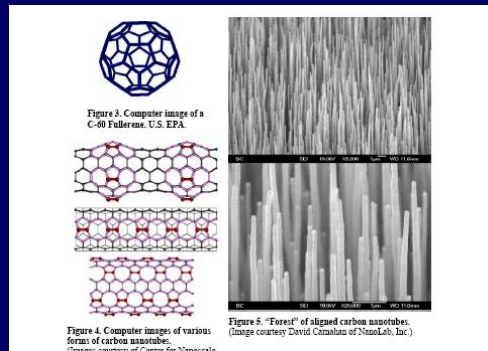
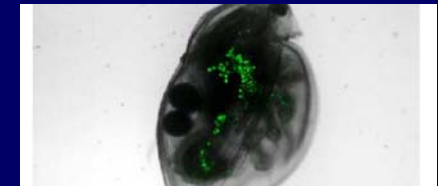
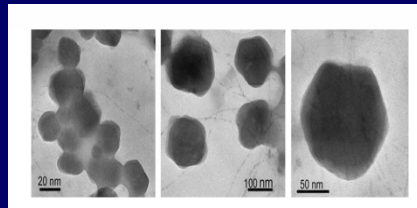
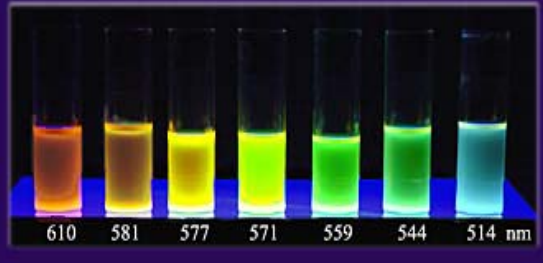


Life Cycle of Nanostructured Materials

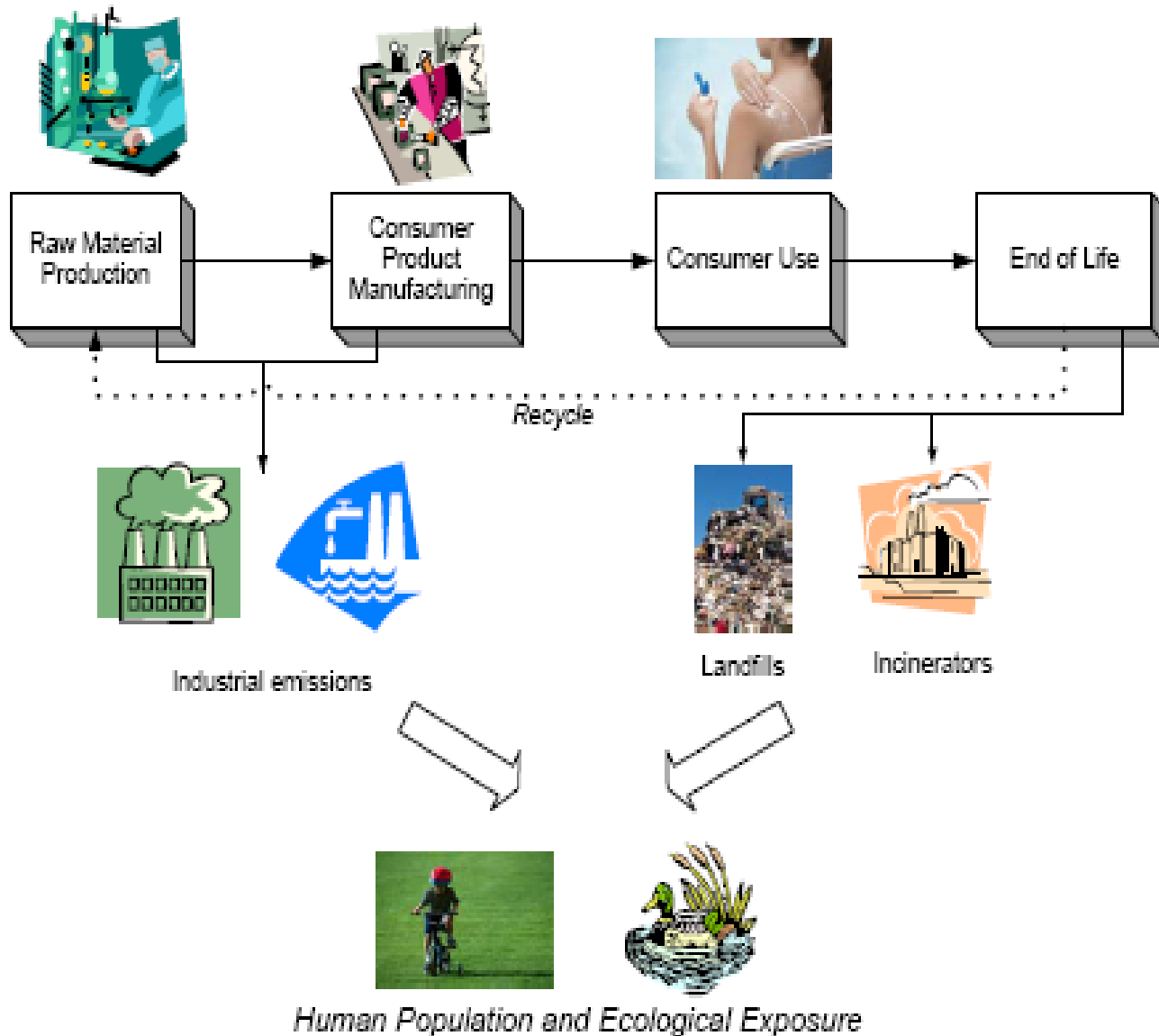
Thomas L. Theis
Institute for Environmental Science and Policy
University of Illinois at Chicago



