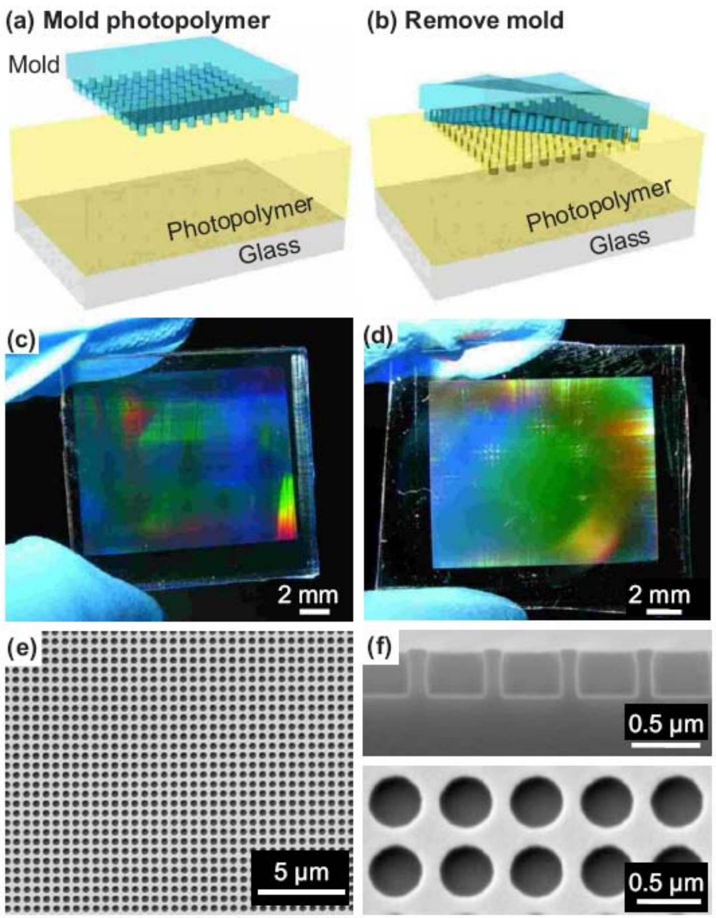
• non-planar surfaces (soft lith; stretchy silicon)

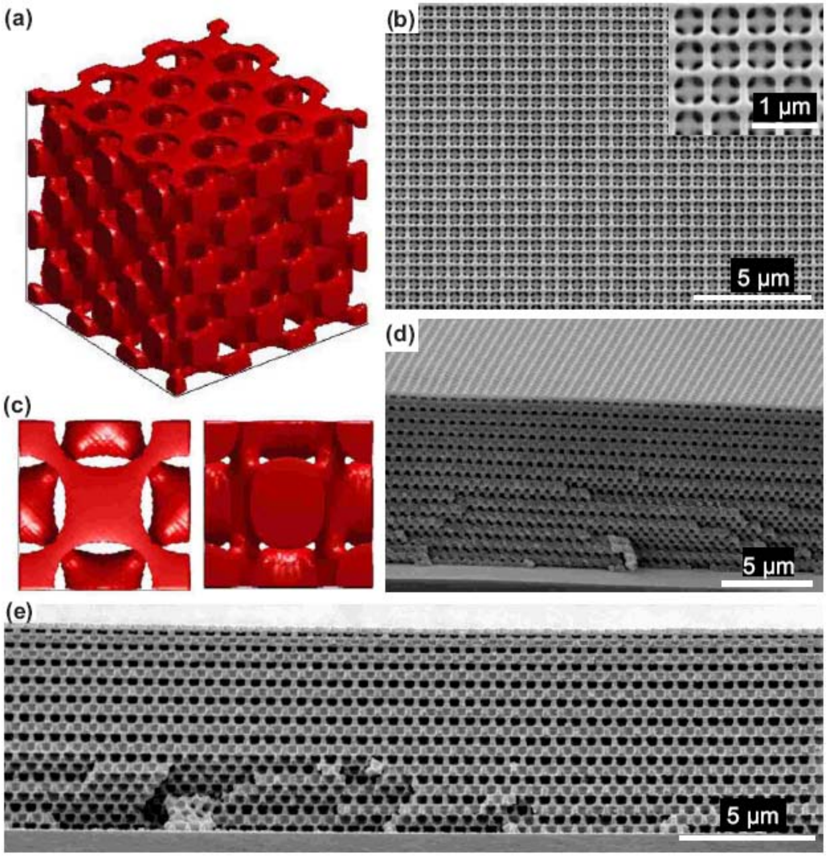
If this works, it saves more than 100 unit process steps from the manufacturing of a modern microprocessor and provides a cost saving of 20-50% (per Infineon and SEMATECH. And Willson)



3D Nanostructures

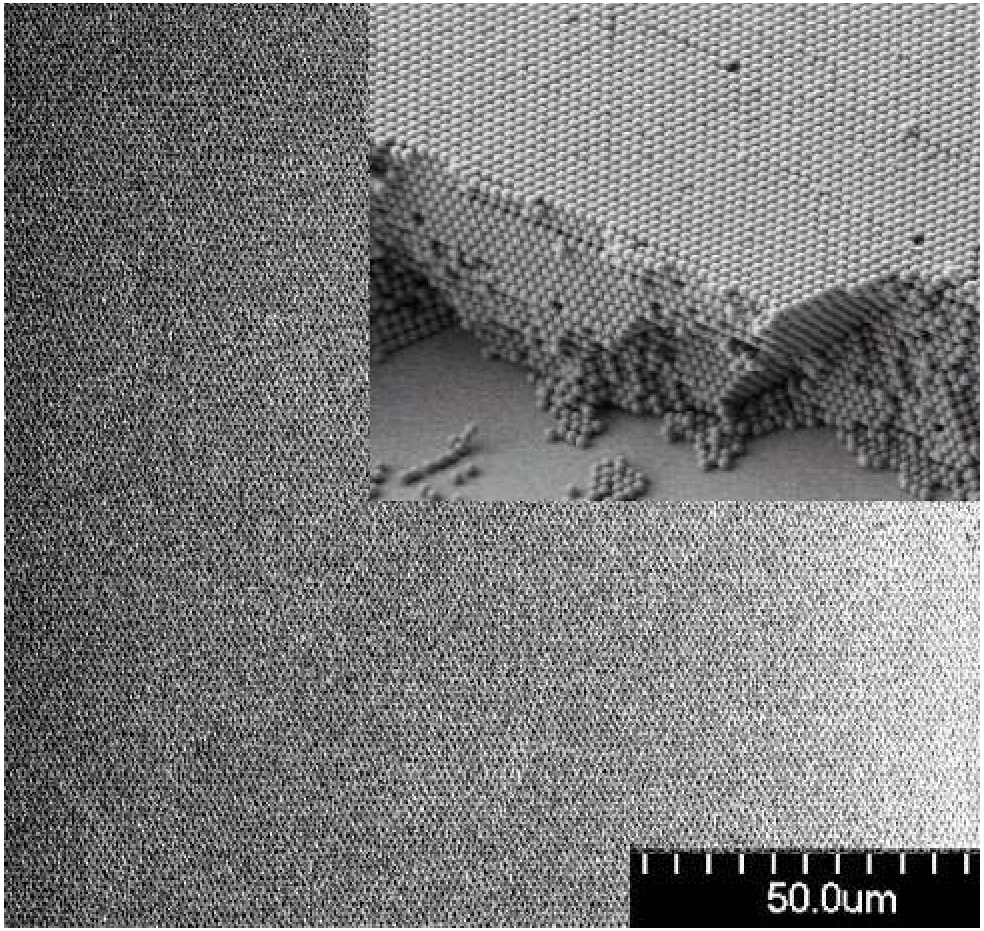
- Tandem nanoimprint & phase-shift lithography yields 3D periodic structures with single imprint



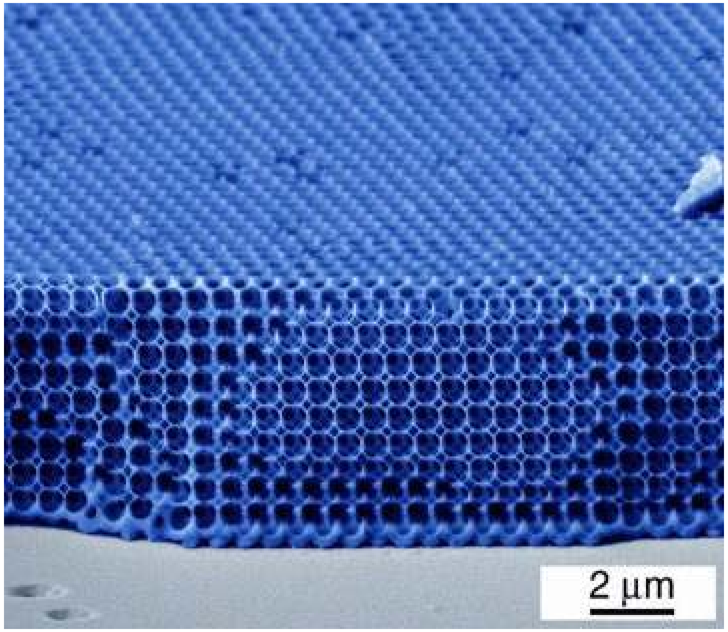


Rogers & coworkers. *Appl. Phys. Lett.* **2009**

Self-Assembly: Opals & Inverse Opal Photonic Crystals



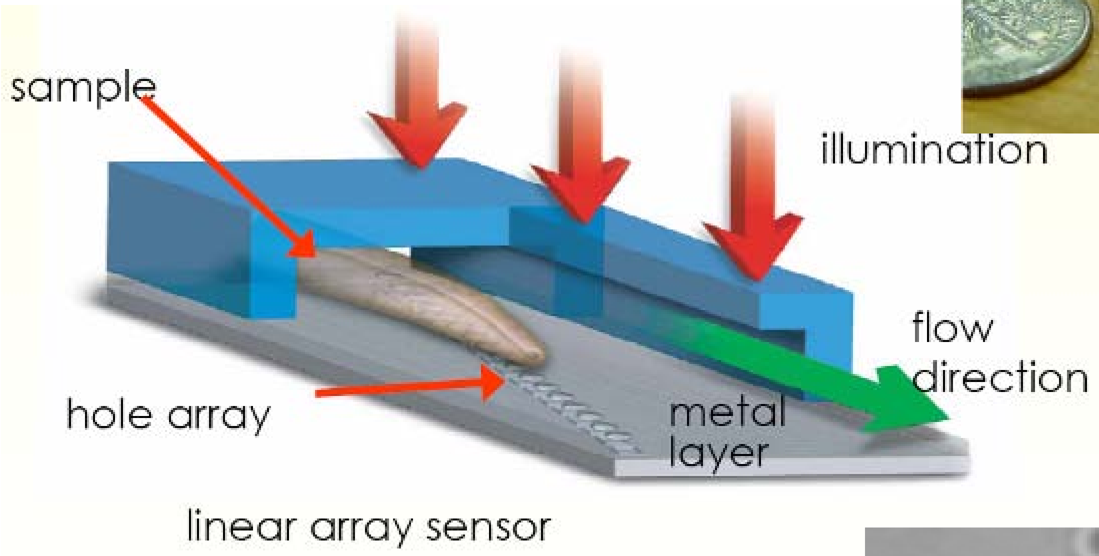
Courtesy of D. Norris, UMN

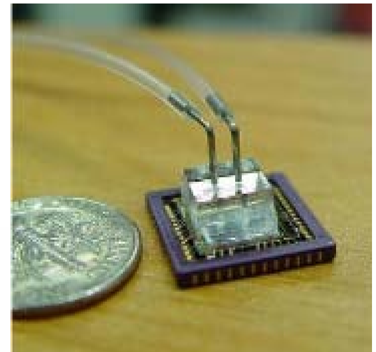


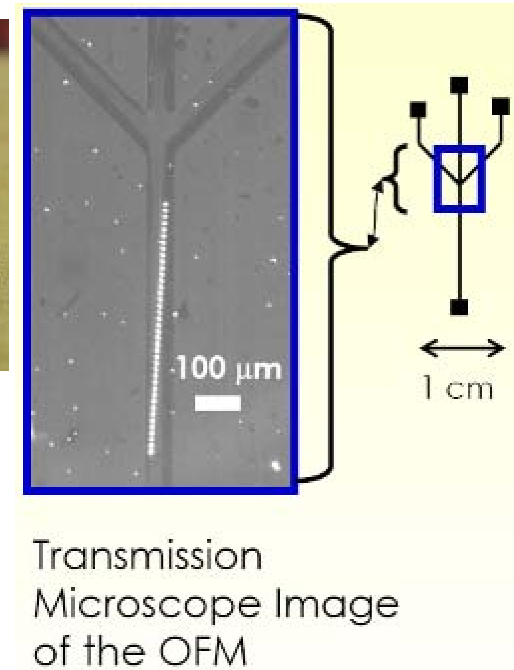
Y. A. Vlasov *et al., Nature* **2001**

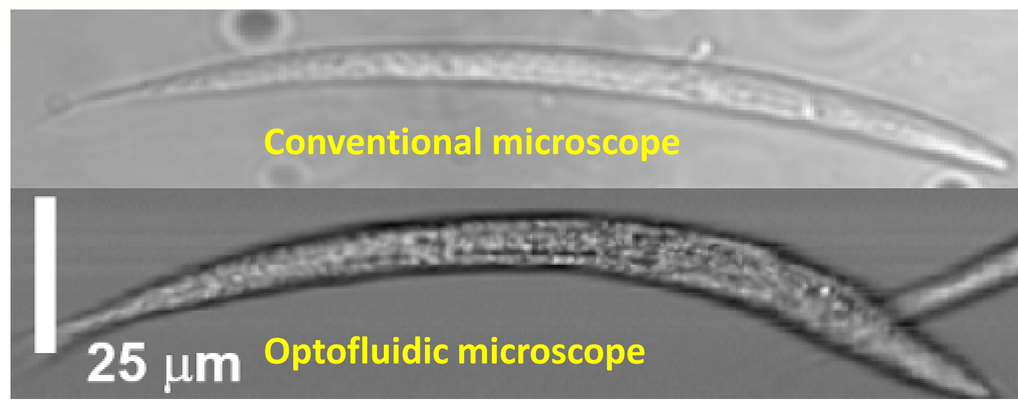
Nanoholes: Optofluidic Microscope

- **Slanted nanohole array**
- **System resolution 490 nm**





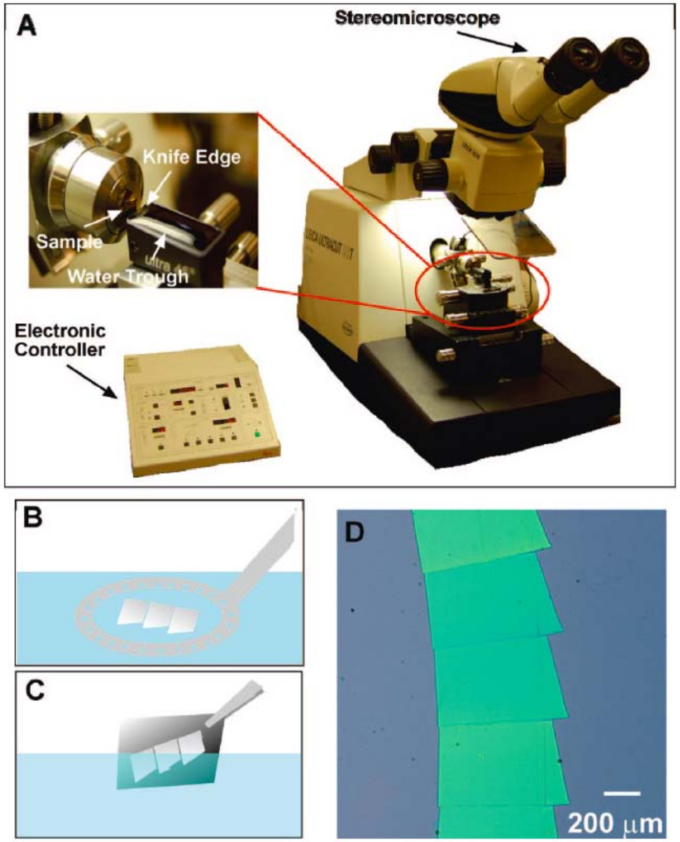


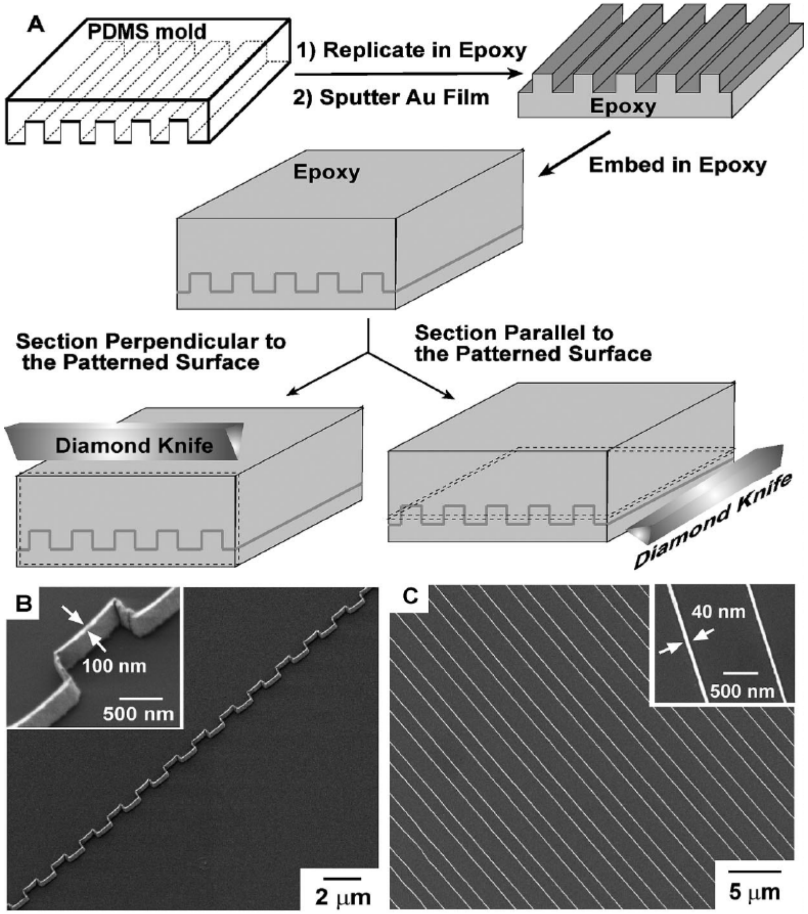


X. Heng, D. Erickson, L. R. Baugh, Z. Yaqoob, P. W. Sternberg, D. Psaltis, and C. Yang, Lab on a Chip 6, 1274 (2006).
X. Cui, X. Heng, J. Wu, Z. Yaqoob, A. Scherer, D. Psaltis, and C. Yang, Optics Letters 31, 3161-3163 (2006).

Nanoskiving

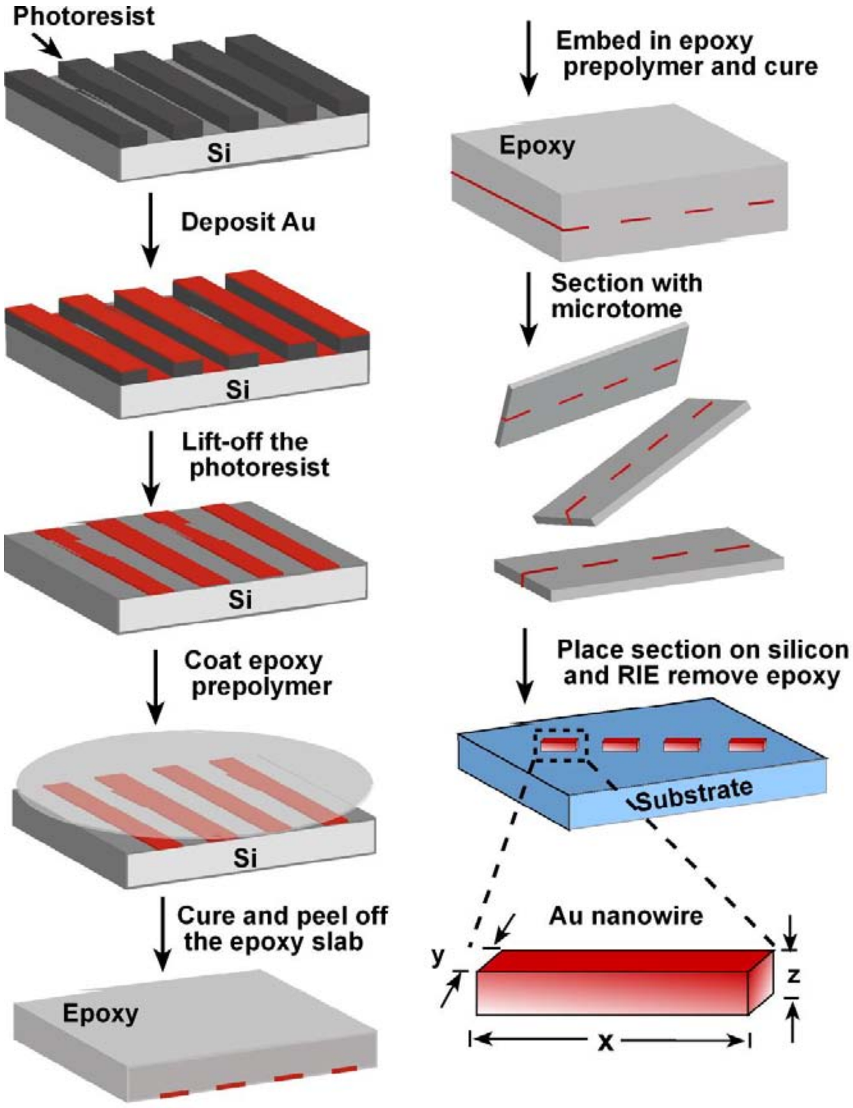
n. The use of an ultramicrotome for nanofabrication

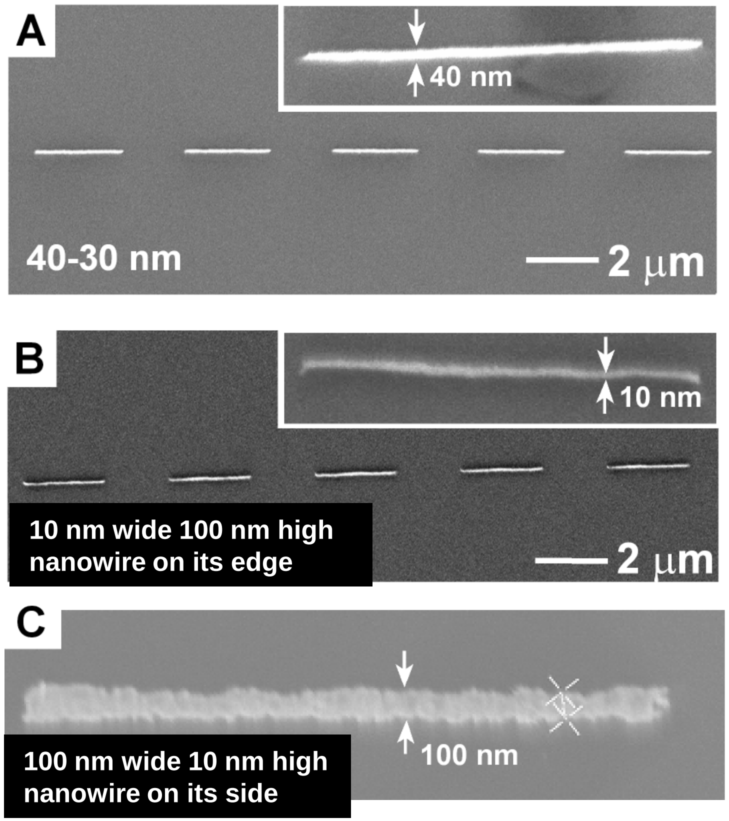




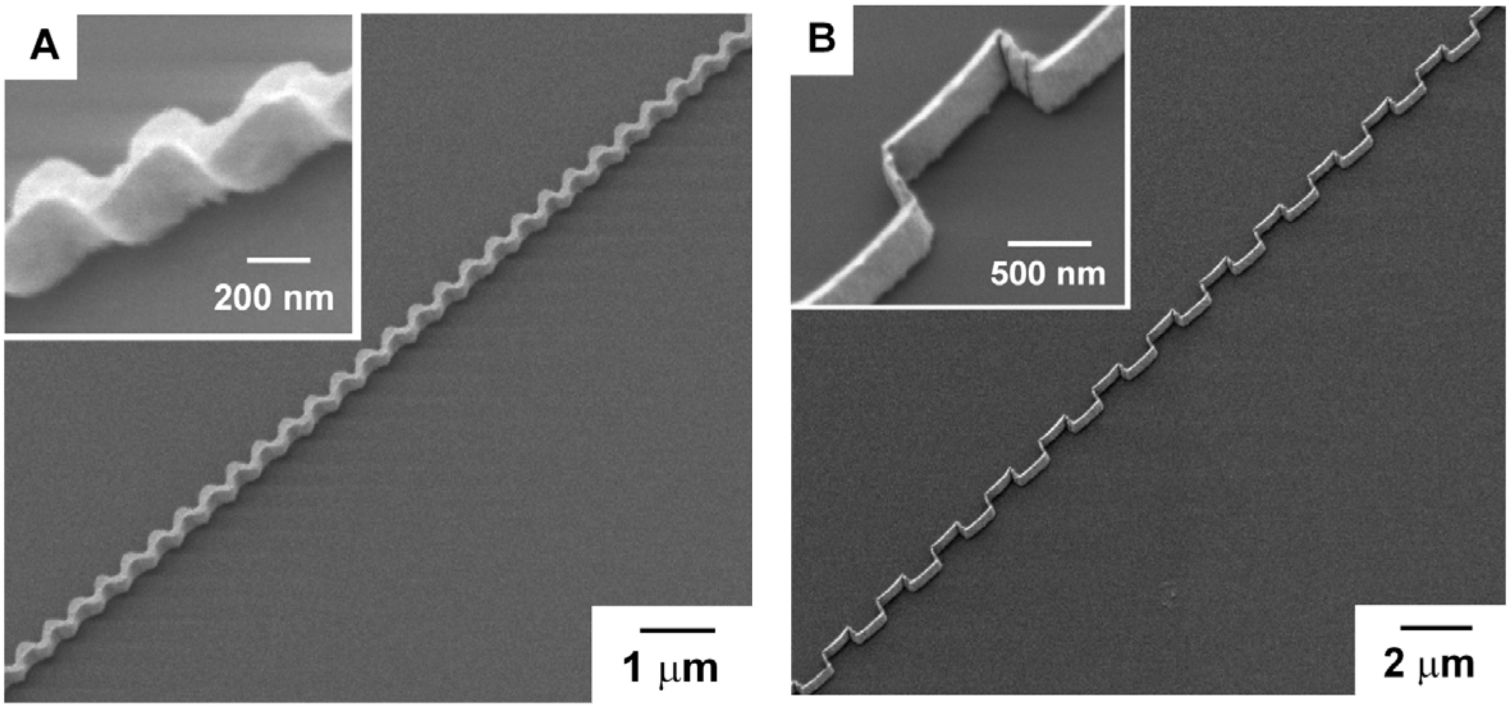
Xu et al. *Acc. Chem. Res.* **2008**

Gold Nanowires Generated by Sectioning Using a Microtome





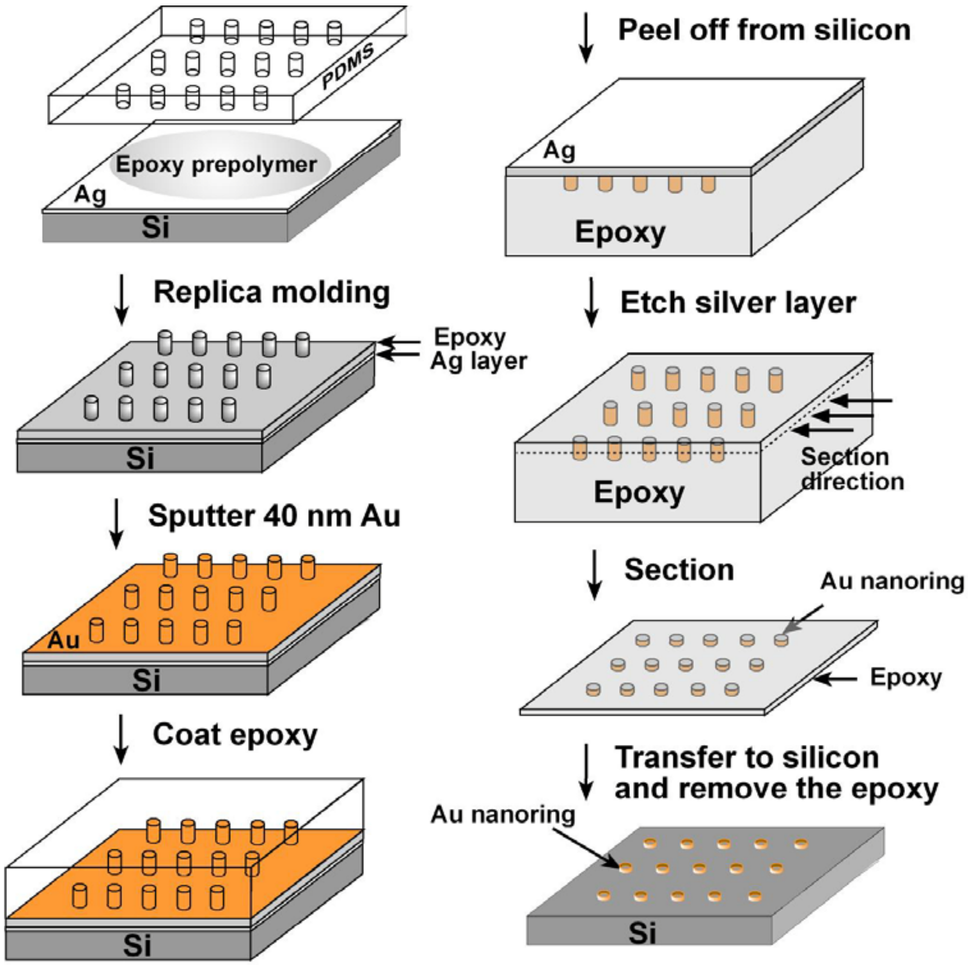
Fabrication of Complex 3-D Nanostructures