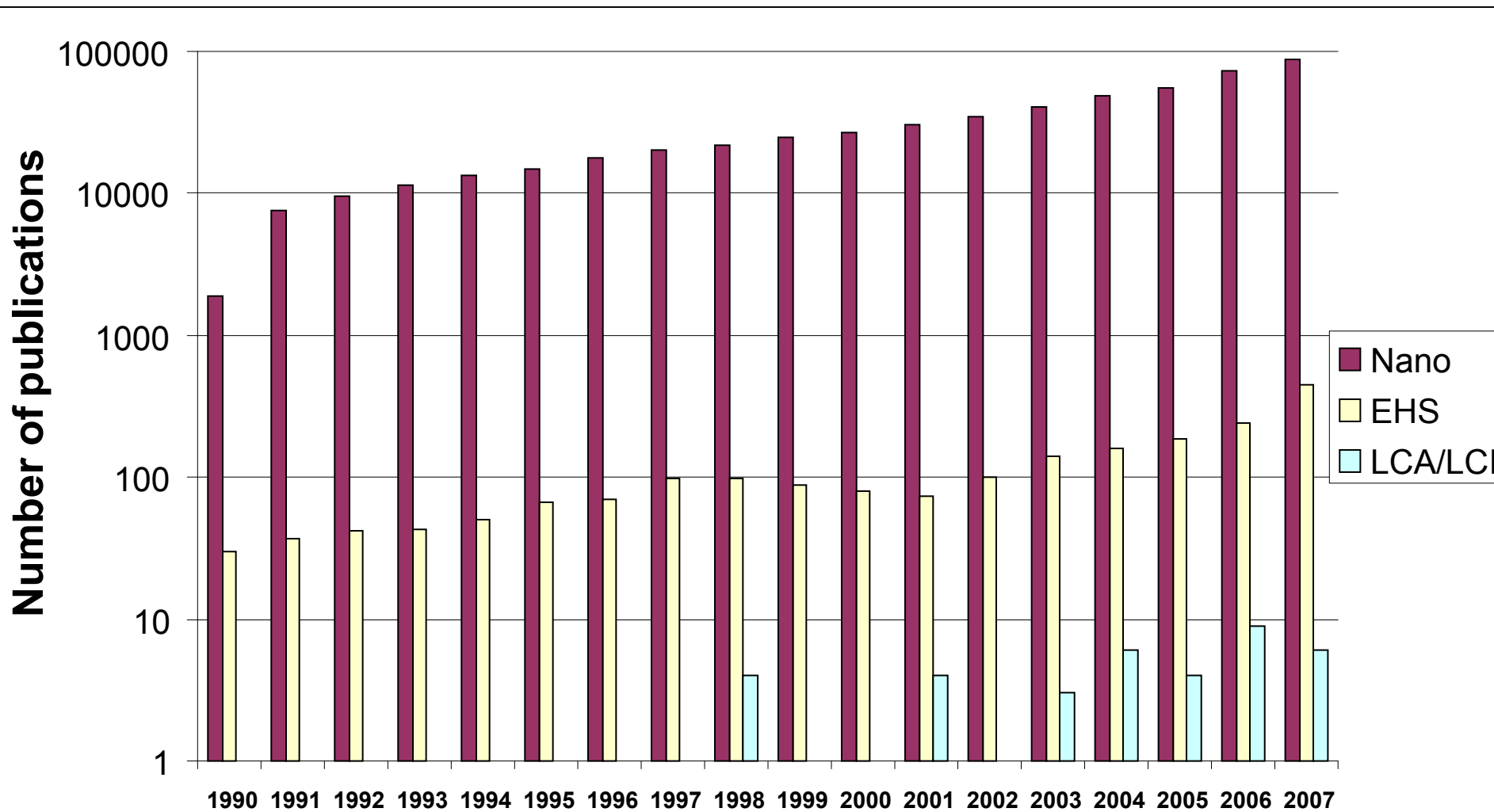
Nano projections

- Projected to generate \$1.1 trillion in economic activity by 2016 (NNI, 2001)
- Production rates $>10^5$ mt/yr by 2020 (Royal Society 2004)
- An “enabling” technology with implications for energy, manufacturing, electronics, transportation, healthcare, pharmaceuticals, environmental control and purification, sensors and national security, chemical processing, and sustainable development

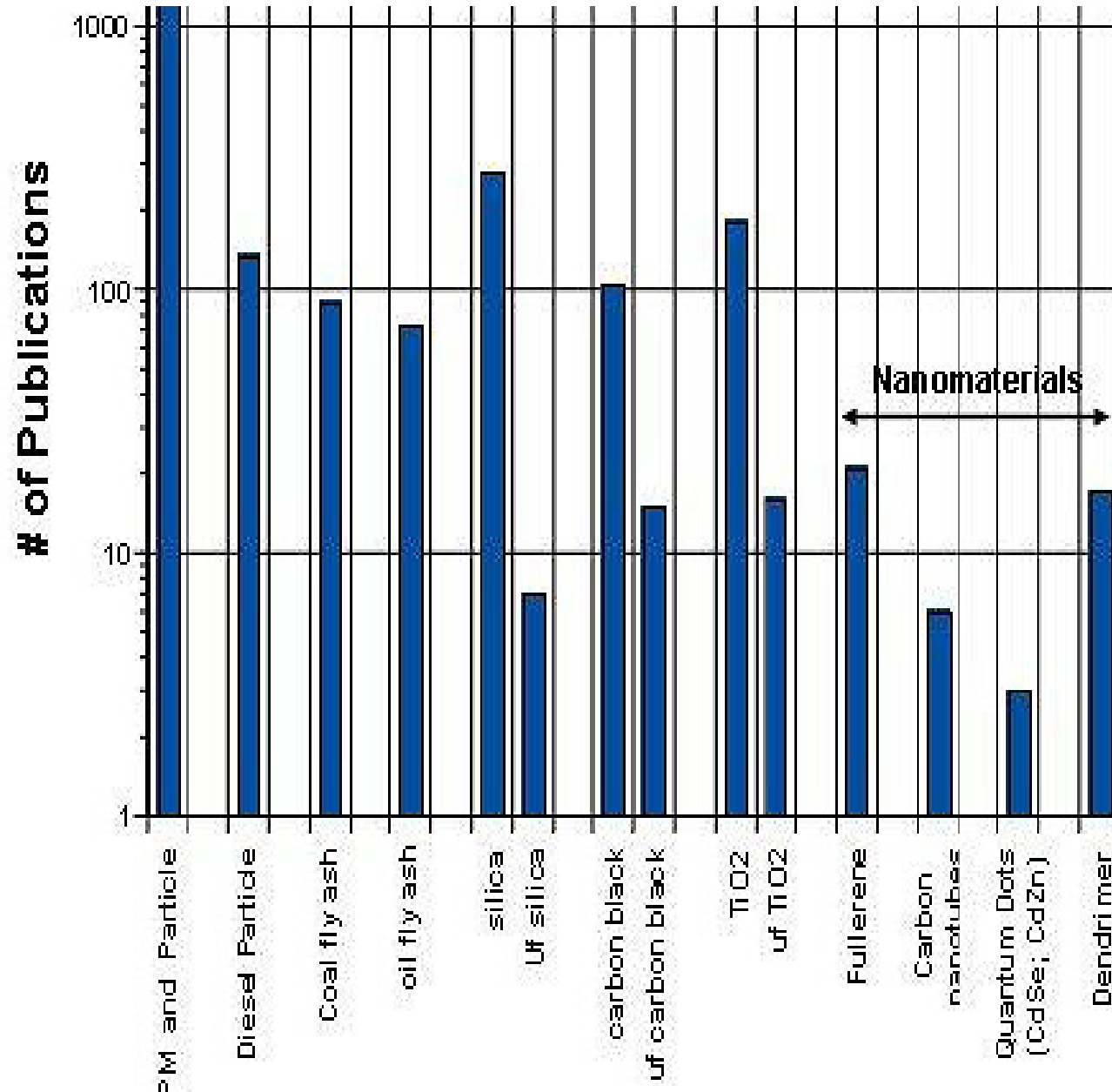
Life Cycle Concept



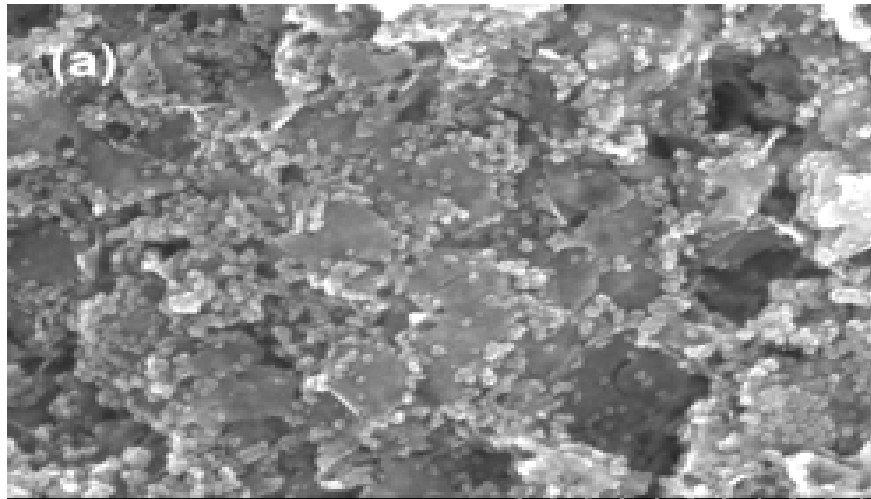
Nano-based publications



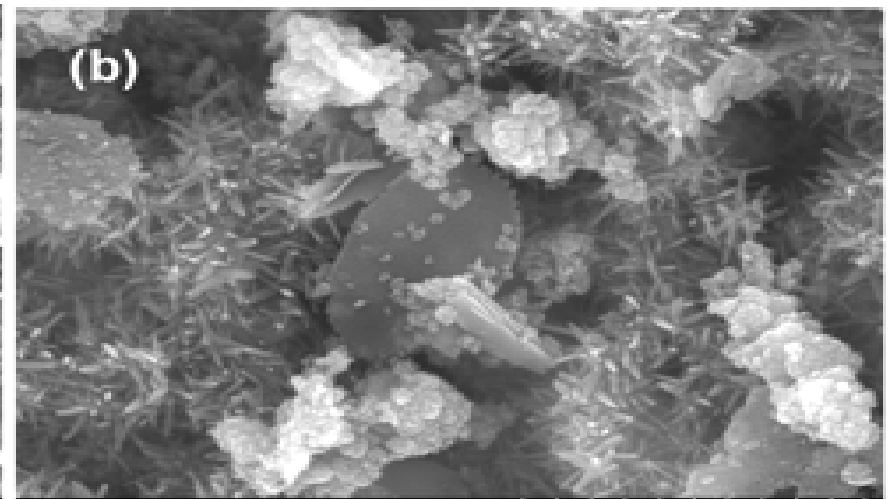
Fine particle toxicity publications (2005)