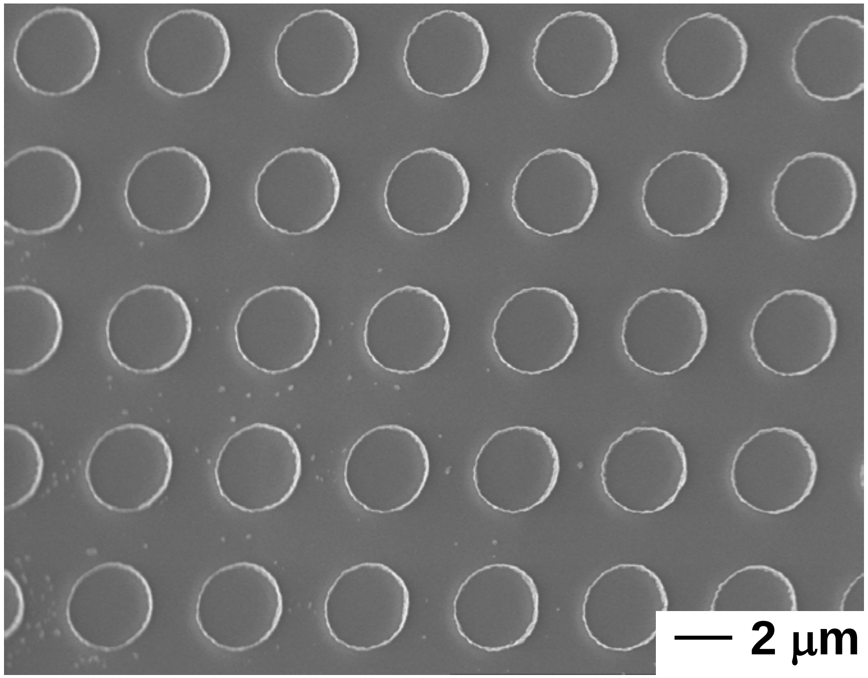


Template from diffraction gratings

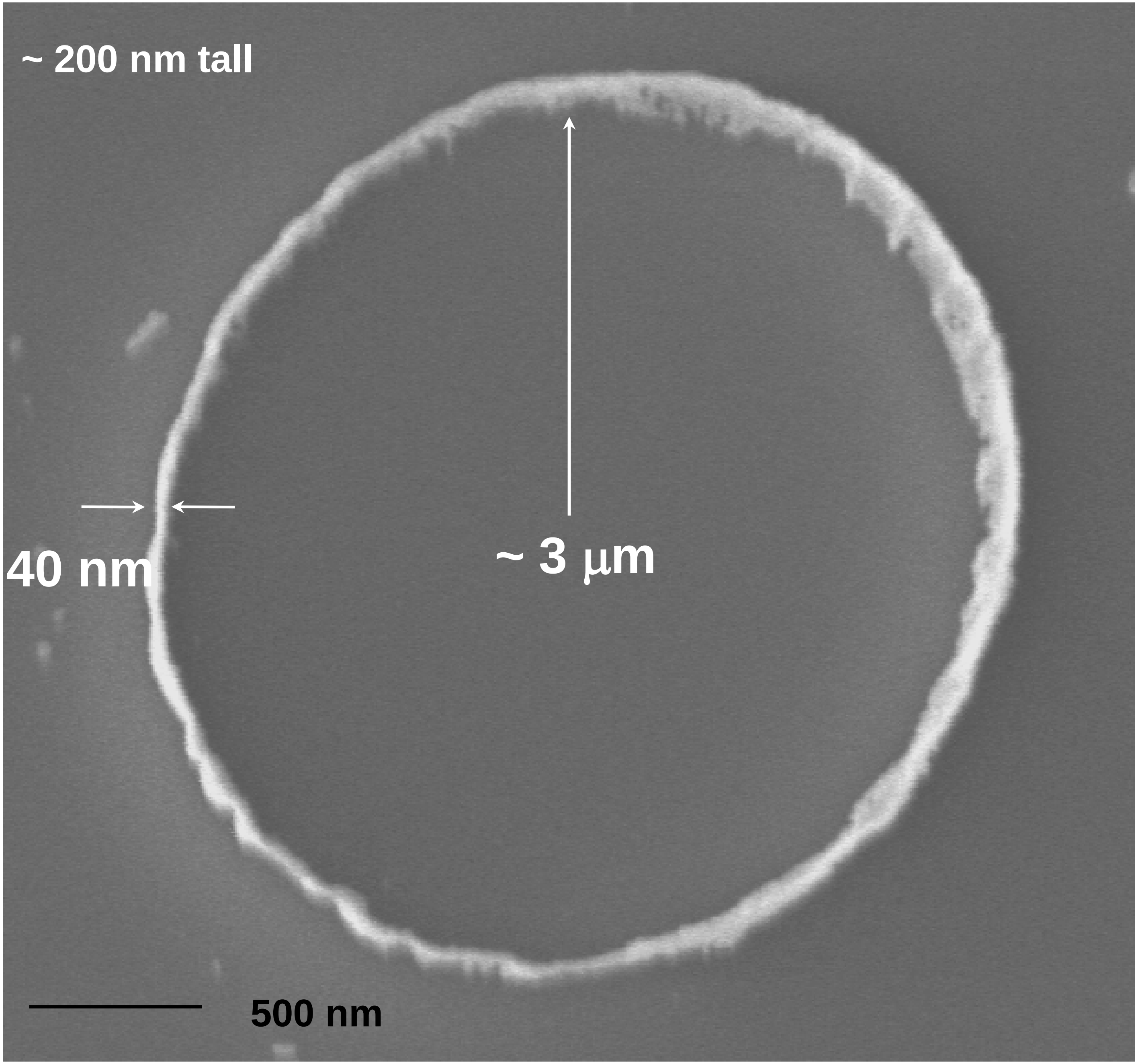
Template from periodic lines

Fabrication of Patterned Metallic Nanostructures over Large Areas

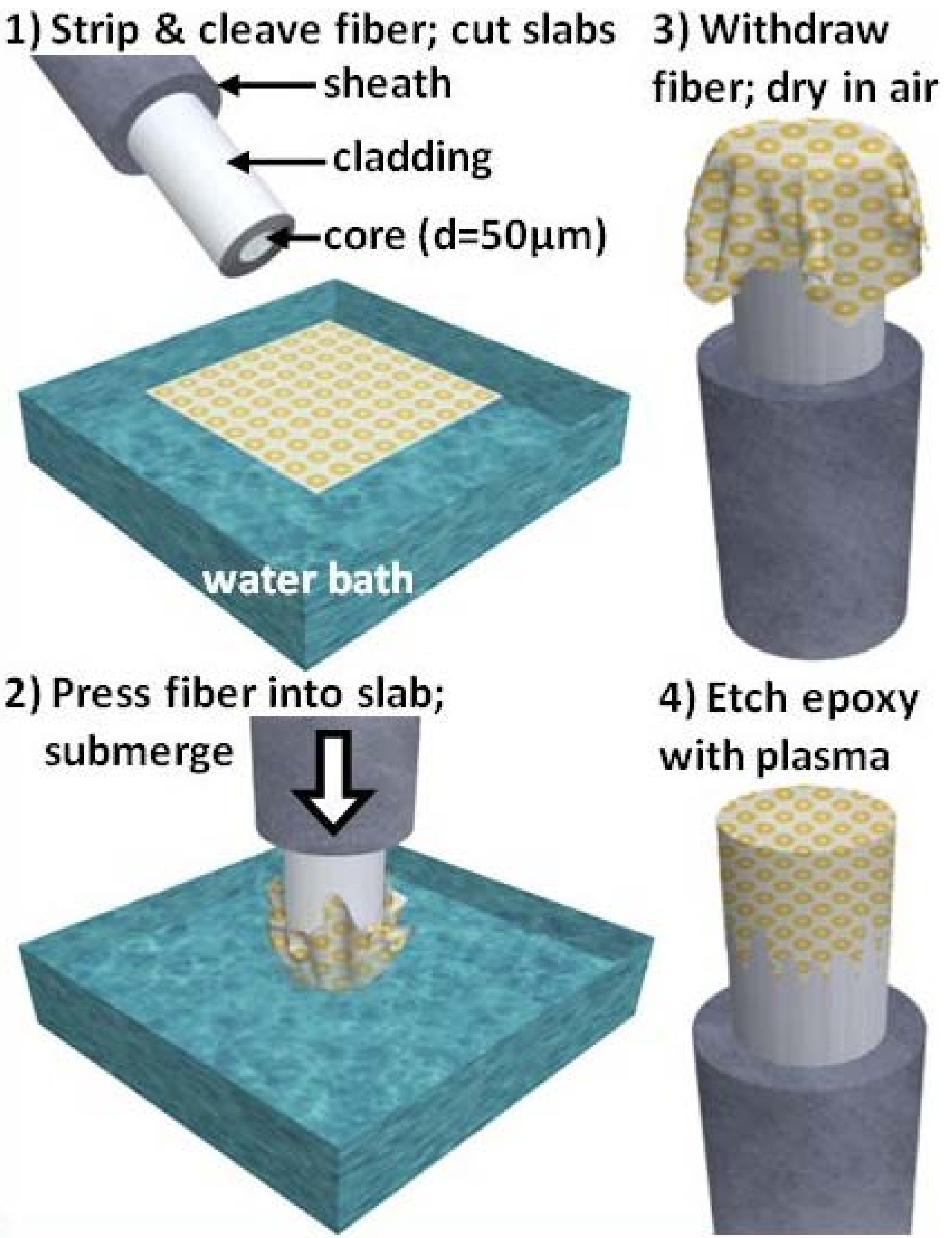


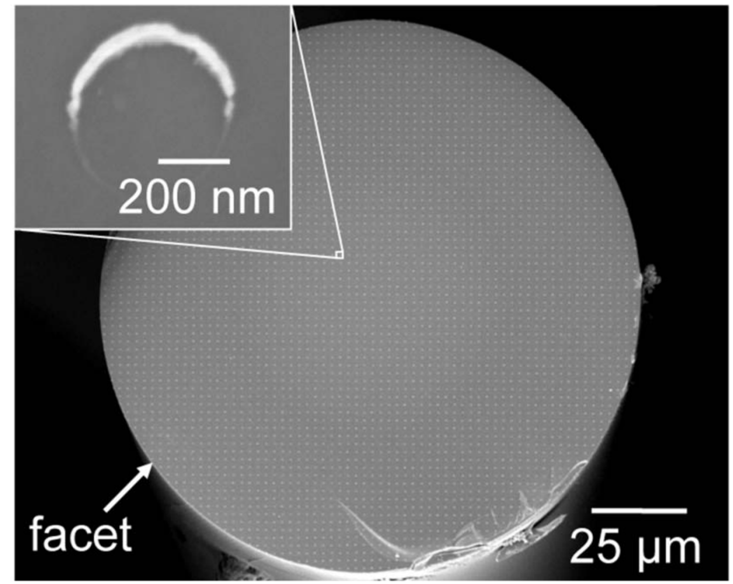


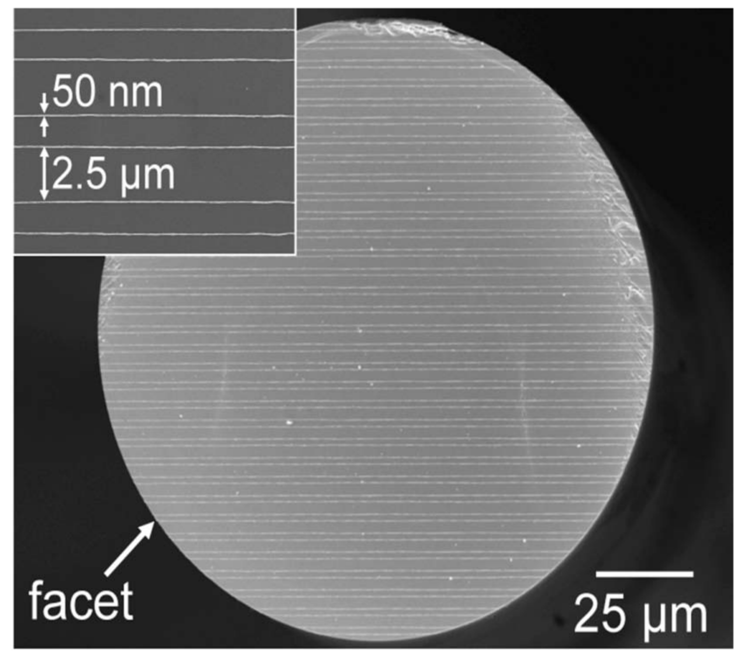
View at an angle 35°


~ 200 nm tall
40 nm
~ 3 μm
500 nm

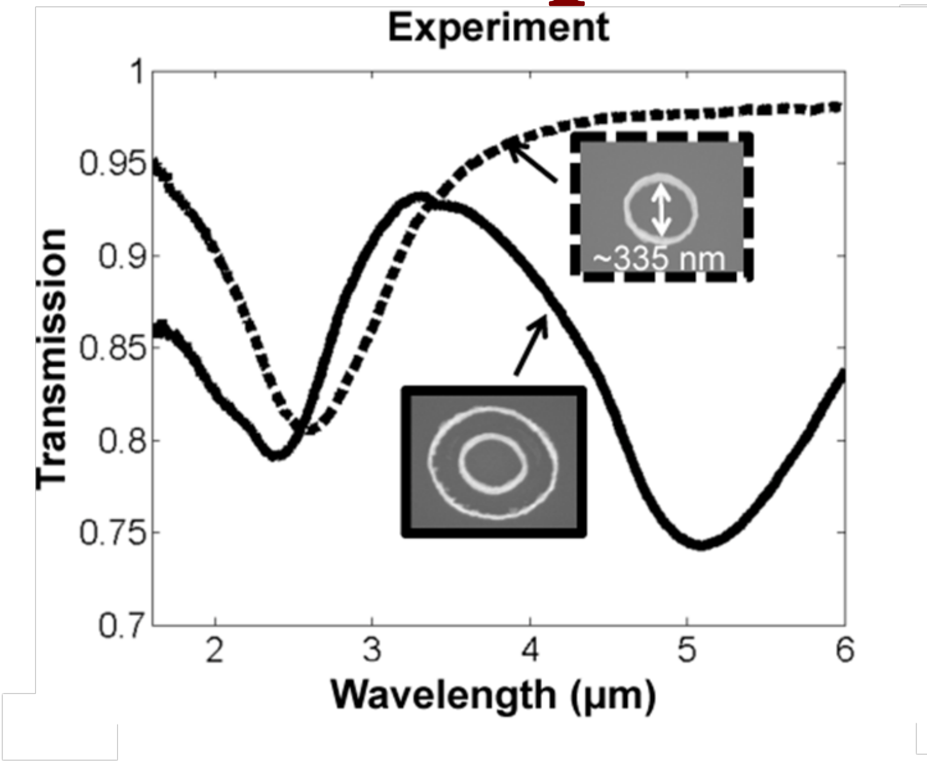
Nanoskiving Capabilities

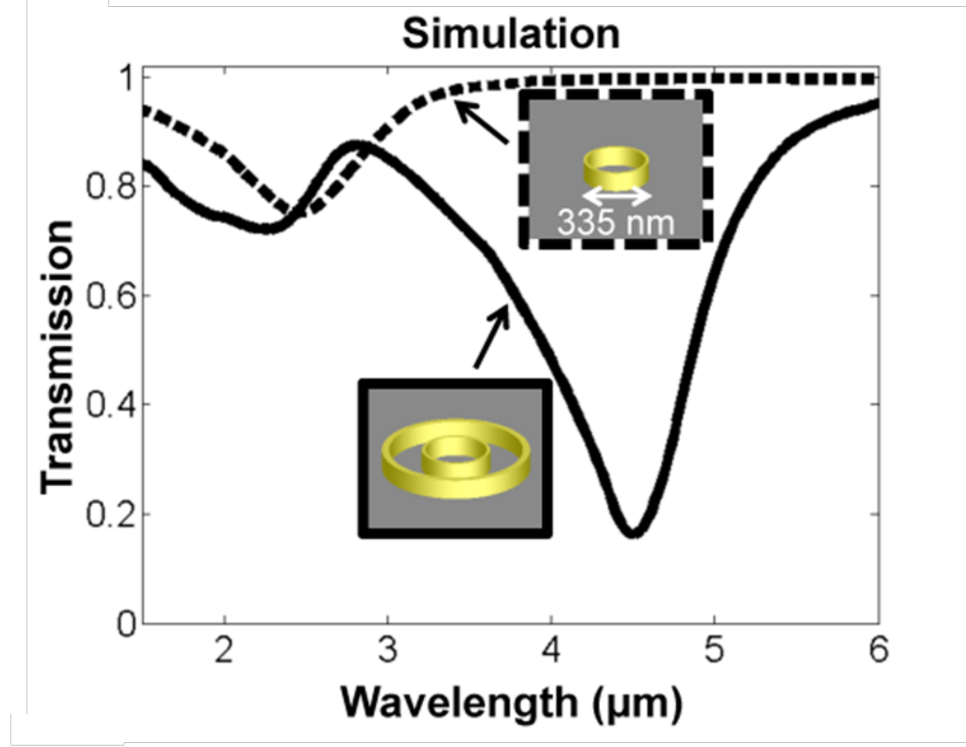


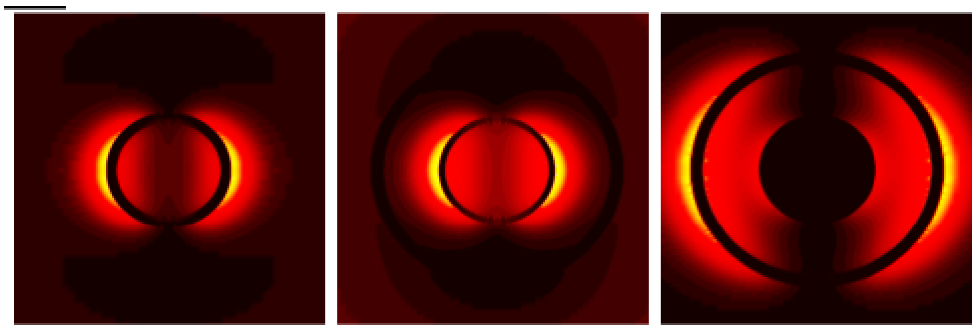




Optical Properties







Single ring
λ ~ 2.5 μm

Double ring
λ ~ 2.2 μm

Double ring
λ ~ 4.5 μm

Some other Observations

- Nanotechnology now seen as a *unifying* field. Technologically useful? *Yes.* Technologically revolutionary? *Not yet.*

- The issues now are *function* and *cost*.

- For many important *potential* functions, we do not know the rules. Heterogeneous catalysis, Nanotoxicology, Aerosols/albedo, Quantum isolation, Charge storage/transport/ interconversion, …

- We should answer the question: “Where does “nano” –rather than “micro” or just “small”—bring unique function or properties or behavior or cost?

And…there is always competition

- Nano..

    or/and

- Catalysis, solar, intelligent machines, stem cells (cancer, replacement), robotics, origin of life, global warming, sustainabilty, green,
- *Jobs, economic competitiveness, costs/benefits of healthcare, "non-conventional conflict," immigration,* outsourcing/globalization, climate change, energy, education…

In the U.S., "nano" is shifting to "applications" from "special emphasis"

The Umbrella Theory of Scientific Managment

1. “Inevitabilities”
2. Specific, Actionable Projects

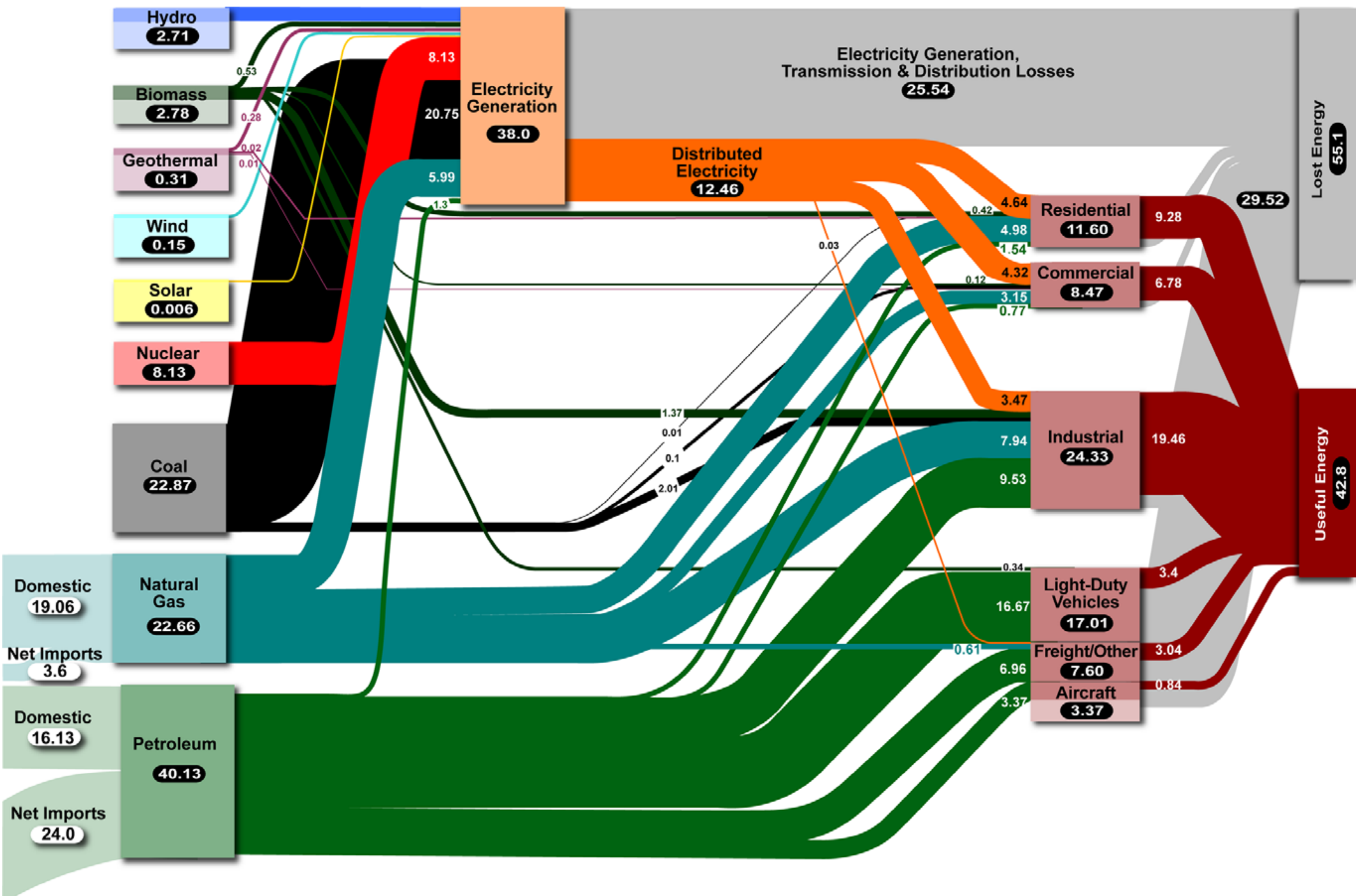
Inevitabilities

- **Areas where it is *certain* that society will need technology**
- **It may be too early to know what ultimate (or even initial) products are**
- **R&D should provide options, and early warning**
- **Examples: six (of perhaps 20)**
- **Keys to success:**
  - **Strategic selection, coupled with specificity**
  - **Critical mass in money, people**
  - **Patience (the www took 40 years; biotech still has not happened)**

1. Commodity Infrastructure: Energy, Water

- Supply/Demand-side technologies.
- Honest, complete, accurate systems analysis
- Biotechnology—finally a use?
- Nanotechnology





Hydro
2.71
Biomass
2.78
Geothermal
0.31
Wind
0.15
Solar
0.006
Nuclear
8.13
Coal
22.87
Domestic
19.06
Natural Gas
22.66
Net Imports
3.6
Domestic
16.13
Petroleum
40.13
Net Imports
24.0
0.53
0.28
0.02
0.01
8.13
20.75
5.99
1.3
Electricity Generation
38.0
Electricity Generation, Transmission & Distribution Losses
25.54
Distributed Electricity
12.46
0.03
1.37
0.01
0.1
2.01
0.42
4.64
4.98
1.54
4.32
0.12
3.15
0.77
3.47
7.94
9.53
0.34
16.67
0.61
6.96
3.37
Residential
11.60
Commercial
8.47
Industrial
24.33
Light-Duty Vehicles
17.01
Freight/Other
7.60
Aircraft
3.37
9.28
6.78
19.46
3.4
3.04
0.84
29.52
Lost Energy
55.1
Useful Energy
42.8

Energy, Climate, Water, Sustainability

Technology provides *options* to society

$$Wellbeing \approx \frac{Energy}{People}$$

Options.

- Generate more energy
- Conserve the energy we now generate.
- Have fewer people

Constraints

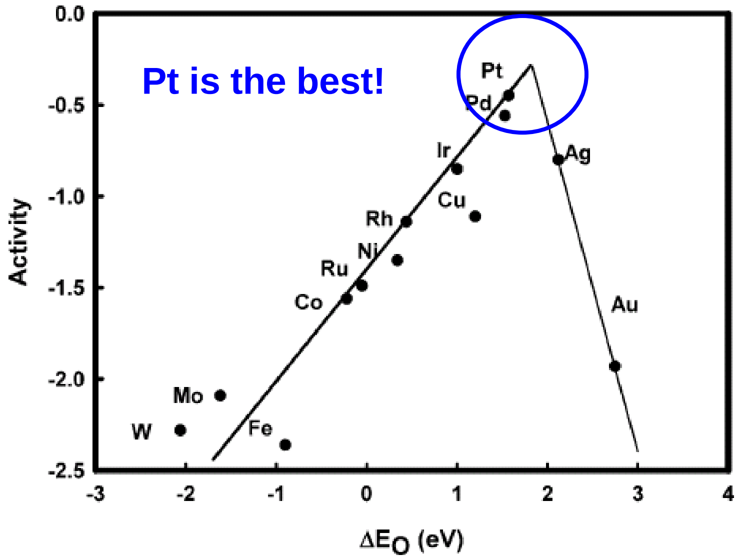
- Energy and Climate
  - Climate change may limit the combustion of fossil fuel
- Energy and Water
  - Water production may become a major use of energy
- Energy and Nuclear
  - Weapons proliferation, reactor safety, waste management

Catalysis: The Oxygen Electrode

Kinetics of cathode reaction are much slower than the anode reaction and limit economic viability of low temperature fuel cells

Cathode reaction: $4e^- + O_2 + 4H^+ \xrightarrow{\text{slow}} 2H_2O$

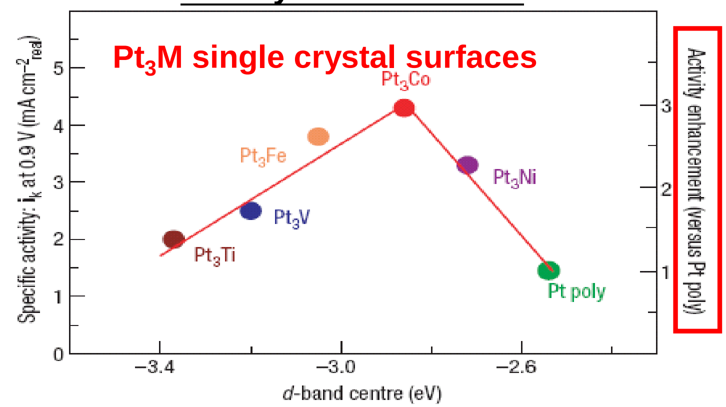
Periodic trends in oxygen reduction activity

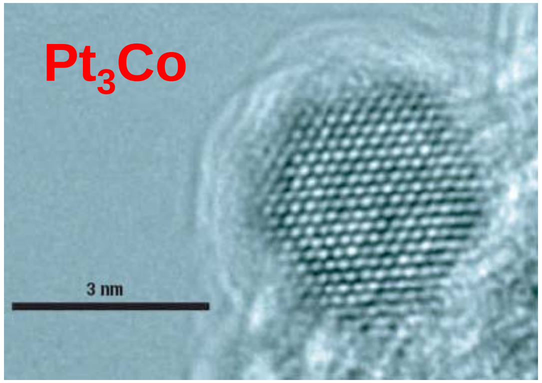


oxygen binding energy

Volcano relationship between activity and oxygen binding energy suggest <u>alloying</u> improve activity

<u>Alloying leads to oxygen reduction activity enhancements</u>





Nørskov et al. J. Phys. Chem. B 108 (2004) 17886

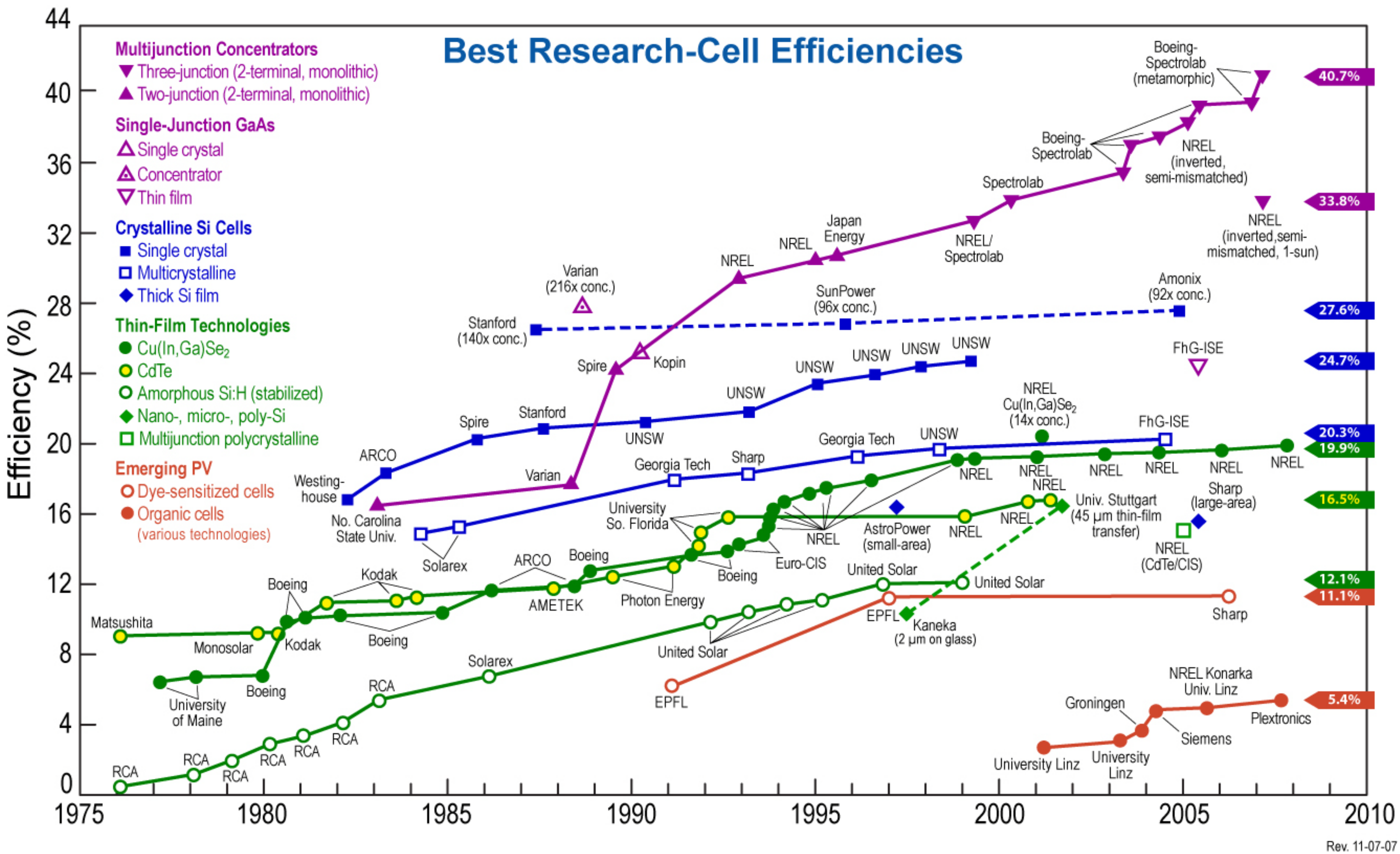
Energy Conservation

Diesel Fuel

http://www.de.nec.d

Boeing 787. Approximately 50% carbon-epoxy composite. (Cost, autoclaves, damage, repair, electromagnetics/lightening, ….