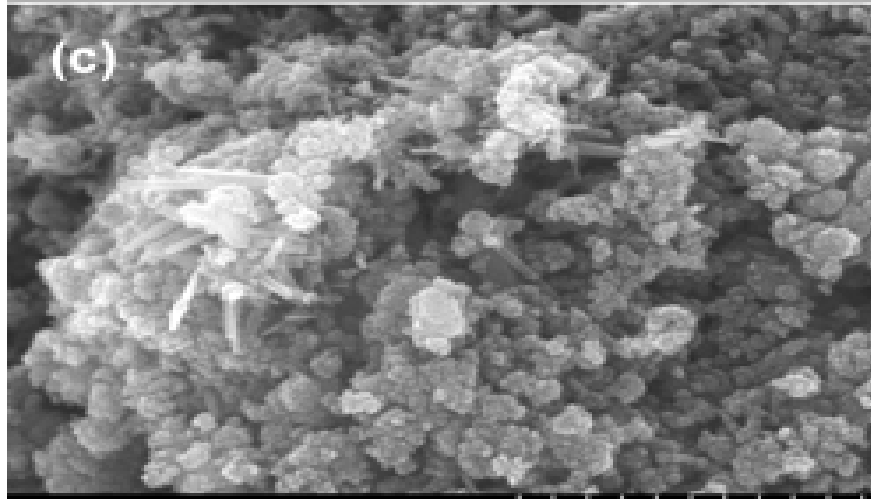
Nano-zerovalent iron



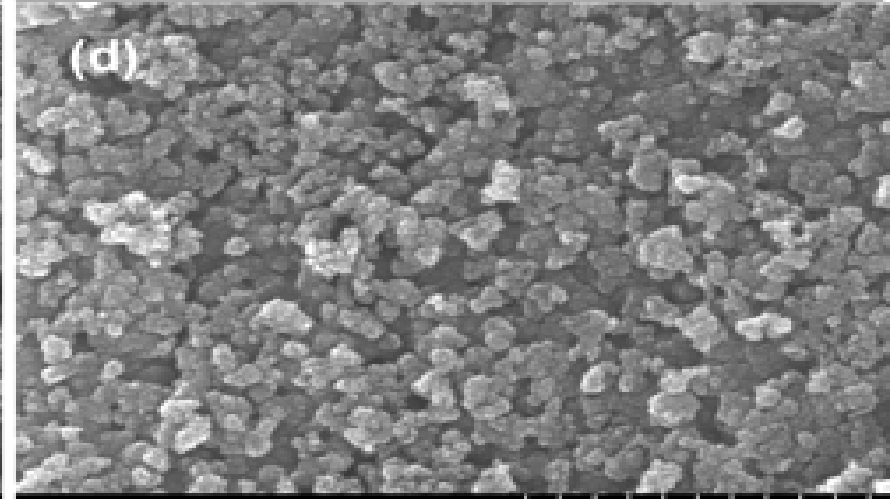
Fe0-blank 15.0kV x50.0k 1.00um



As3NZVI-7d 15.0kV x50.0k 1.00um



As3NZVI30d 15.0kV x50.0k 1.00um



As3NZVI60d 15.0kV x50.0k 1.00um

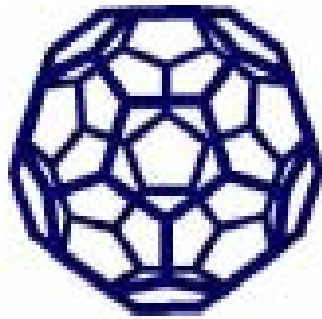


Figure 3. Computer image of a C-60 Fullerene. U.S. EPA.

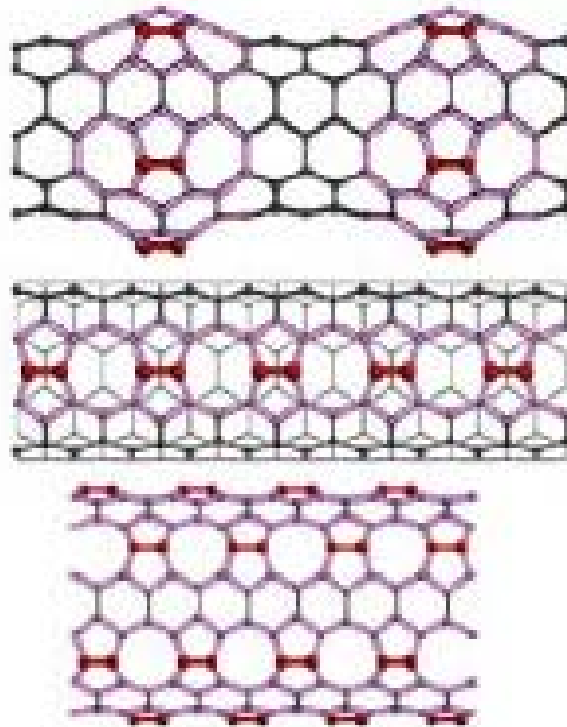


Figure 4. Computer images of various forms of carbon nanotubes.
(Images courtesy of Center for Nanoscale