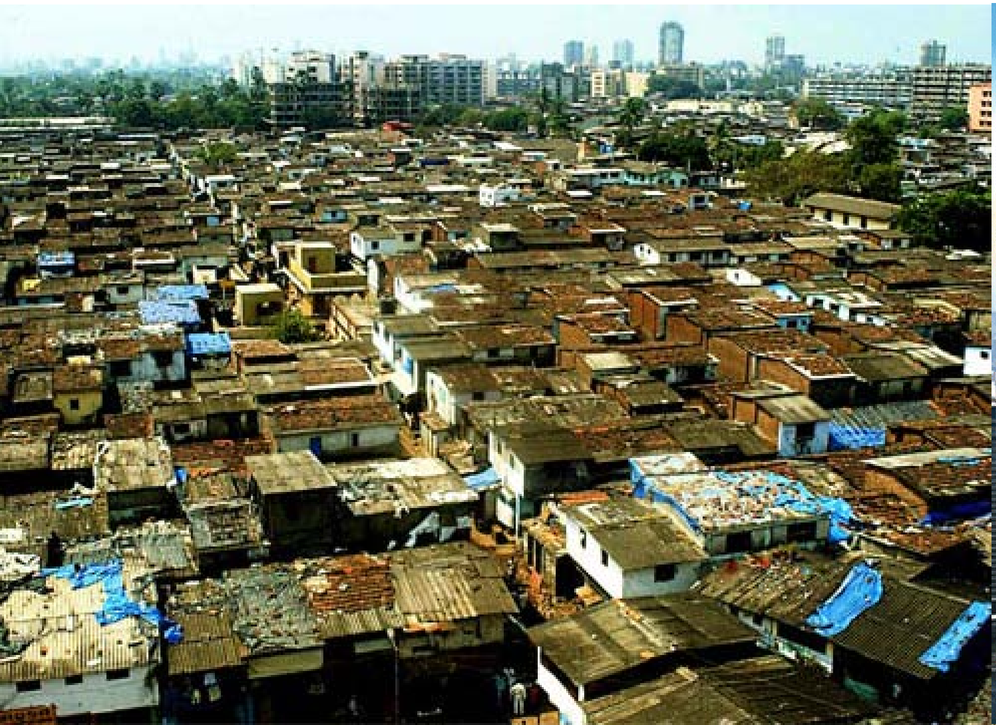
Performance in Photovoltaics:
Cost vs. Efficiency Tradeoff



NREL

2. Global Stewardship

- CO_2 and atmospheric management
- Population, “crowding”, future megacities
- (Education)



"Geoengineering"

- **Sulfuric Acid Sols**
  - **Tambora (1815) and the "year without a summer"**

- **CO_2 for control**
  - **Inject CO_2 into atmosphere for "feedback" climate control**

3. Information Technology

- **Consumerization; globalization of information**
- **Education, Entertainment**

4. Health Care

- Cost reduction: Prevention, Anticipation
- Developing world
- Is the patient important any more?

Vs.

5. Building the Global Middle Class

- **The fusion of capitalism and socialism, with a 50- to 100-year time-scale**
- **National Security: Conflict and nation-building**

Middle class in India

6. Robotics: Replacing Human Labor

BigDog, *Boston Dynamics*

LittleDog, *Boston Dynamics*

http://www.bostondynamics.com/content/sec.php?section=BigDog

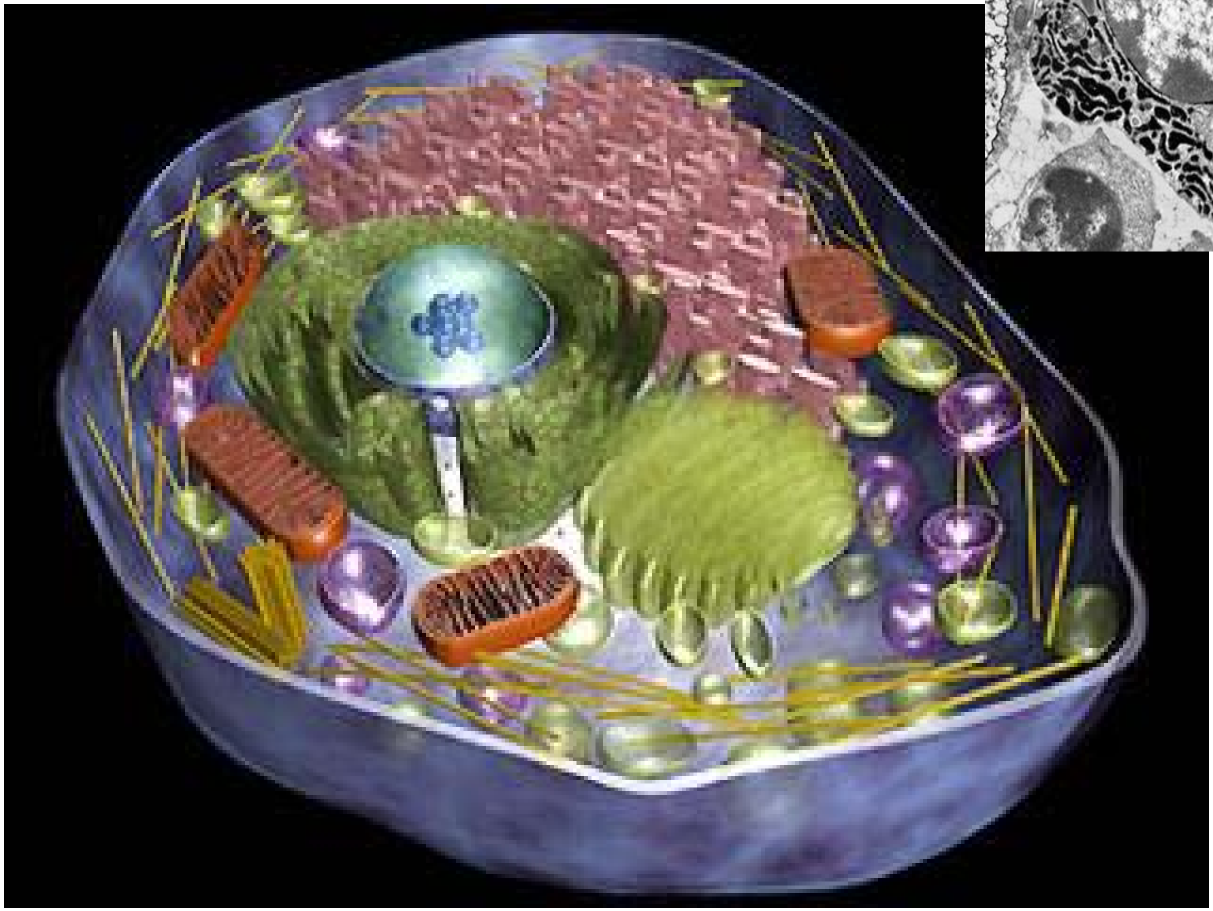
http://www.bostondynamics.com/content/sec.php?section=LittleDog

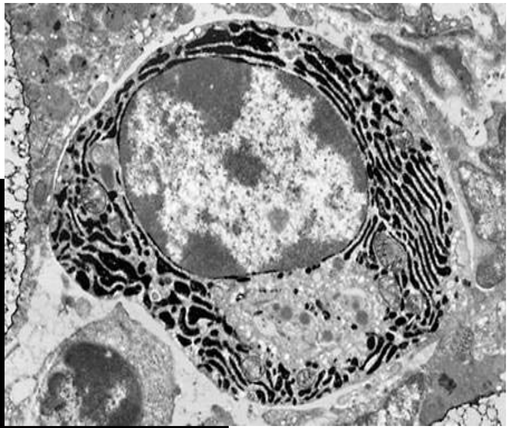
A “Next Big Thing”

- Robotics: Changes the way we work. Work often defines what it is to be human.
- Investment:
  - Competition with low labor-rate competitors
  - Military
- Turing test

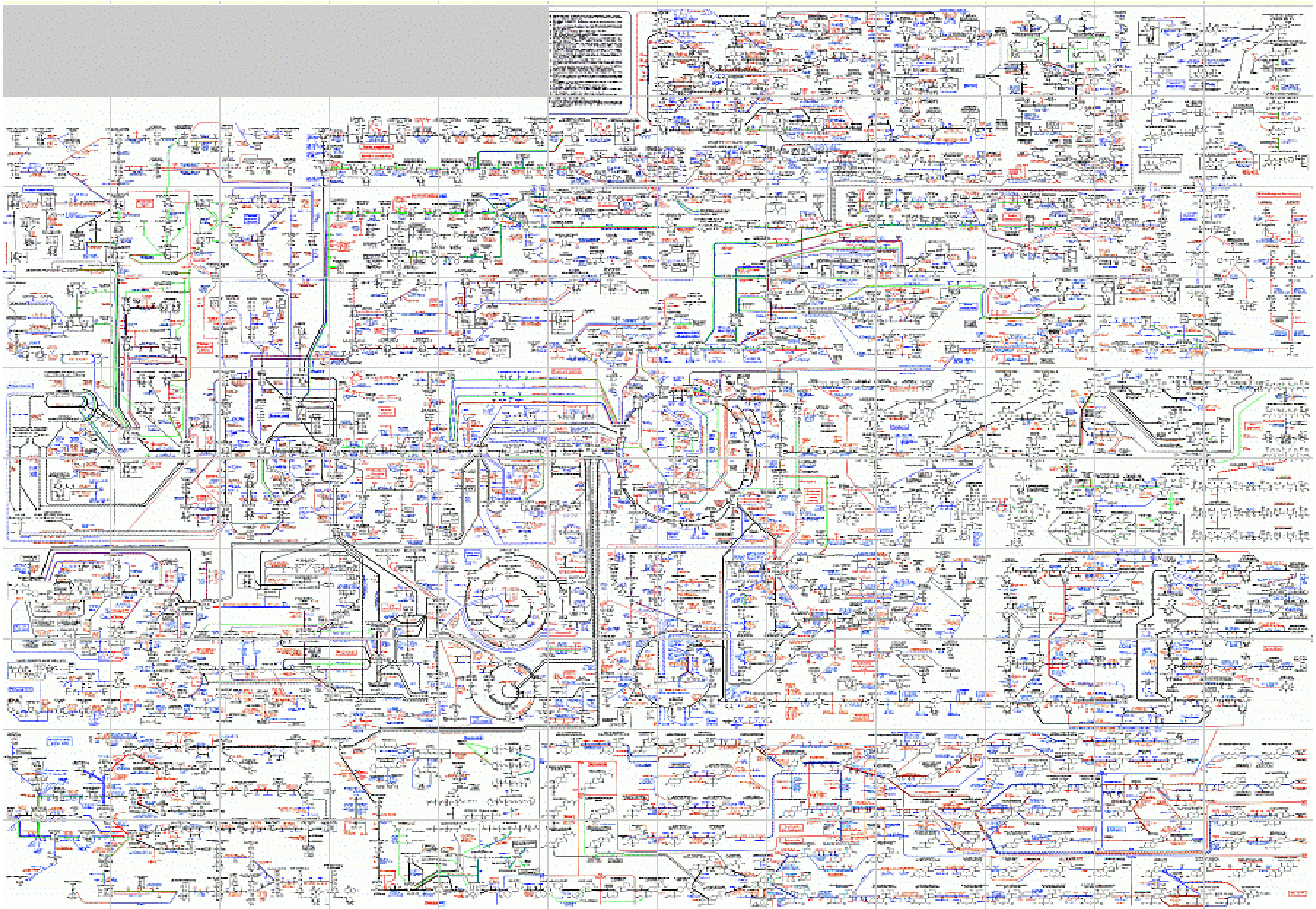
Robotics: Replacing Human Labor

Fundamental/Basic Science: The Cell





Systems: “What is life?”



Origin of Life: Peribiotic Earth

- **Little/no? land**
- **Unformed continental plates**
- **Extensive vulcanism; geothermal activity; Mn/Fe/NiS colloids**
- **Cool, uv-rich sun**
- **Continuing impaction**
- **$CO_2/N_2/H_2O$ atmosphere (~10 atm); overall redox neutral; large uncertainties in NH_4^+, CH_4, O_2, …**
- **Acidic, mildly reducing ocean; Fe^{+2}**
- **“Pond scum”; in-fall from space + geosynthesis**

Summary: Opportunities

- **Nano has developed as integrative rather than revolutionary**
- **It is developing the tools needed to focus on *function*.**
- **Many connections to large-scale problems: Energy, water, climate change, health-care cost reduction, information technology**
- **Rich source of new materials and processes**
- **Tools and concepts for fundamental science, especially in catalysis, biology, charge-transport, optics, interfacial chemistry, materials science**

For Nano and Nanochemistry, Fundamentals are Sound:

- **Atoms/Molecules—*"Nano"*—Meso/Macro-scale Matter; the least-understood scale of matter.**
- **Charge transport (Energy generation/storage): occurs across nm-scale interfaces**
- **Assemblies in the cell are nanoscale**
- **Heterogeneous catalysis: "catalysis by design" must involve nano for empiricism to science**
- **Surface science is nanoscale, and ubiquitous: electrochemistry, plasmonics, membrane separations (RO/H_2O, CO_2, CH_4), fuel cells/batteries/capacitors, solar cells**
- **The environment: Micro/nanoparticles, aerosols**
- **New materials and characterization: Graphene, nanorods, quantum dots, nanoresists, photovoltaics…SPM, tribology, corrosion, grain boundaries, phase-change materials**

Some Generalizations about Nano: “Then” and “Now”

- Then
  - Generally: structure
  - “New” nanoelectronics
  - Nanosensors
  - Atomic/molecular-scale visualization
  - “Nanomedicine”
  - The cell
  - “Nanobots”; the “self-assembler”

- Now
  - Search for Function (Saalfeld Criterion)—energy, consumer electronics, optics..
  - Materials (graphene,..)
  - Nanoelectronics (materials support)
  - Energy/sustainability/ climate/energy storage…
  - Search for applications in biomedicine (NIH, VCs): imaging; research; environmental nano
  - Search for a lead in heterogeneous catalysis

Acknowledgements

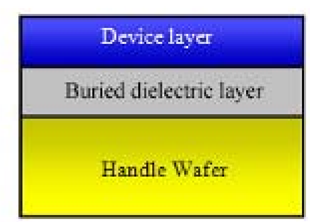
- Darren Lipomi
- Roger York
- Sindy Tang
- Audrey Ellerbee (Stanford)
- Zhihong Nie
- Ben Wiley (Duke)
- Qiaobing Xu
- Michael Dickey (U. North Carolina)
- Rob Rioux (Penn State)

Six big ideas

1. Applications: Electronics, Energy, Water
2. New materials
3. Information/globalization
4. The cell, biology, and medicine
5. Single atoms and molecules
6. Quantum phenomena, both fundamental and applied

Opportunities: Lateral Transfer Electronics → Chemistry

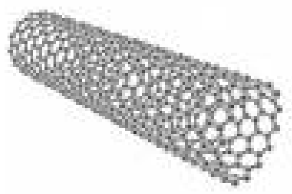
- **Phase-shifting and immersion optics**
- **Spin-coating**
- **Resists and thin films**
- **Chemical vapor deposition**
- **Chemical mechanical polishing**
- **Si on oxide**
- **High K materials**



SOI cross section

Opportunities: Lateral Transfer Chemistry → Electronics

- **Nanomolding**
- **Buckytubes/nanotubes**
- **High h+ mobility materials**
- **Phase-change materials for electronics**
- **Thin films; CVD**



Opportunities: Energy

- **Catalysis**
- **Materials**
- **Band-gap Engineering**
- **Separations**

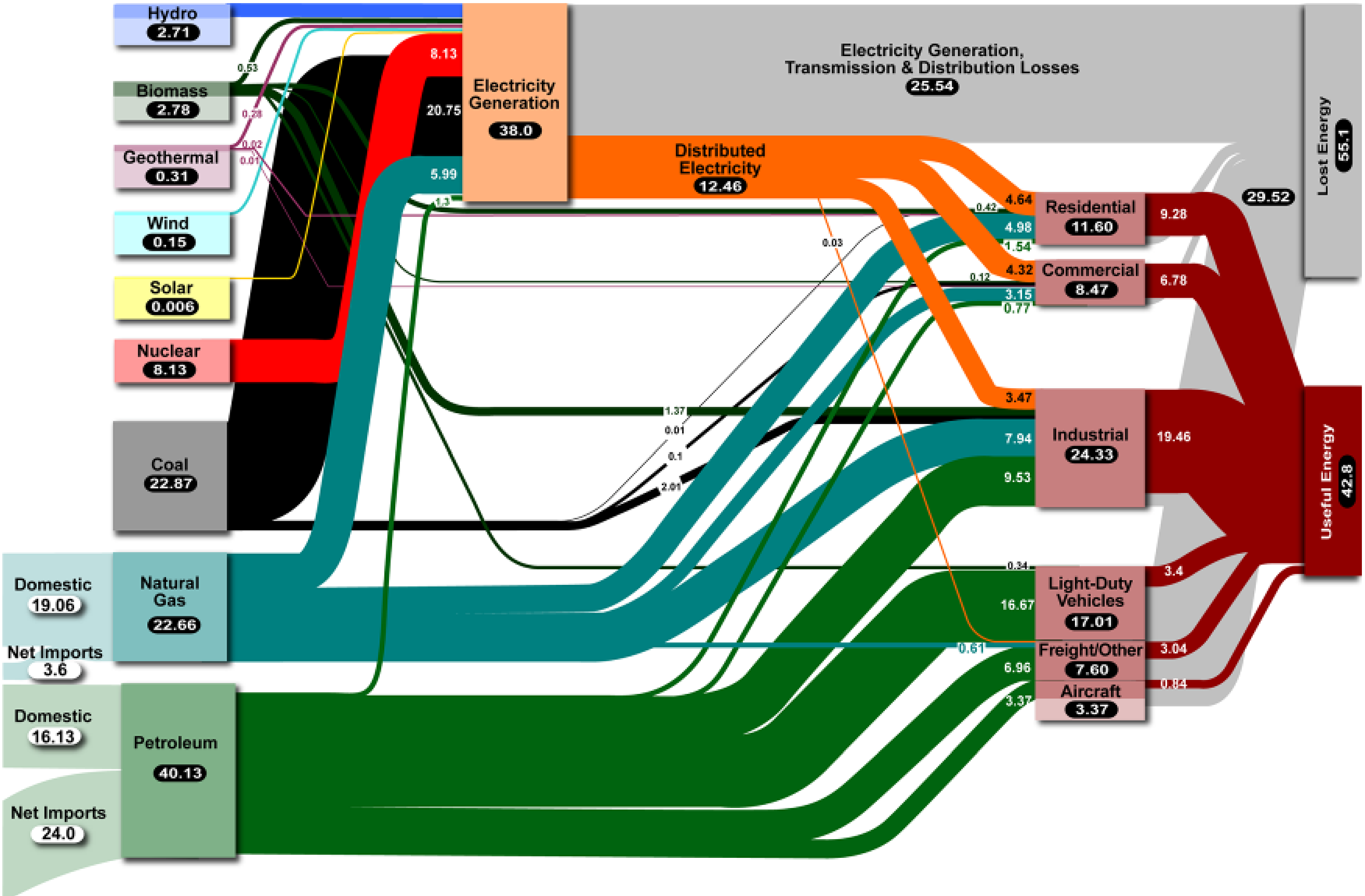
Energy:

Thermal (high T is good)

Electrochemistry ($P = i^2R = IV$)

Conservation

Light weight, strong, corrosion resistant



Hydro
2.71
Biomass
2.78
Geothermal
0.31
Wind
0.15
Solar
0.006
Nuclear
8.13
Coal
22.87
Domestic
19.06
Natural Gas
22.66
Net Imports
3.6
Domestic
16.13
Petroleum
40.13
Net Imports
24.0
8.13
20.75
5.99
Electricity Generation
38.0
Electricity Generation, Transmission & Distribution Losses
25.54
Distributed Electricity
12.46
4.64
4.98
1.54
Residential
11.60
4.32
3.15
0.77
Commercial
8.47
3.47
7.94
9.53
Industrial
24.33
16.67
Light-Duty Vehicles
17.01
0.61
Freight/Other
7.60
6.96
3.37
Aircraft
3.37
9.28
6.78
19.46
3.4
3.04
0.84
29.52
Lost Energy
55.1
Useful Energy
42.8

Efficient Use of Energy

spiral type compact fluorescent light bulb

Diesel Fuel

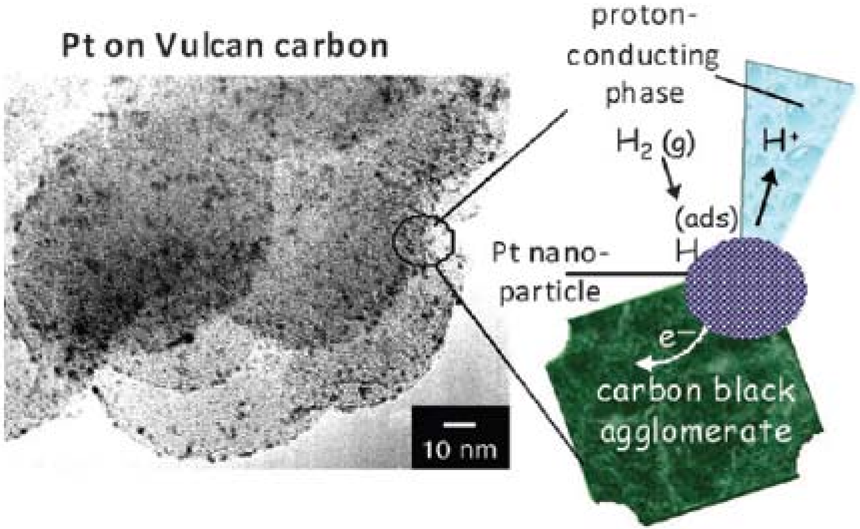
http://www.de.nec.de/

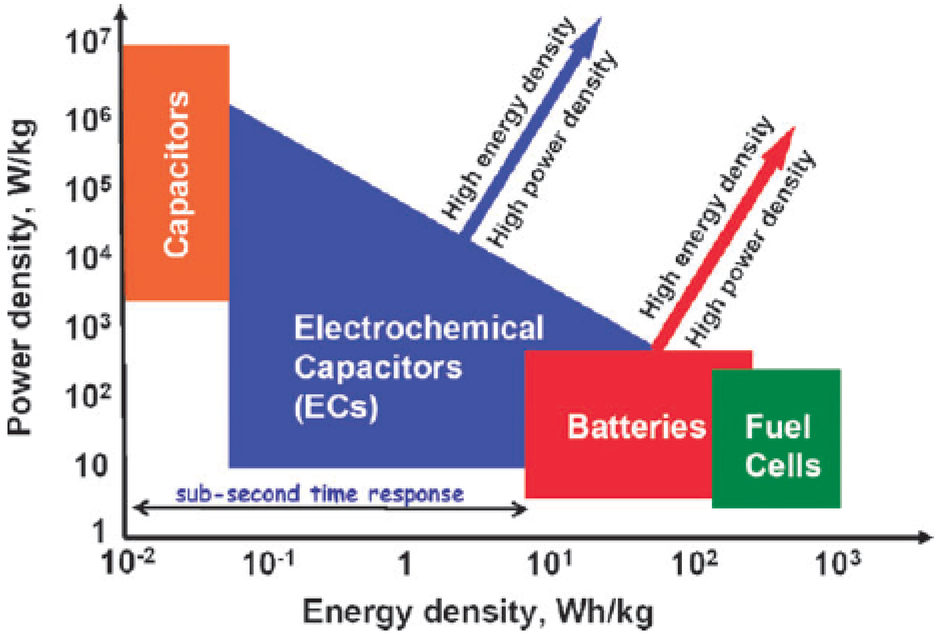
Materials in Energy

Nanotechnology may have many roles in energy challenge

Multifunctional 3D nanoarchitectures for energy storage and conversion†

Debra R. Rolison,*[a] Jeffrey W. Long,*[a] Justin C. Lytle,[a] Anne E. Fischer,[b] Christopher P. Rhodes,[c] Todd M. McEvoy,[d] Megan E. Bourg[a] and Alia M. Lubers[a]





Chemical Society Reviews, **2009**

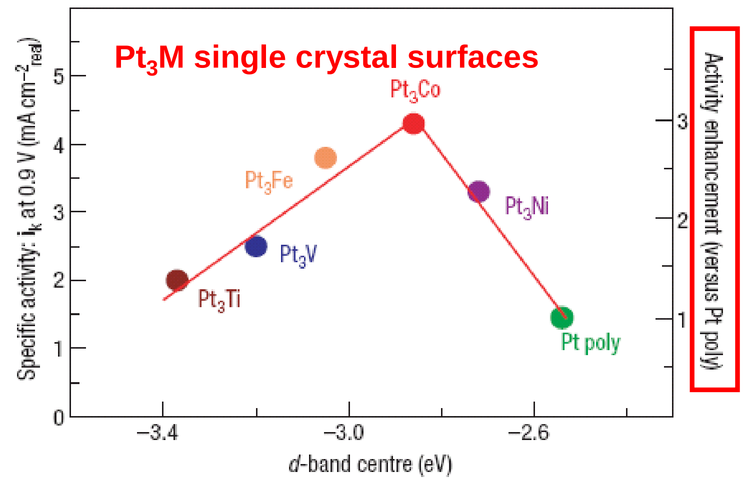
Is it Possible to Design Catalysts?

Tuning surface electronic structure of nanoparticle surface by alloying leads to improved reduction kinetics – Aided by *surface science* and *nanoscience*

Fundamental

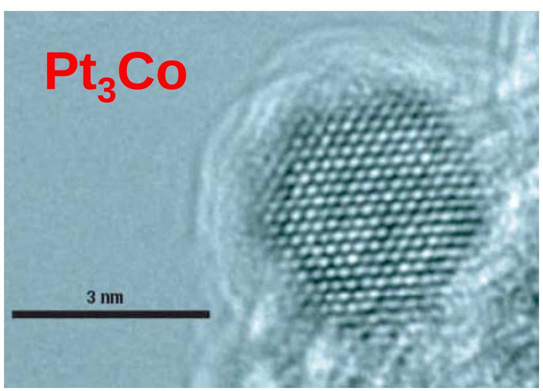
Research…

Alloying leads to reduction activity enhancements



DFT calculated surface electronic structure

new generation of oxygen reduction catalysts



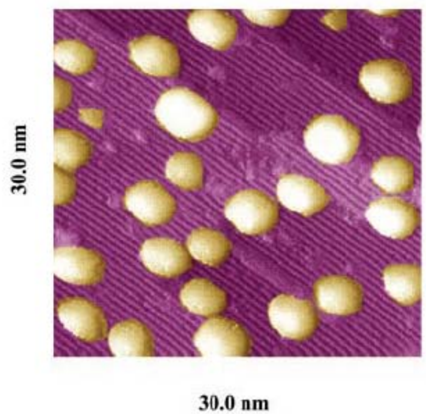
…coupled with nanoscience leads to the design

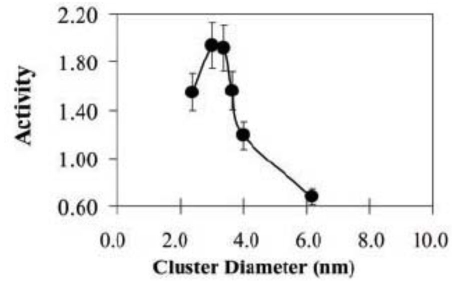
of better O_2 reduction catalysts

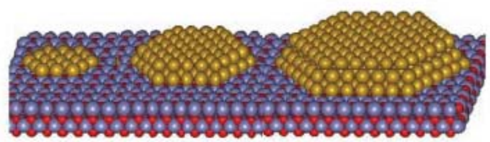
Nanoscience: Enabling Catalysis by Design

<u>Particle size</u> and <u>shape</u> is critical for activity and selectivity

$CO + ½ O_2 \rightarrow CO_2$







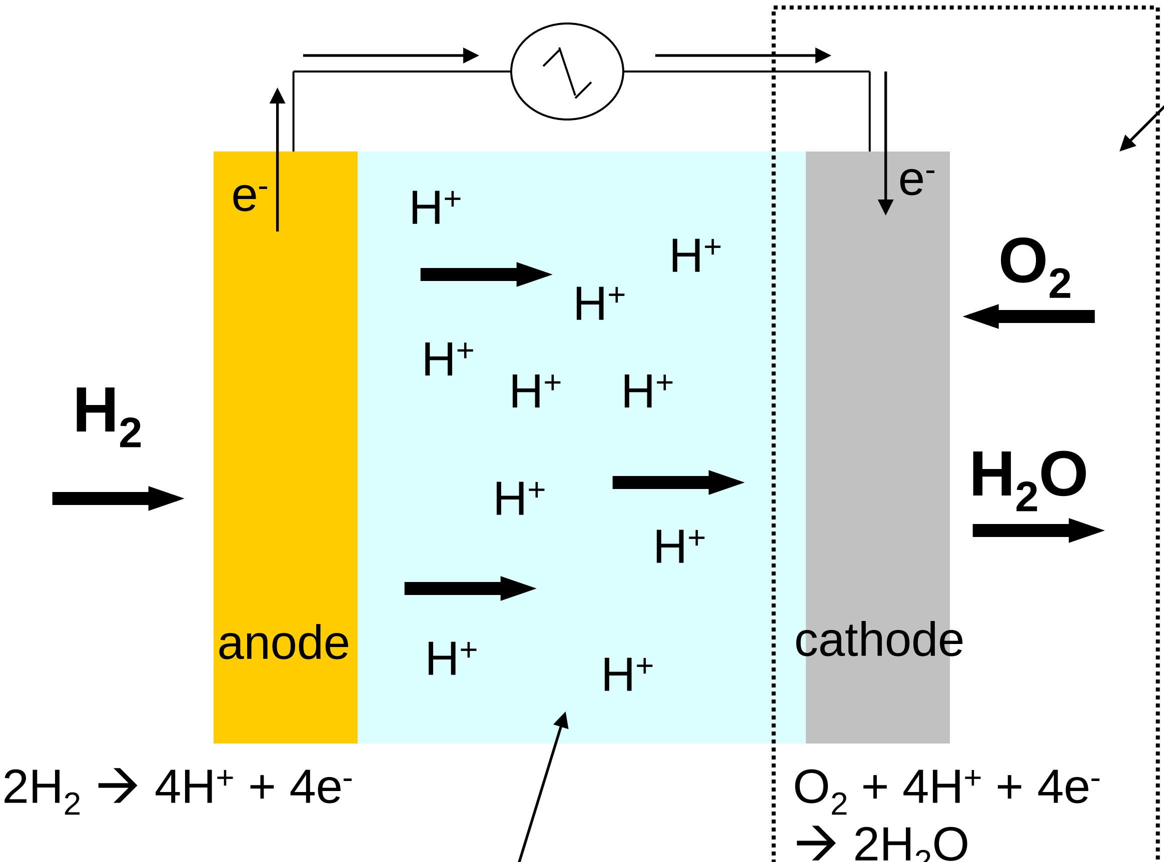
M. Valden et al. *Science* **281** (1998) 1647.

- **Relatively inert Au becomes active once the particle size reaches an optimal diameter.**

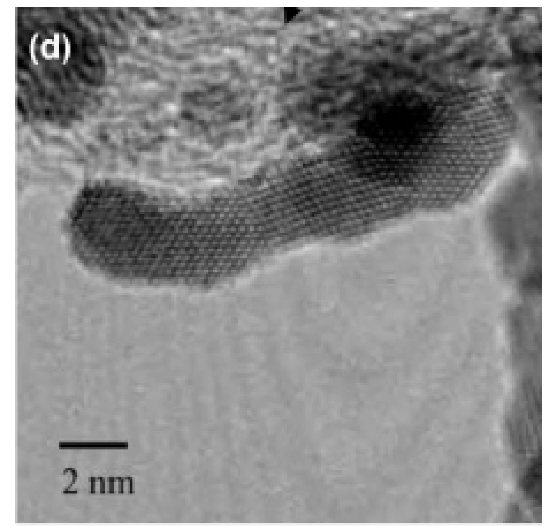
- **Methods of surface science are still critical for understanding how catalyst operates, but the complexity of real catalysts must be integrated into model catalyst design**

Supported Nanoparticles to Catalyze Reduction of O_2 in Proton Exchange Membrane Fuel Cells

O_2 reduction is the rate-limiting step…



Polymer membrane "electrolyte"
(doped perfluorocarbon)

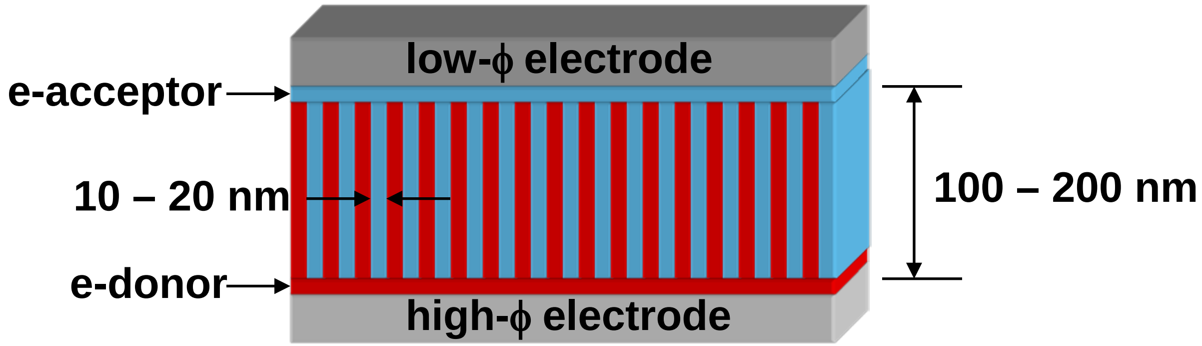


Nanostructured Photovoltaic Cells

- **Solar materials**

  - Cheap semiconductors (organics, nanocrystals, etc.) have poor exciton and/or carrier lifetimes

  - Nanostructuring is essential



Ordered bulk heterojunction

Opportunities: Functional Materials

Nanotubes, Nanowires and Nanoparticles:

- **Electronic & optical properties**
  - **Low defects**
  - **Metamaterials**
  - **Quantum confinement**
- **Mechanical properties**
  - **Much different than bulk materials**
- **Thermal properties**
  - **New forms of conductivity (diamond, graphite, aerogels)**
- **Chemical properties**
  - **Exploiting high surface-to-volume ratios**

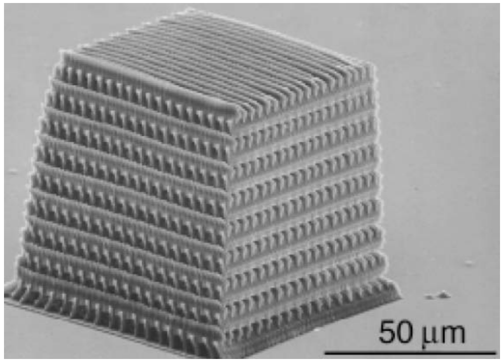
Opportunities: Optics, especially for IT

Nanochemistry is developing alongside nanooptics

- **Optical systems**
  - More defect-tolerant than electronics

- **New science**
  - Plasmonic waveguiding
  - Single-photon sources and detectors

- **New synthetic challenges**
  - 3D fabrication
  - High-quality nanocrystals



Two-Photon Woodpile Crystal
B. H. Cumpston *et al.*,
Nature ***398*, 51 (1999)**

Opportunities: Biology and Biomedicine

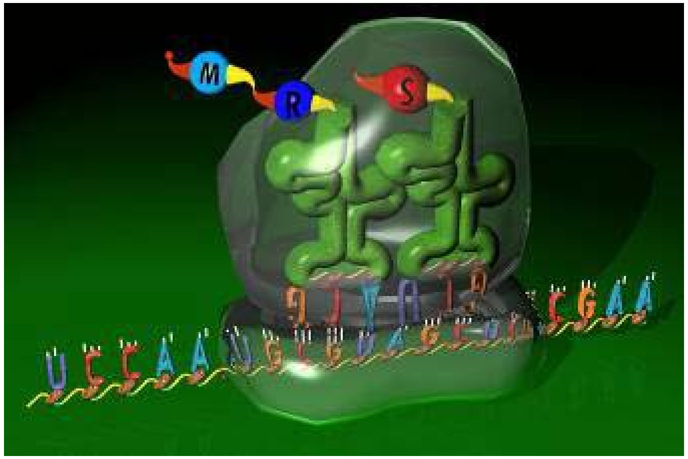
Learning the Functions of Bionanostructures

Nature-provides examples of actuation, sensing, signaling, information processing, and intelligence at the nanoscale

Ribosome = molecular assembler

blueprints

functional product



ribosome

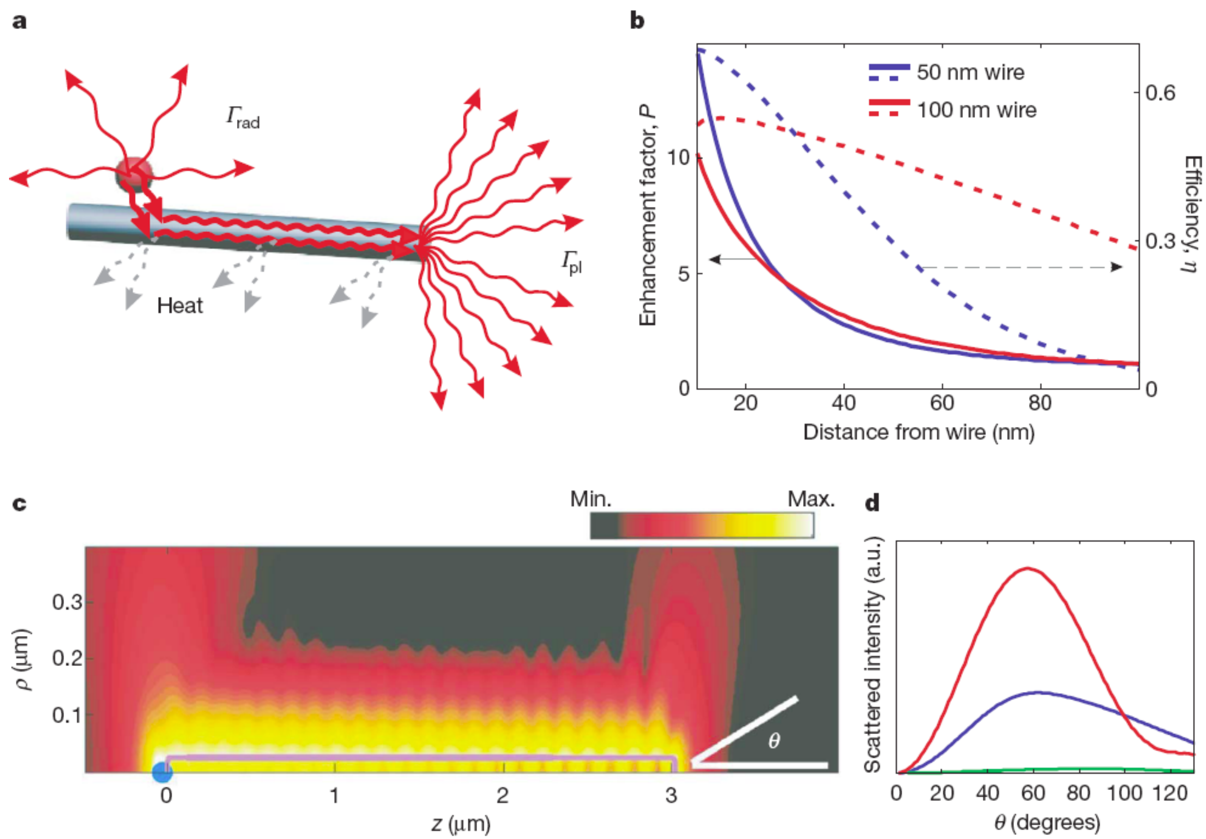
assembly line

Additional Material…

Quantum

Generation of single optical plasmons in metallic nanowires coupled to quantum dots

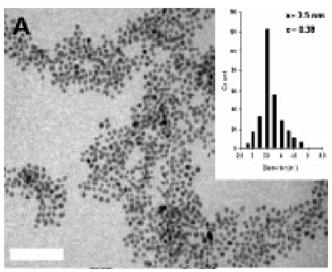
A. V. Akimov[1,4]*, A. Mukherjee[1]*, C. L. Yu[2]*, D. E. Chang[1], A. S. Zibrov[1,4], P. R. Hemmer[3], H. Park[1,2] & M. D. Lukin[1]



Chemical Control of Catalytic Particles

Design of Catalytic Nanostructures

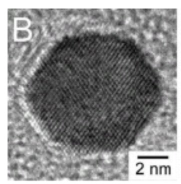
Size control



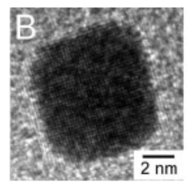
K. Niesz et al. *Nano Lett.* 5 (2005) 2238

Shape control

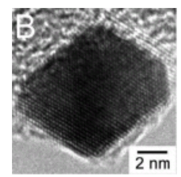
Pt cuboctahedra



Pt cubes



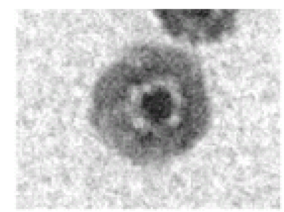
Pt octahedra



H. Song et al. *J.PC B* 109 (2005) 188

Morphology control

Pt nanoparticle embedded in hollow CoO shell

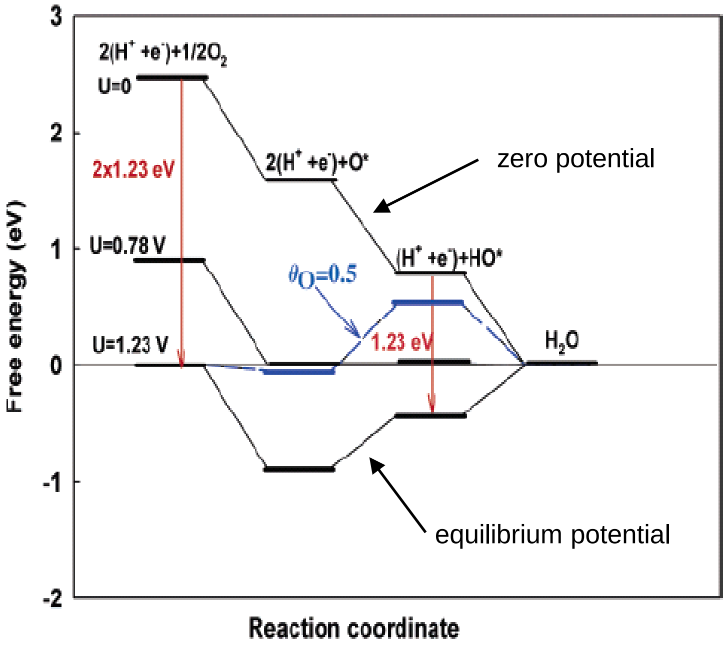


The Oxygen Electrode

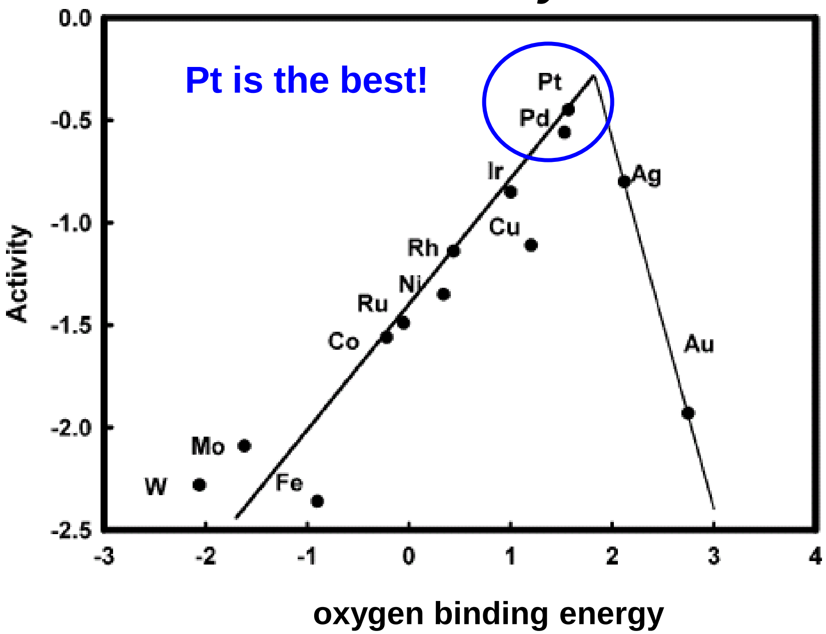
Kinetics of cathode reaction are much slower than the anode reaction and limit economic viability of low temperature fuel cells

Cathode reaction: $4e^- + O_2 + 4H^+ \xrightarrow{\text{slow}} 2H_2O$

Free-energy diagram for O_2 reduction on Pt



Periodic trends in oxygen reduction activity



Volcano relationship between activity and oxygen binding energy suggest <u>alloying</u> improve activity

Nørskov et al. J. Phys. Chem. B 108 (2004) 17886

Challenges

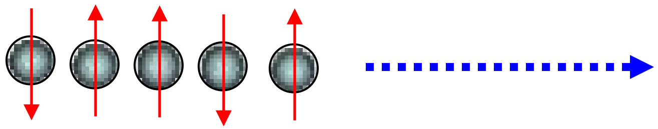
- Defect-free assemblies
- Large-area assemblies
- Fine-tuning of interparticle spacing
- Precise manipulation of assemblies

Vital to applications in optics and electronics

Need Solutions

- A combination of 'bottom-up' and 'top-down' methods
- Nature-developed approaches (biological templates)
- New opportunities?