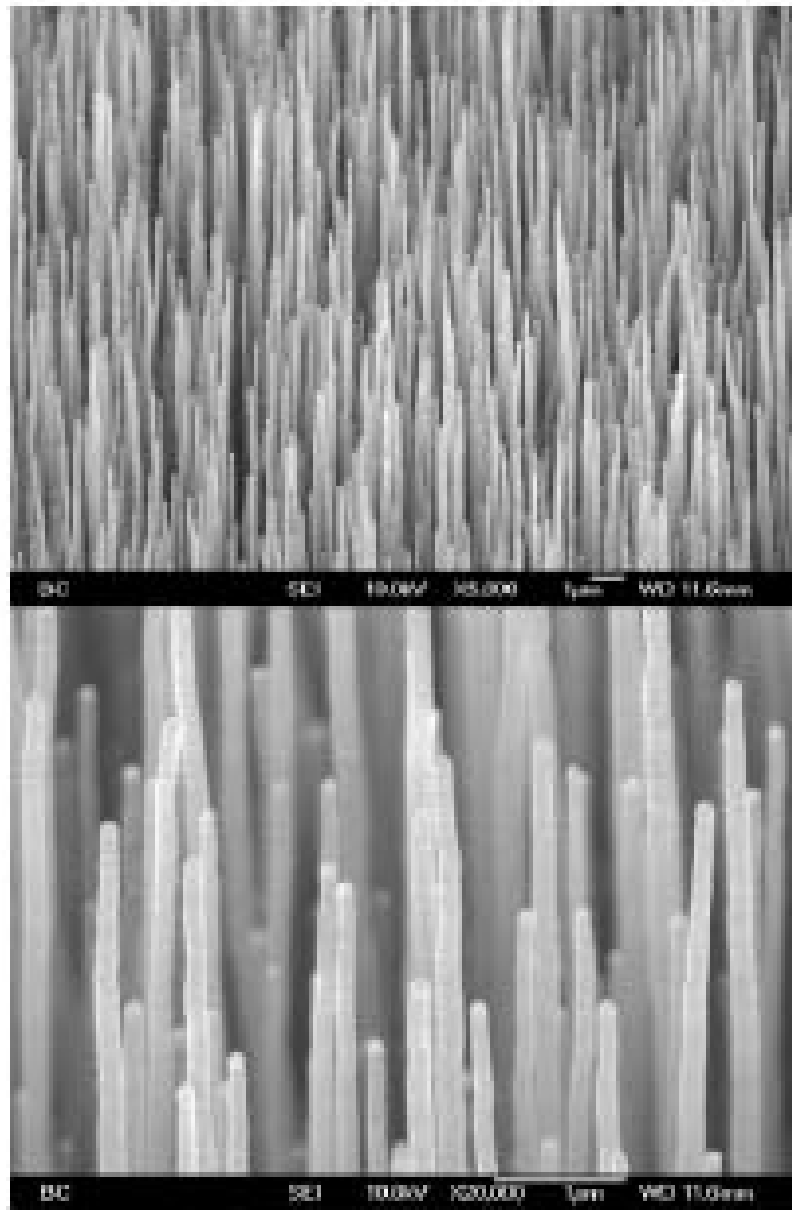
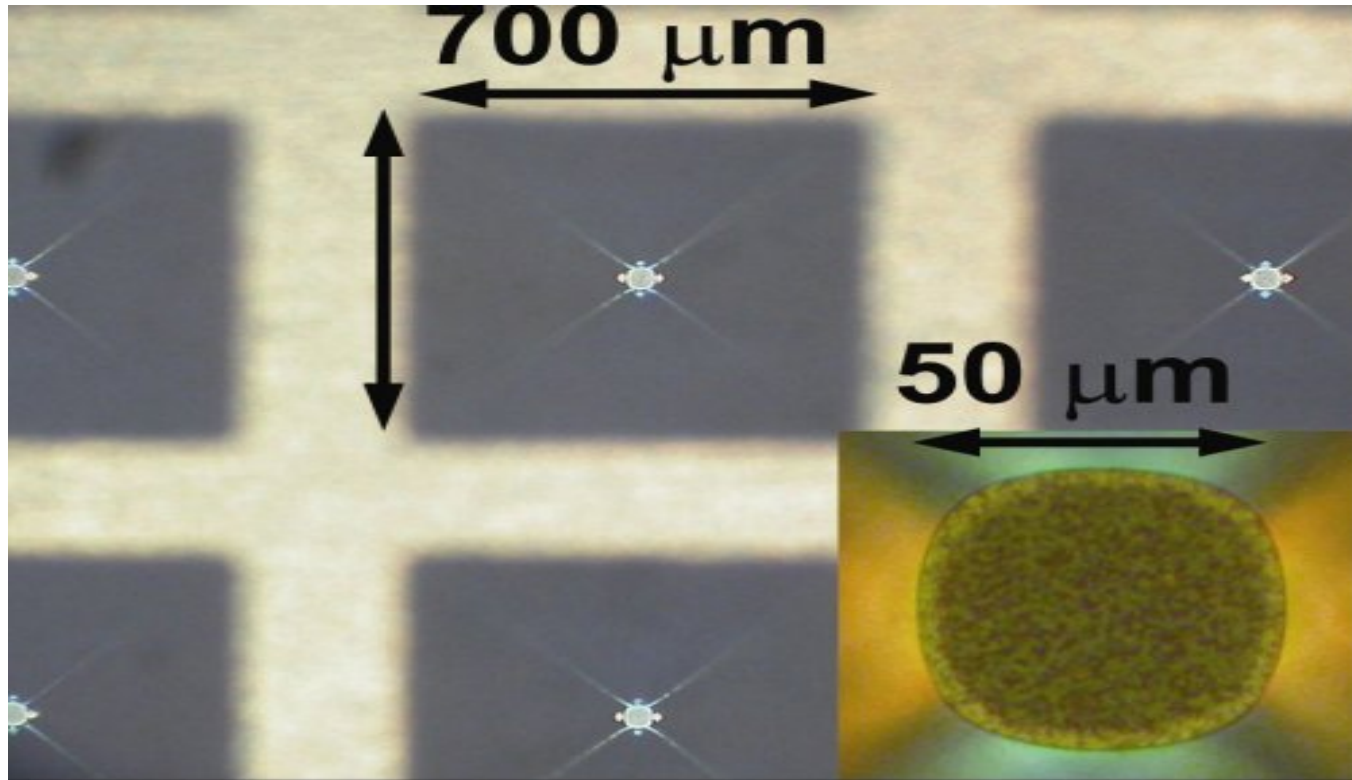


Figure 5. "Forest" of aligned carbon nanotubes.
(Image courtesy David Camahan of NanoLab, Inc.)

Membrane technology



Holt et al. Fast Mass Transport Through Sub-2-nanometer Carbon Nanotubes
Science 19 May 2006: 1034-1035