Quantum Computing



2^{400} **classical registers**

400 qubits

- Binary digit ("bits") replaced by a two-level quantum system ("qubits") allowing for infinite superpositions of states
- Quantum operation could compute not just on one machine state at once!
- Factoring a 100-digit number

Factoring a 400 digit number would take 10^{10} years with today's fastest computers, but only 3 years with quantum computers!

Conclusions

The most important problems in nanoscience depend on chemistry

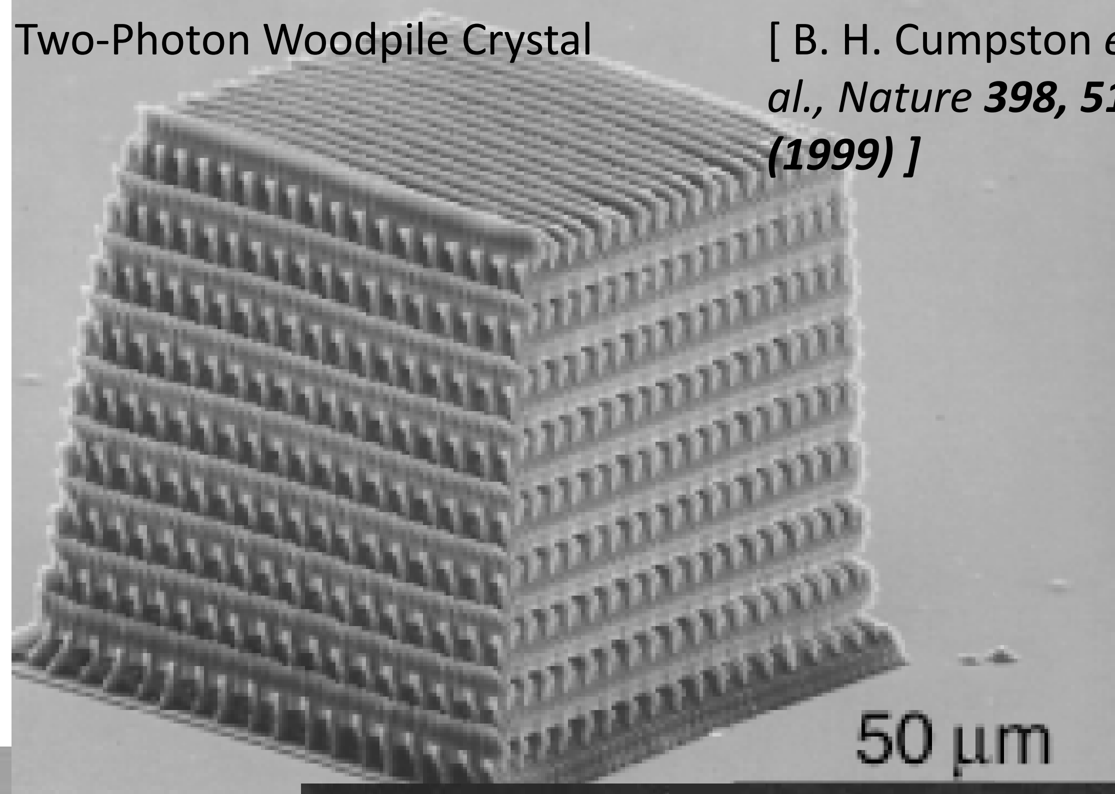
***New* chemistry is essential**

One final thought: *Risk*

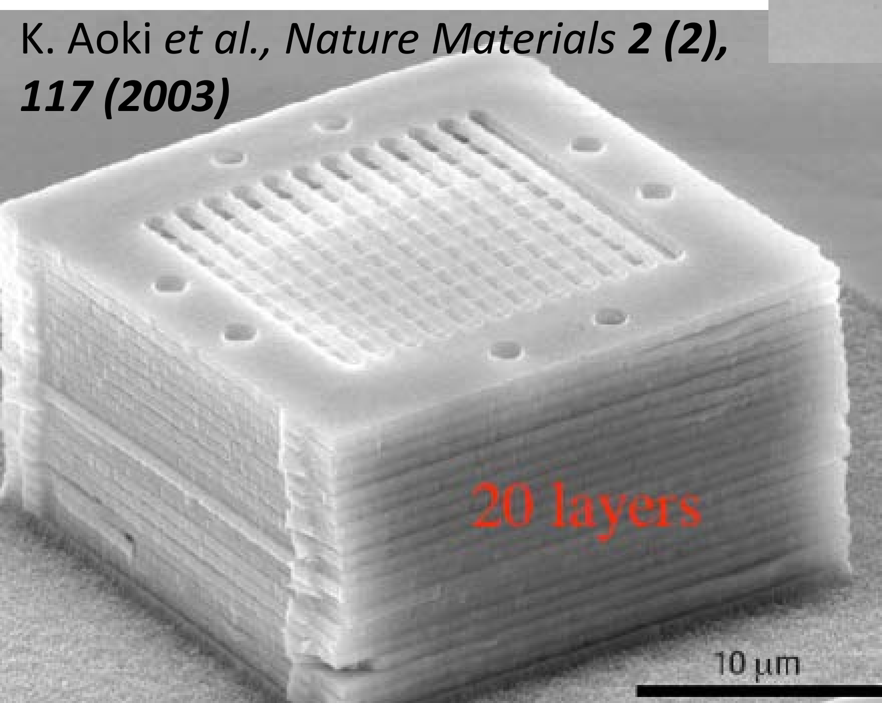
	Successful?	
Problem	**Yes**	**No**
Important	+ + +	+
Unimportant	-	- - -

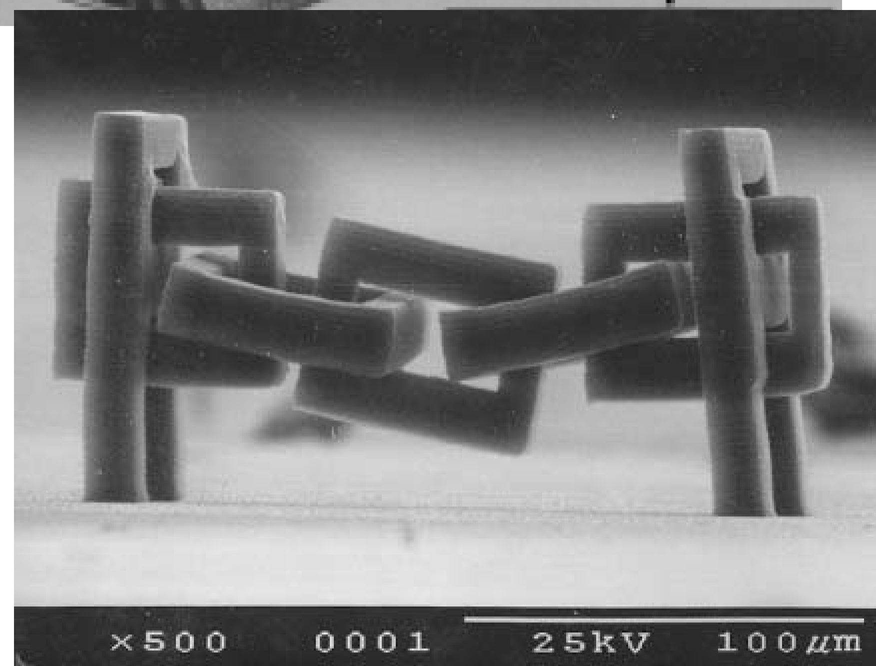
Two-Photon Woodpile Crystal

[B. H. Cumpston *et al., Nature* ***398, 51 (1999)***]

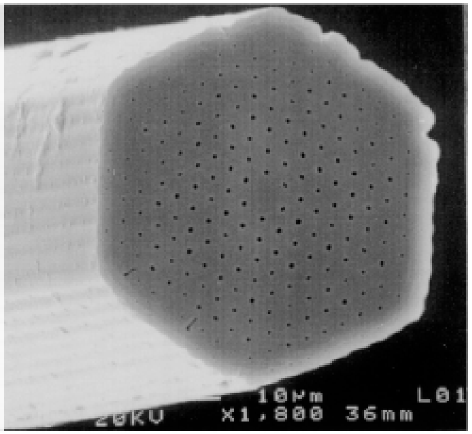


K. Aoki *et al., Nature Materials* ***2 (2), 117 (2003)***



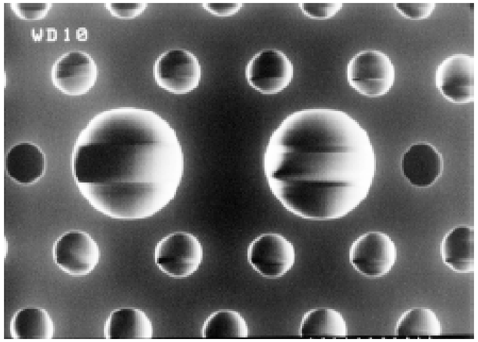


Holey fibers



endlessly single-mode

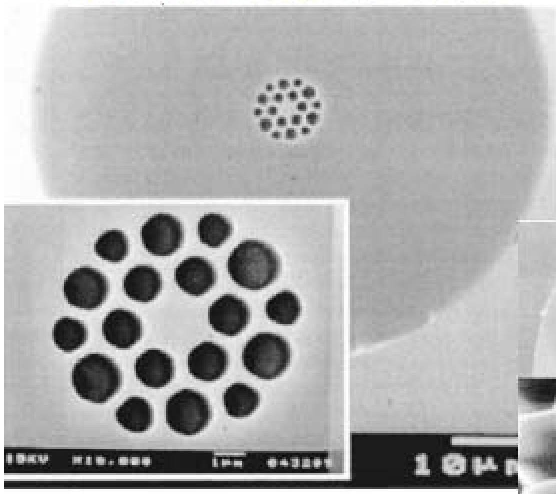
[T. A. Birks *et al.*, *Opt. Lett.* **22**, 961 (1997)]



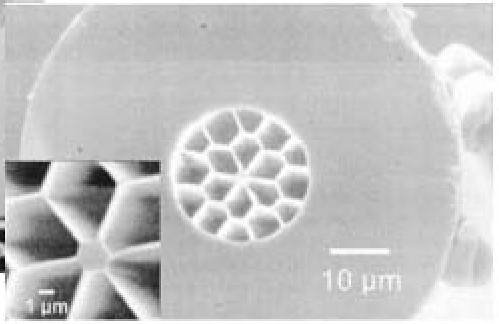
polarization -maintaining

[K. Suzuki, *Opt. Express* **9**, 676 (2001)]

nonlinear fibers

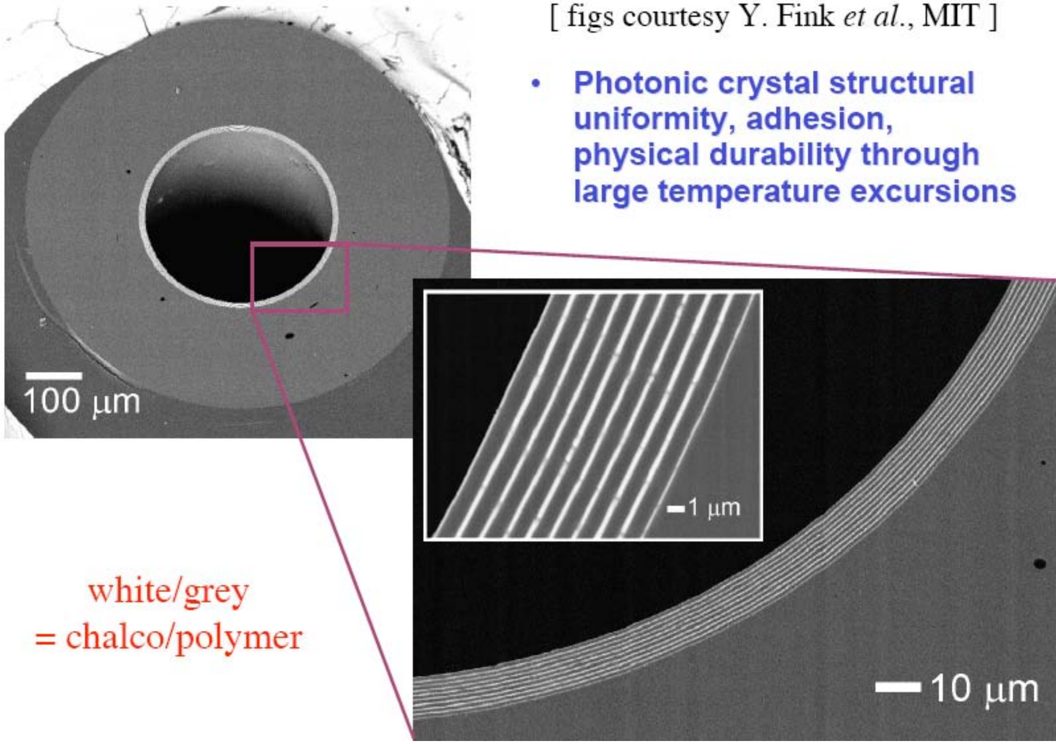


[Wadsworth *et al.*, *JOSA B* **19**, 2148 (2002)]



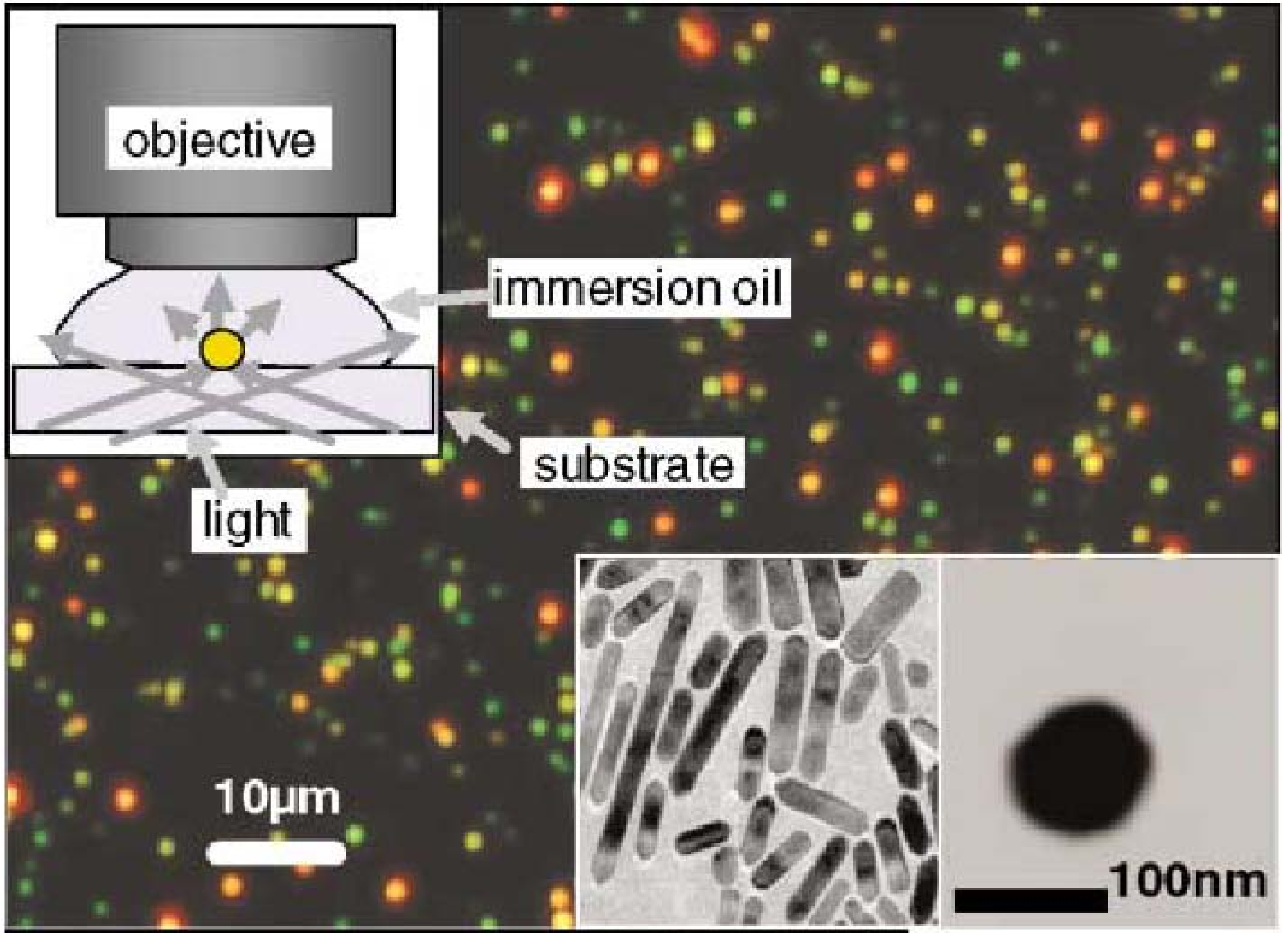
[figs courtesy Y. Fink *et al.*, MIT]

- Photonic crystal structural uniformity, adhesion, physical durability through large temperature excursions



white/grey = chalco/polymer

Optical Properties of Metal Nanostructures

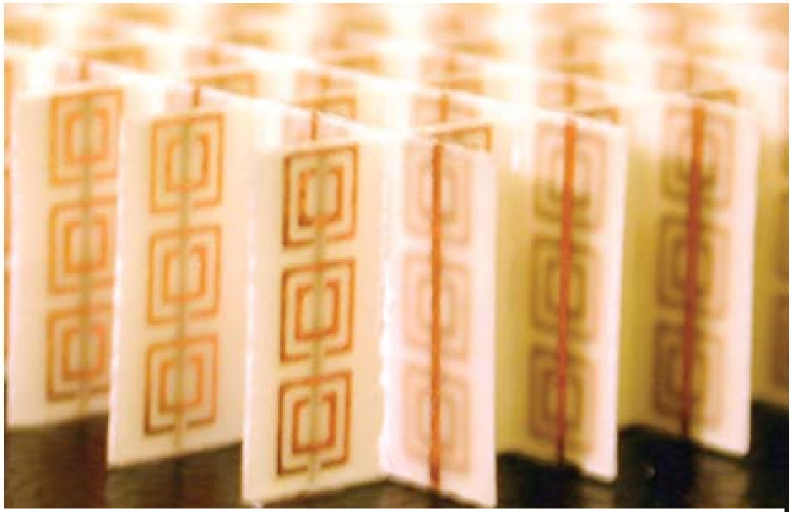


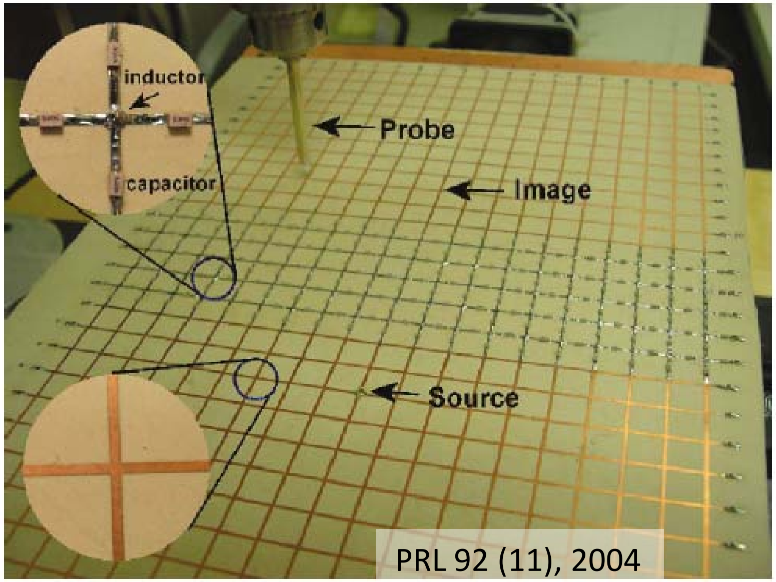
Gold Nanorods (red) and 60nm Gold Nanospheres (green) under Dark-field Illumination

From: Sonnichsen et al, Phys. Rev. Lett., vol. 88, no. 7, pp. 077402 (2002)

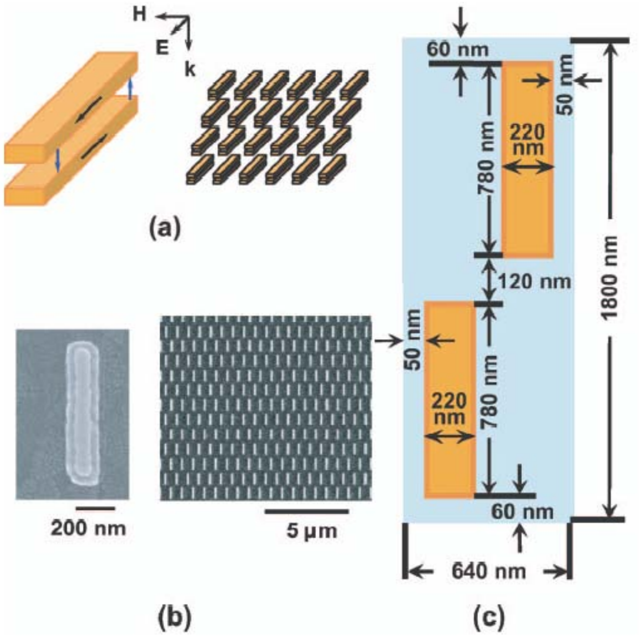
Negative index materials

Science 292, 77 (2001)

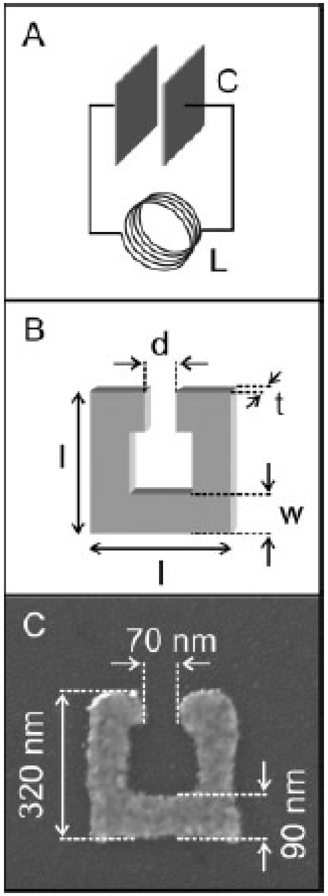




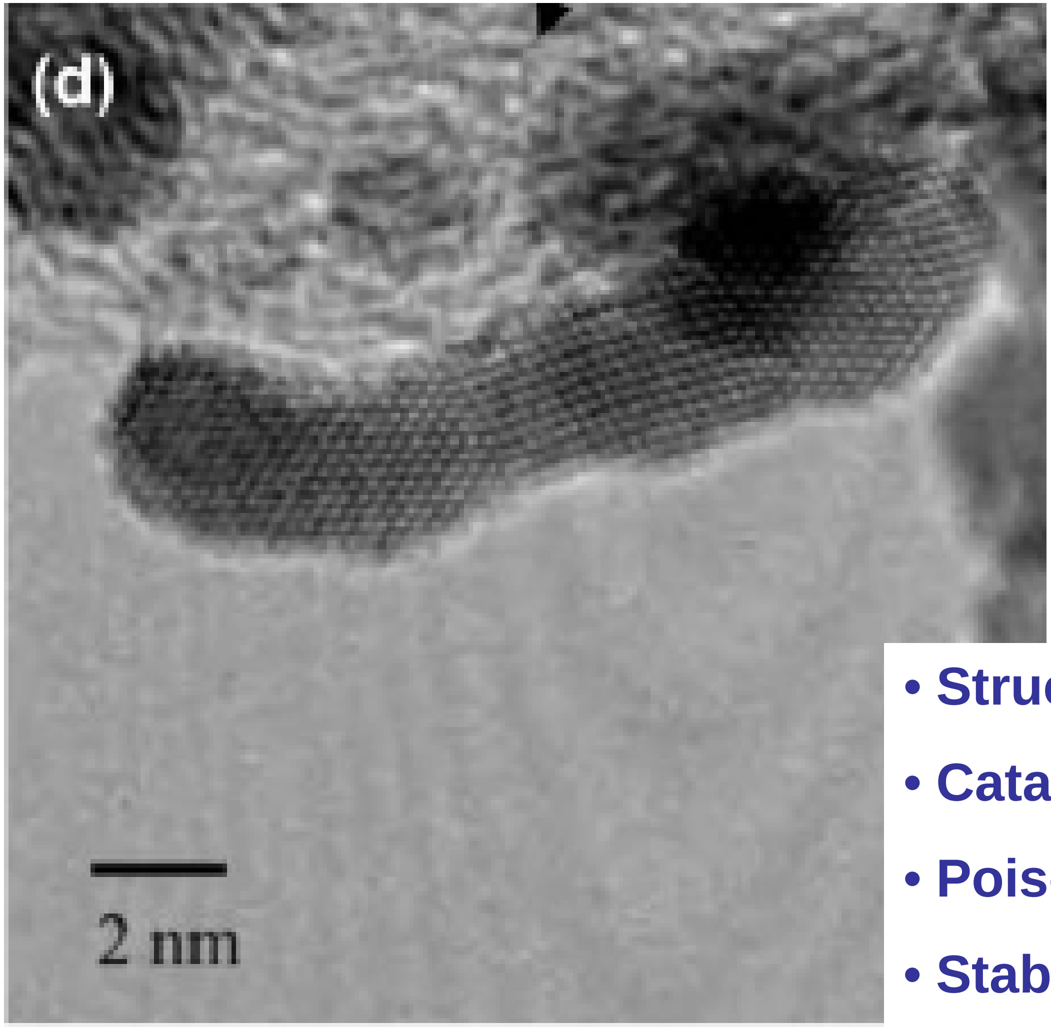
PRL 92 (11), 2004



Optics letters, 30, 24, 3356 (2005)



S. Linden, C. Enkirch, M. Wegener, J. Zhou, T. Koschny, C. M. Soukoulis, *Science* **2004**, *306*, 1351.



- Structure-reactivity relations
- Catalyst-support interactions
- Poisoning and Activation
- Stability
- Mass transport

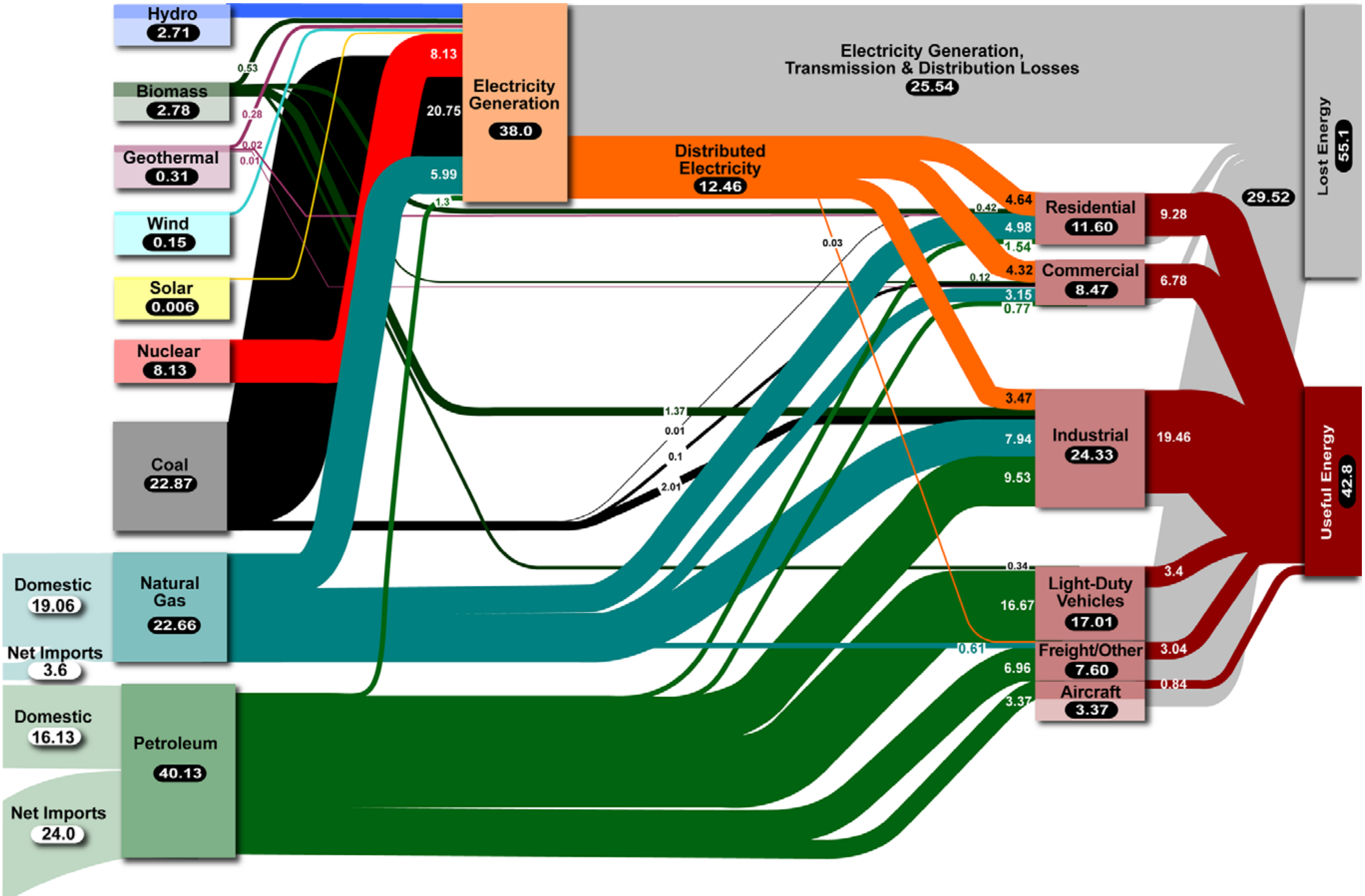
Nanotechnology in Energy

Berkeley, CA:
www.nrel.gov

A stack of 36 PEM fuel cells

Schatz Energy Research Center:
www.humboldt.edu/~serc/animation.html

Plasma Display:
http://www.de.nec.de/pressfiles/42vp4_plasma_display.jpg


Hydro
2.71
Biomass
2.78
Geothermal
0.31
Wind
0.15
Solar
0.006
Nuclear
8.13
Coal
22.87
Domestic
19.06
Natural
Gas
22.66
Net Imports
3.6
Domestic
16.13
Petroleum
40.13
Net Imports
24.0
0.53
0.28
0.02
0.01
8.13
20.75
5.99
1.3
Electricity
Generation
38.0
Electricity Generation,
Transmission & Distribution Losses
25.54
Distributed
Electricity
12.46
0.03
1.37
0.01
0.1
2.01
0.34
0.61
4.64
0.42
4.98
1.54
4.32
0.12
3.15
0.77
3.47
7.94
9.53
16.67
6.96
3.37
Residential
11.60
Commercial
8.47
Industrial
24.33
Light-Duty
Vehicles
17.01
Freight/Other
7.60
Aircraft
3.37
9.28
6.78
19.46
3.4
3.04
0.84
29.52
Lost Energy
55.1
Useful Energy
42.8

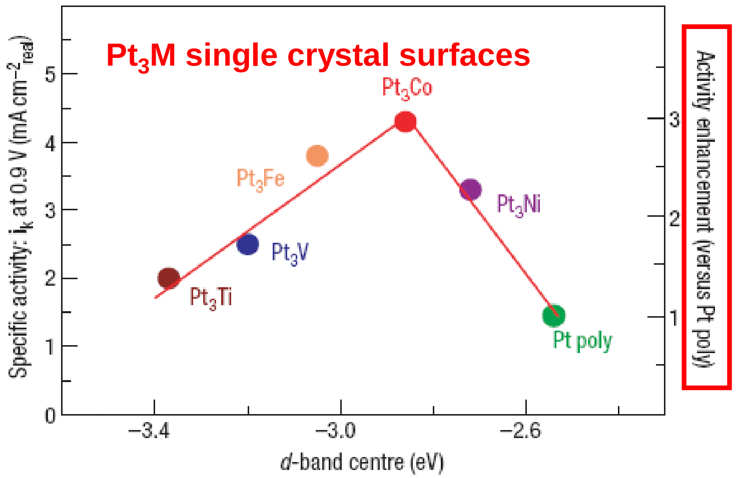
Is it possible to design catalysts?

Tuning surface electronic structure of nanoparticle surface by alloying leads to improved reduction kinetics – Aided by *surface science* and *nanoscience*

Fundamental

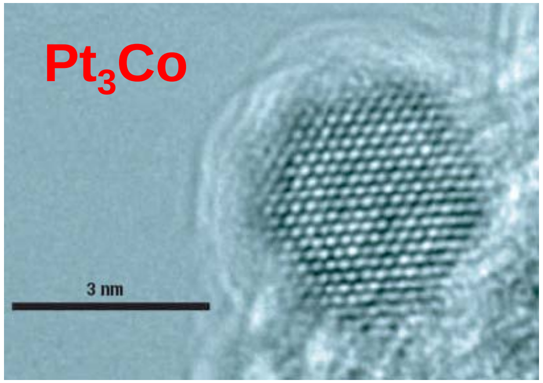
Research…

Alloying leads to reduction activity enhancements



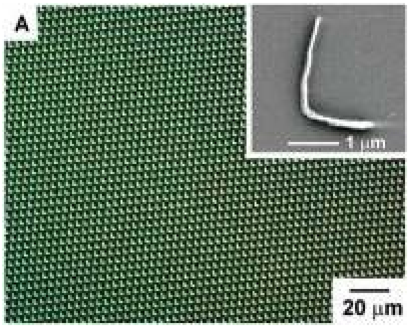
DFT calculated surface electronic structure

new generation of oxygen reduction catalysts

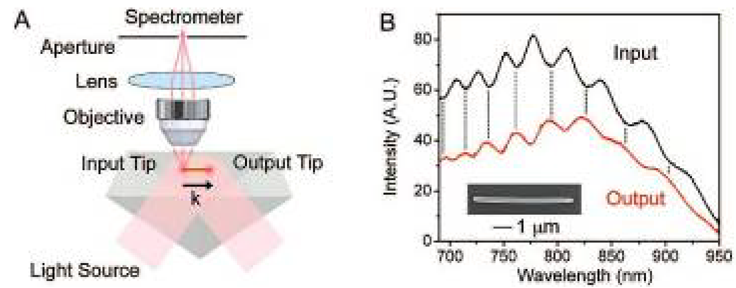


…coupled with nanoscience leads to the design of better O_2 reduction catalysts

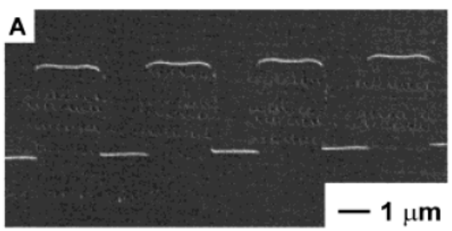
Applications of Nanoskiving



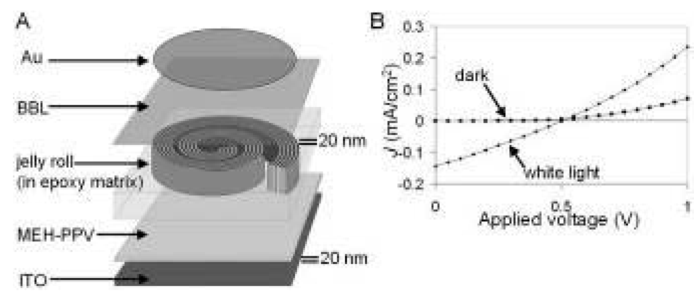
Frequency-selective surfaces
Xu et al. *Nano Lett.* **2007**



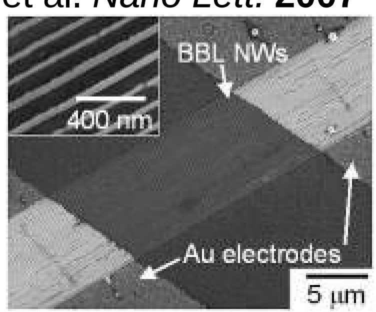
Single-crystal nanowire plasmonic waveguides
Wiley et al. *Nano Lett.* **2008**



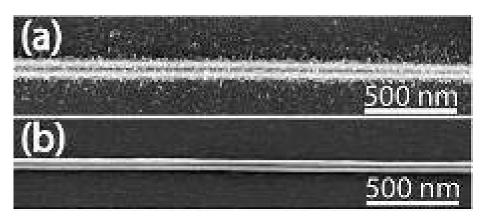
Electrodes for electrodeposition
Xu et al. *Nano Lett.* **2007**



Organic photovoltaic device
Lipomi et al. *Adv. Funct. Mater.* **2008**



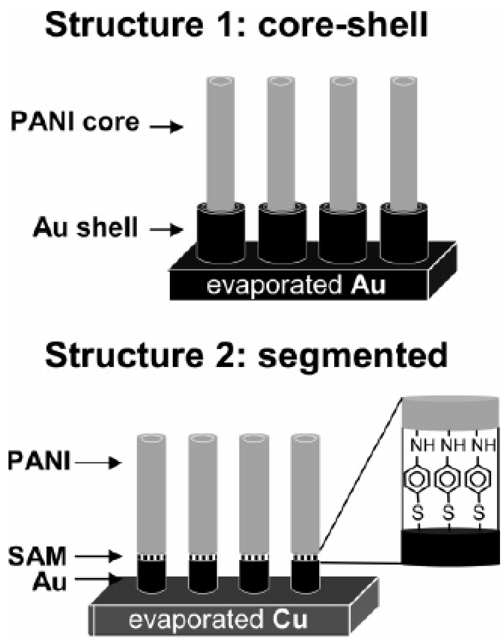
Conducting polymer nanowires
Lipomi et al. *Nano Lett.* **2008**

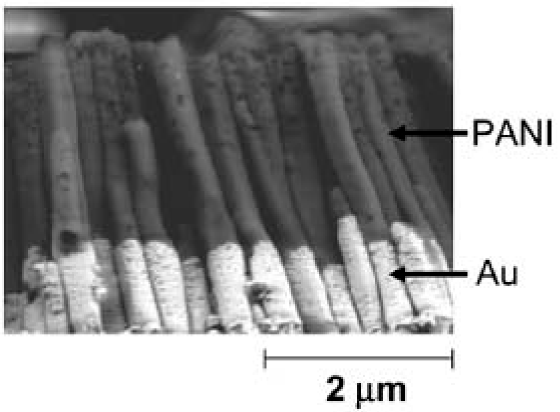


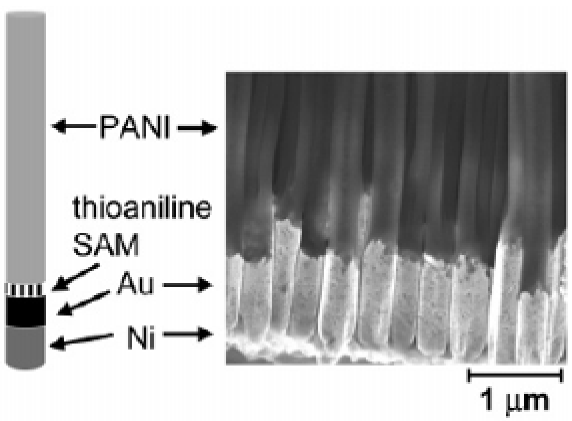
Electrically addressable parallel nanowires
Dickey et al. *Nano Lett.* **2008**

Templating

- Example: electrochemical growth of core-shell and segmented metallic and polymeric tubes in anodic alumina membranes







C. Martin

Lahav et al. *Nano Lett.* **2006**

Applications of Self-Assembled Particles

- **Sensing**
  - **Chemi- and biosensors**
  - **Plasmonic rulers**
- **Multifunctional carriers for delivery**

Developing quickly

- **Data storage devices**
- **Optoelectronic devices**
  - **Plasmon waveguides**
  - **Focusing lenses**
  - **Light generators**
  - **Optical switches**
- **Nanoelectronics**

Developing slowly

Self-Assembly: Combining Top-down and Bottom-up

- **Assembly in solutions – “artificial molecules”**
  - Balance of attraction and repulsion forces
  - Molecular recognition