Environmental Sensors

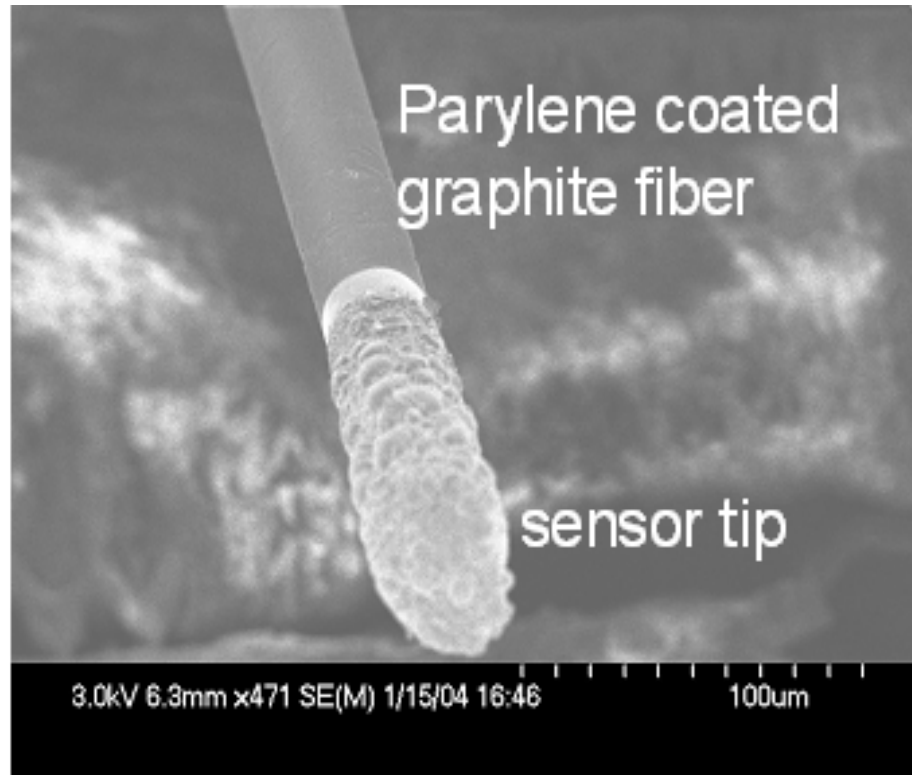


Figure 3.C.5-11 *SEM image of a potentiometric nitrate microsensor comprising a nitrate-doped polypyrrole membrane electropolymerized on a graphite carbon fiber; the fiber above the tip has been sheathed in parylene C to limit the active sensor surface to the tip of the fiber, and to provide structural reinforcement to the brittle graphite fiber.*

Nano-based Energy Savings

**Table 3. Potential U.S. Energy Savings from Eight Nanotechnology Applications
(Adapted from Brown, 2005 a)**

Nanotechnology Application	Estimated Percent Reduction in Total Annual U.S. Energy Consumption**
Strong, lightweight materials in transportation	6.2 *
Solid state lighting (such as white light LED's)	3.5
Self-optimizing motor systems (smart sensors)	2.1
Smart roofs (temperature-dependent reflectivity)	1.2
Novel energy-efficient separation membranes	0.8
Energy efficient distillation through supercomputing	0.3
Molecular-level control of industrial catalysis	0.2
Transmission line conductance	0.2
Total	14.5

*Assuming a 5.15 Million BTU/ Barrel conversion (corresponding to reformulated gasoline – from EIA monthly energy review, October 2005, Appendix A)

**Based on U.S. annual energy consumption from 2004 (99.74 Quadrillion Btu/year) from the Energy Information Administration Annual Energy Review 2004

Nanomanufacturing

Definition: The fabrication of nanostructures, or the use of nano-based methods to manufacture a product

Two types: “Top-down” and “Bottom-up”
(*Royal Society, 2004*)

Top-down

Etching/milling

- **Etching**
- Wet etching (chemical etching)
- Dry etching
 - reactive ion etching
 - plasma Etching
 - sputtering
- **Milling**
- Mechanical milling
- Mechanical alloying
- Cryomilling
- Mechanochemical bonding

Electrospinning

Lithography

- Conventional lithography
- Photolithography
- E-beam lithography

- Next-generation lithography*
- Immersion lithography
- Lithography with lower wavelengths than photolithography
- Extreme ultraviolet (soft X-ray) lithography
- X-ray lithography
- Lithography with particles
- e-beam lithography
- Focused ion-beam lithography
- Nanoimprint lithography
- Soft lithography

Bottom-up

Vapor-phase deposition

- Vapor phase epitaxy
- Metal organic chemical vapor deposition
- Molecular beam epitaxy
- Plasma enhanced chemical vapor deposition
- Sputtering
- Evaporation

Nanoparticle synthesis

- Evaporation
- Laser ablation
- Flame synthesis
- Arc discharge

Liquid phase

- Precipitation
- Sol-gel
- Solvothermal synthesis
- Sonochemical synthesis
- Microwave irradiation
- Reverse micelle