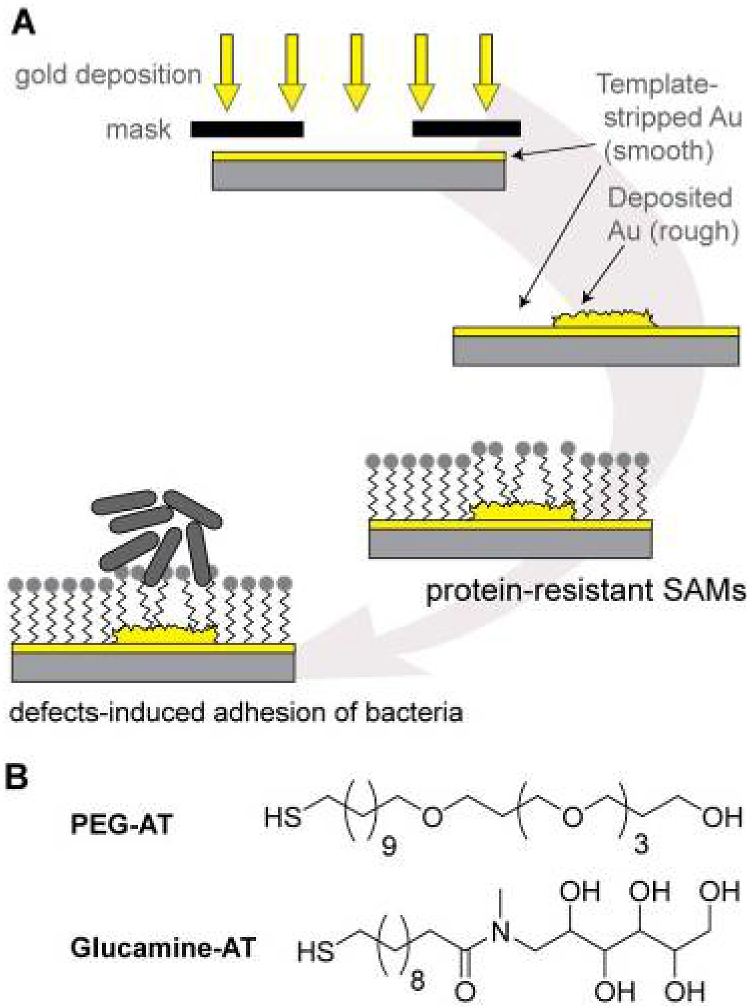
- **Assembly using templating methods**
  - Hard template: nanotubes, nanowires, nanofabricated templates
  - Soft template: synthetic polymers, proteins, DNA or viruses

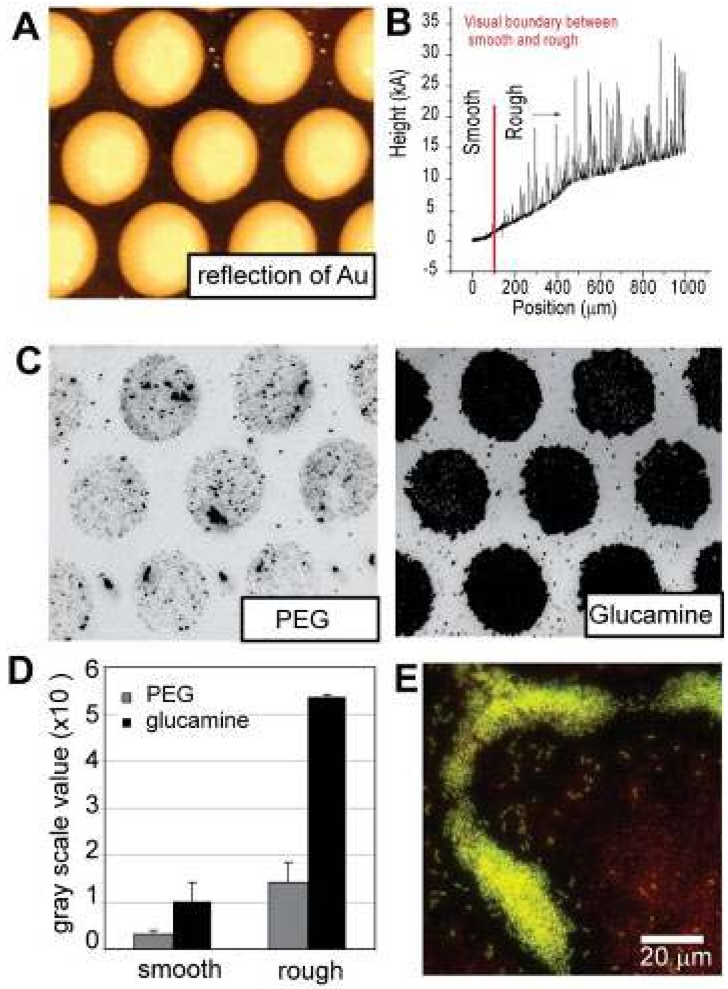
- **Assembly at interfaces**
  - Langmuir-Blodgett technique
  - Sedimentation or evaporation-induced self-assembly
  - Adsorption of nanoparticles

- **Assisted assembly of nanoparticles**
  - Electric or magnetic fields
  - Shear forces
  - Light irradiation

SAMs

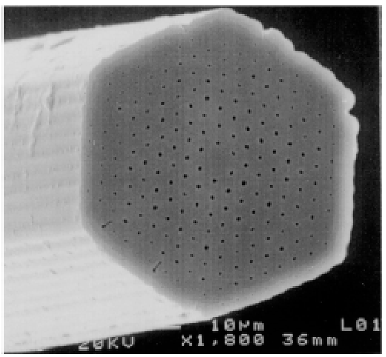
- Influence of defects in organic monolayers on growth of biofilms





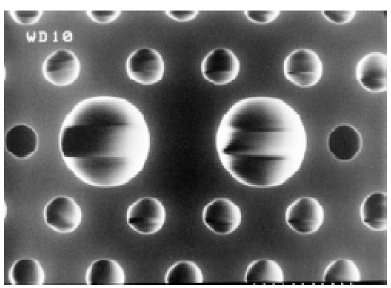
York et al. in prep

Holey Fibers



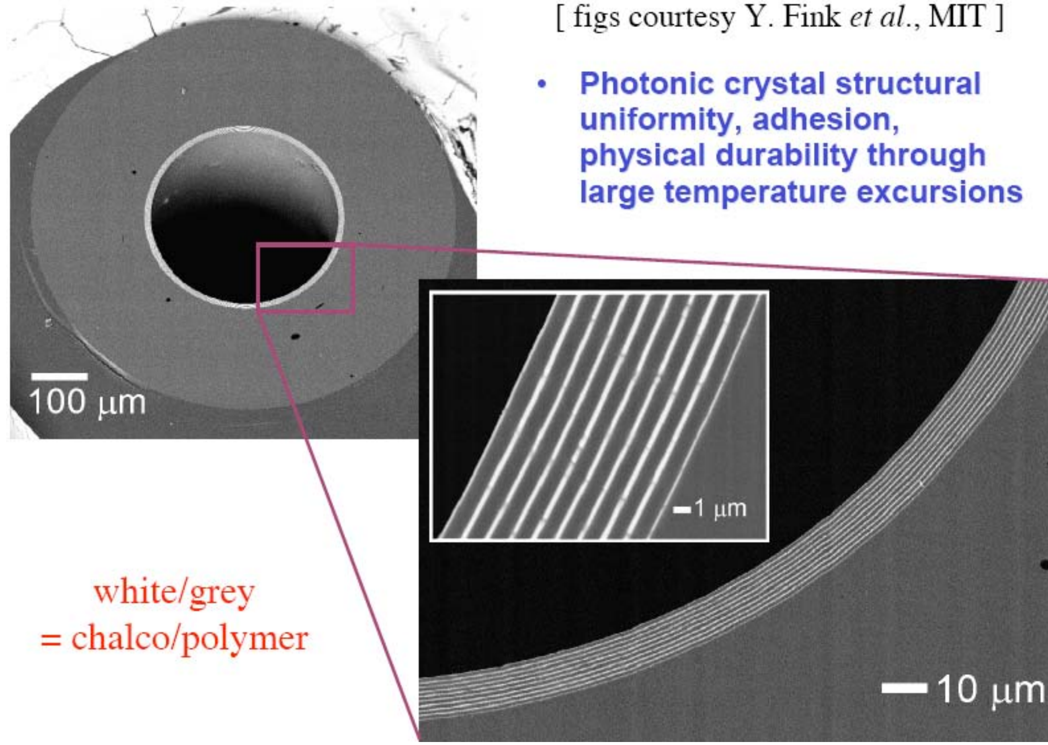
endlessly
single-mode

[T. A. Birks *et al.*,
Opt. Lett. **22**,
961 (1997)]



polarization
-maintaining

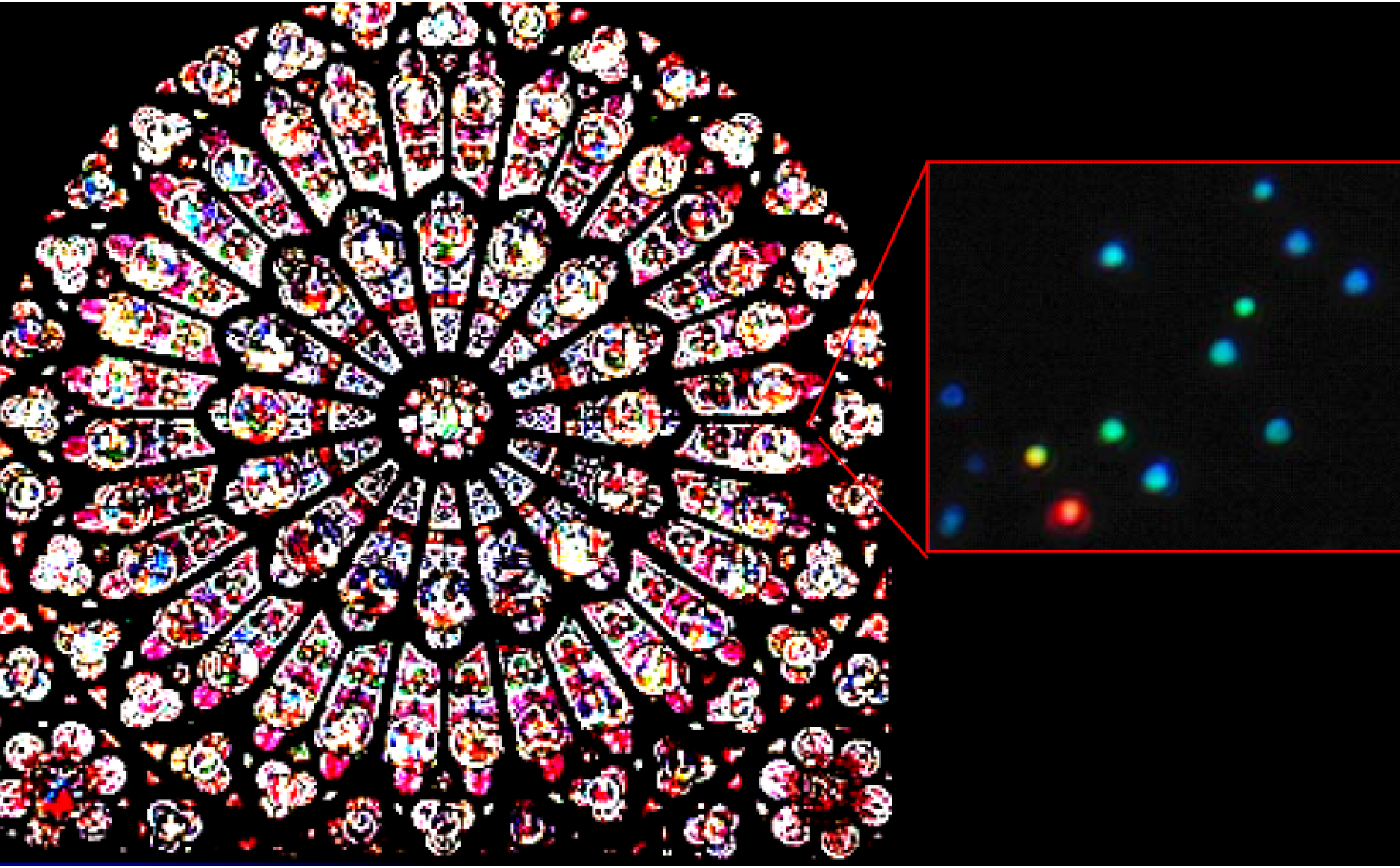
[K. Suzuki,
Opt. Express **9**,
676 (2001)]



[figs courtesy Y. Fink *et al.*, MIT]

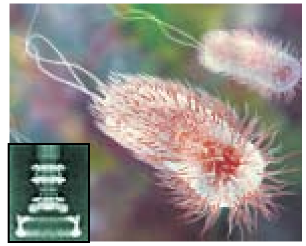
- **Photonic crystal structural uniformity, adhesion, physical durability through large temperature excursions**

http://ab-initio.mit.edu/photons/tutorial/L5-fiber.pdf



Biology: Proving Function at the Nanoscale

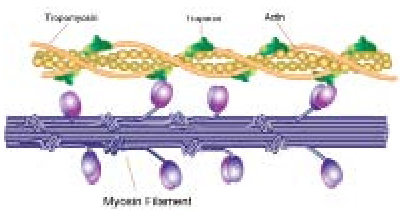
rotary motor



bacteria flagellum

electric motor

linear motor



actin / myosin

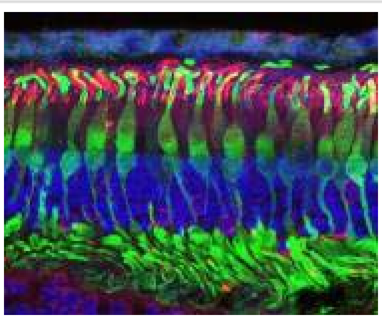
rack and pinion

energy transducer

ATP synthase

steam engine

photo-transducer

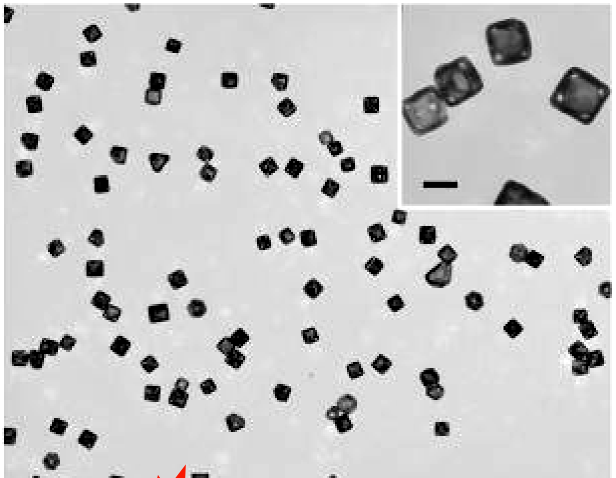


rhodopsin

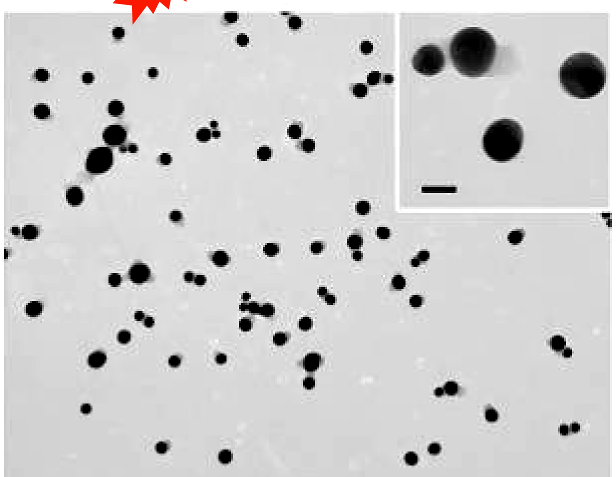
photodiode

Particles for EM Heating

In air, gold nanocages melted under camera flash as the temperature was raised by 200 degrees. In water, the temperature increase was enough to kill breast cancer cells targeted by gold nanocage at a laser (l=820 nm) power density of 0.9 W/cm^2.

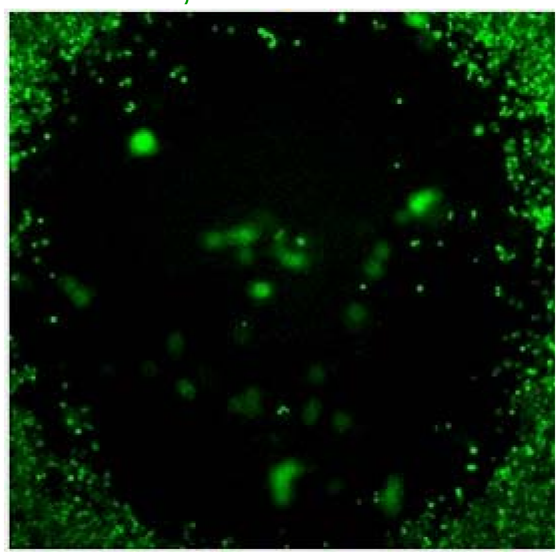


Camera flash

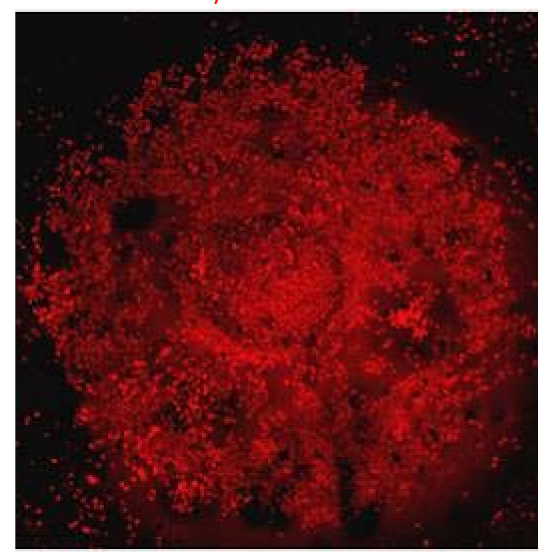


100 nm

Live cells, calcein-AM stain



Dead cells, EthD-1 stain



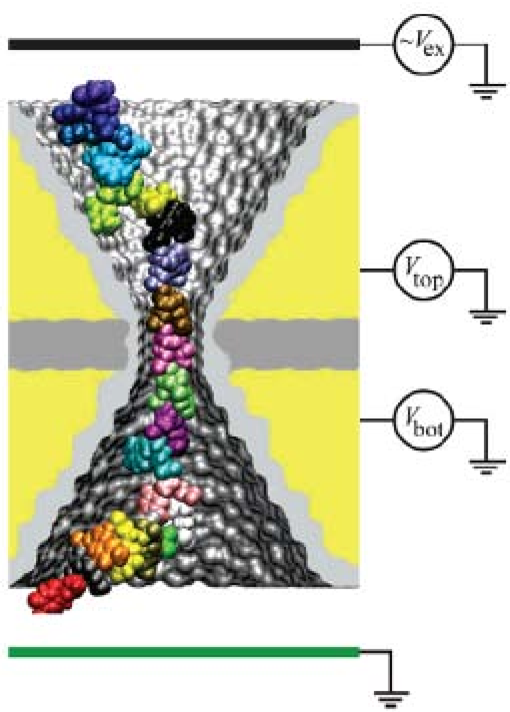
500 μm

Chen, Wang, Xi, Au, Siekkinen, Warsen, Li, Zhang, Xia & Li, *Nano Lett.* **2007**

Nanoholes: DNA Sequencing

Detection of DNA Sequences Using an Alternating Electric Field in a Nanopore Capacitor

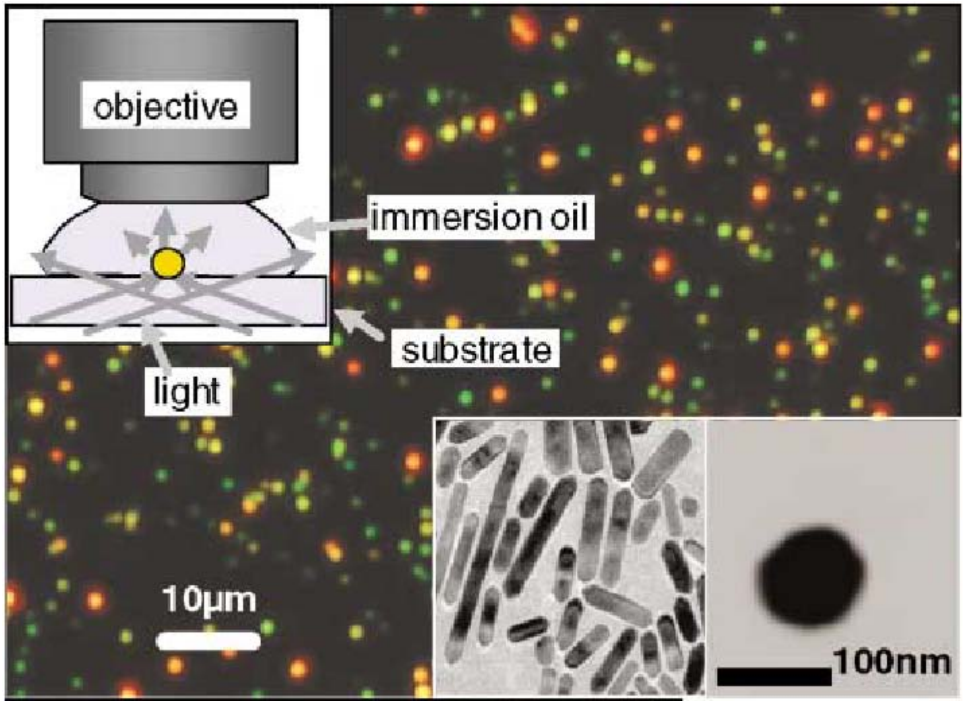
Grigori Sigalov,[†] Jeffrey Comer,[†,‡] Gregory Timp,[†] and Aleksei Aksimentiev*[,†,‡]



Nano Letters, **2008**

Nanooptics

- **Optical properties of metallic nanostructures**



Gold Nanorods (red) and 60nm Gold Nanospheres (green) under Dark-field Illumination

Sonnichsen et al, Phys. Rev. Lett., vol. 88, no. 7, pp. 077402 (2002)

The Cell