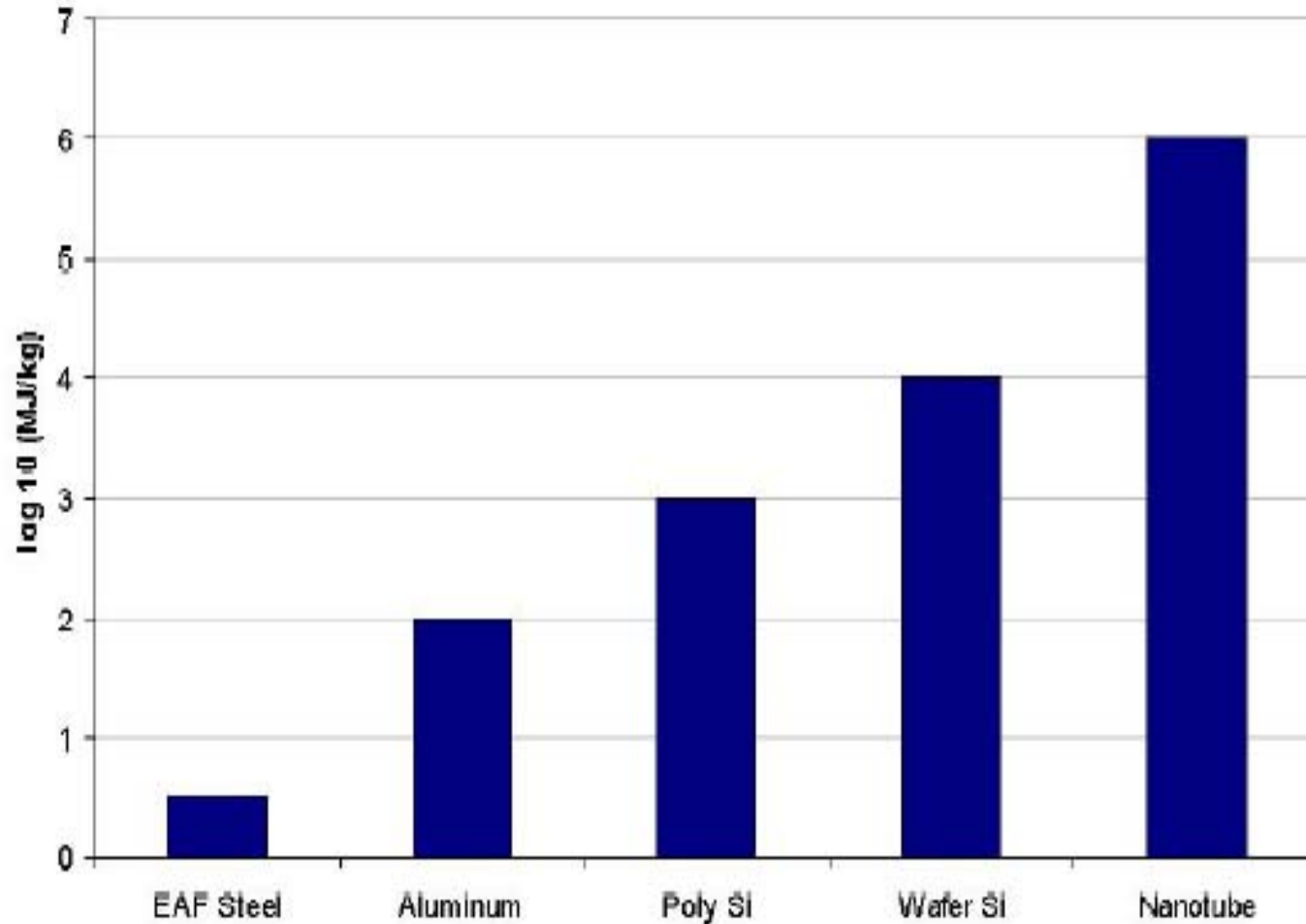
Sources of nanomanufacturing impacts

- **Strict purity requirements and less tolerance for contamination during processing than more conventional manufacturing processes (up to “nine nines”).**
- **Low process yields or material efficiencies**
- **Repeated processing, postprocessing, or reprocessing steps of a single product or batch during manufacturing**
- **Use of toxic/basic/acidic chemicals and organic solvents (eg. As, Ga, In, Cd, Zn, Sn, Sb, Hg, solvents, chlorinated and perfluorinated compounds, etc.)**

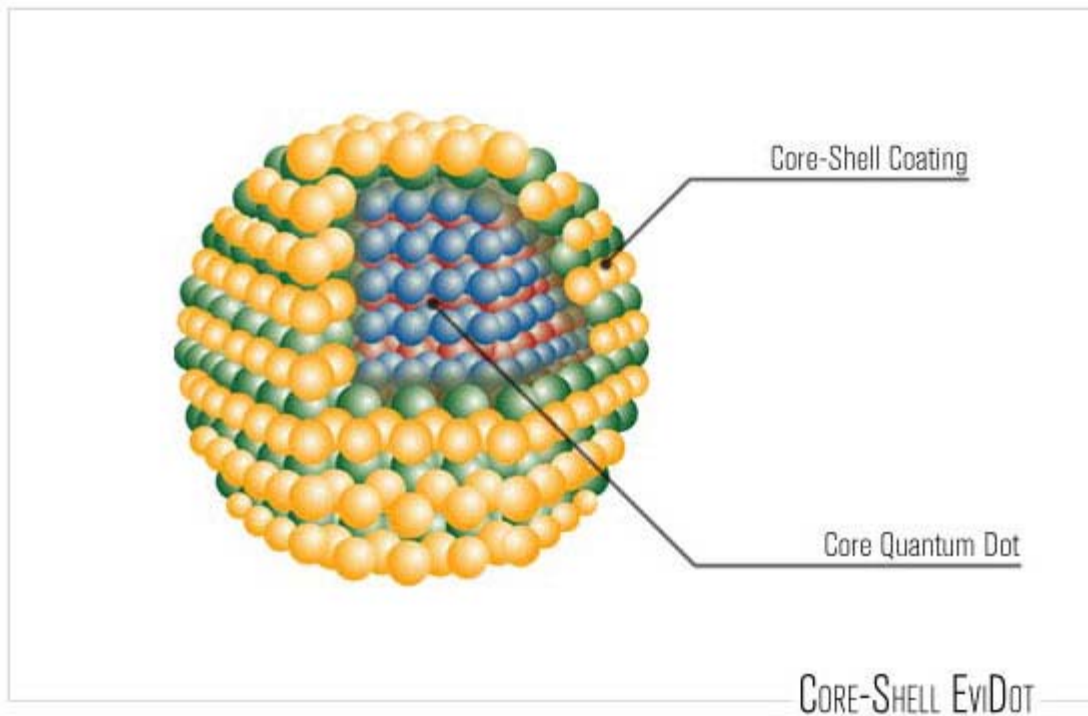
Sources of nanomanufacturing impacts

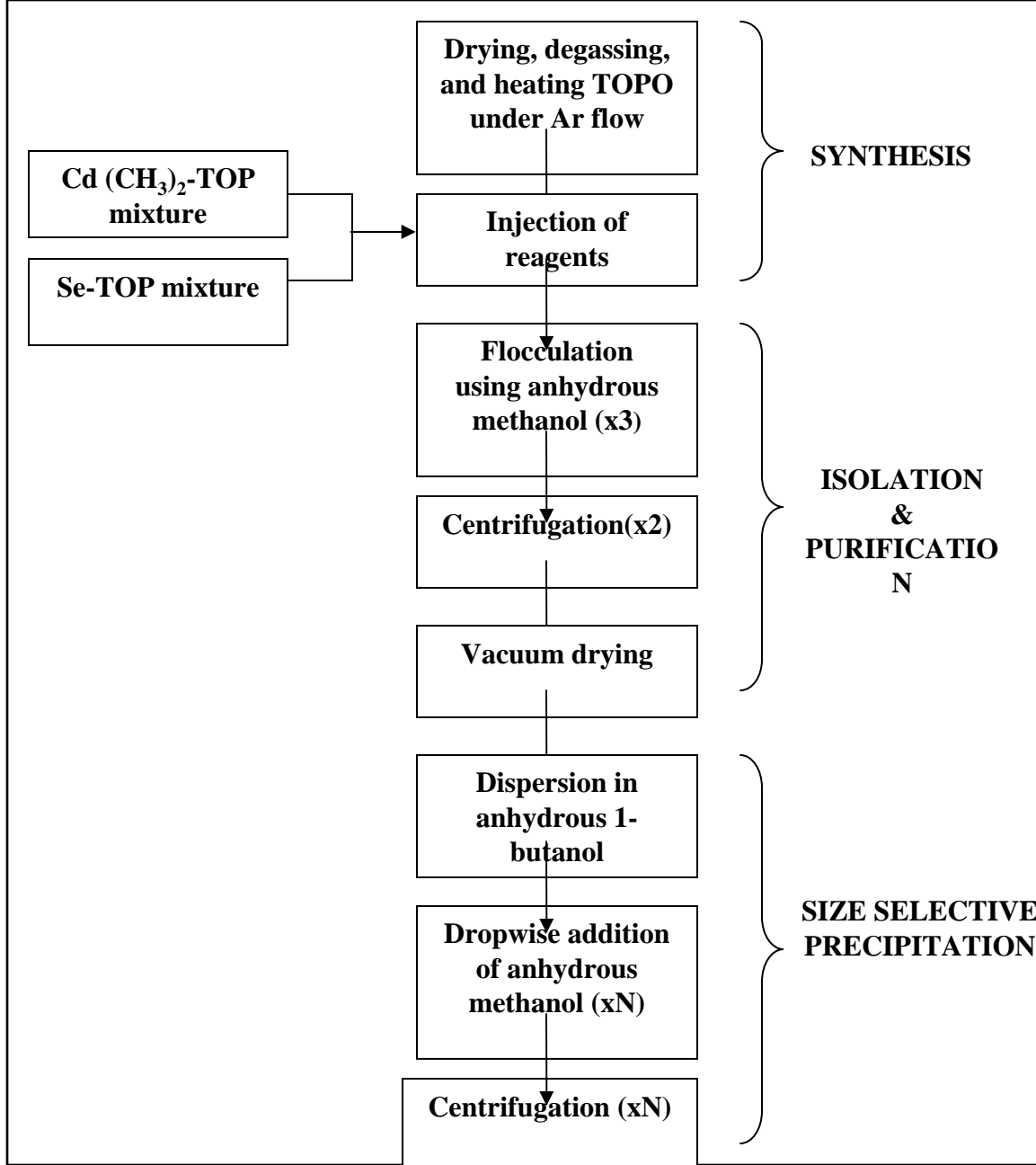
- **Need for moderate to high vacuum and other specialized environments such as high heat or cryogenic processing**
- **Use of or generation of greenhouse gases (directly or through energy consumption)**
- **High water consumption**
- **Chemical exposure potential in the workplace and through technological/natural disasters**

Energy requirements of materials

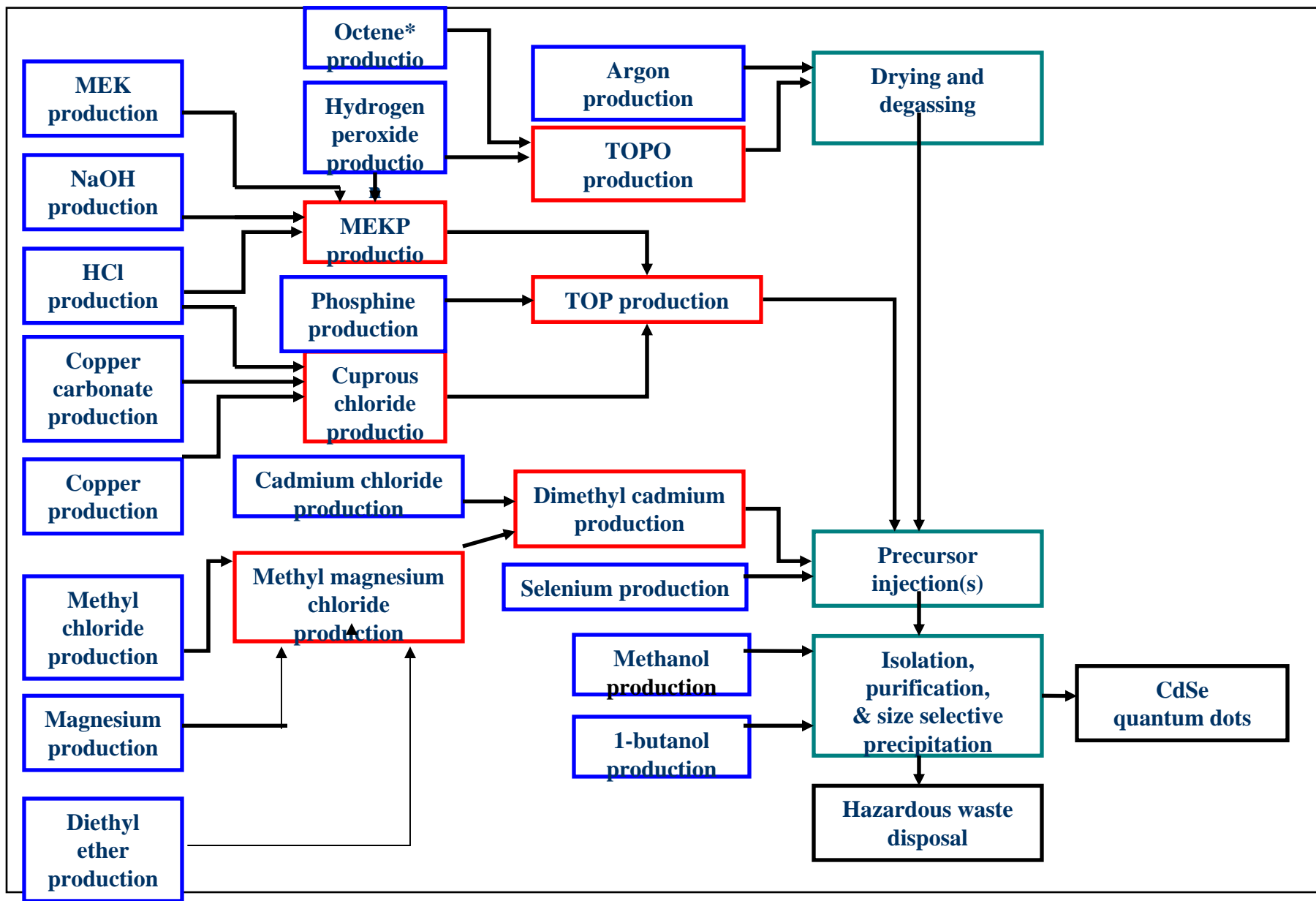


Quantum dots



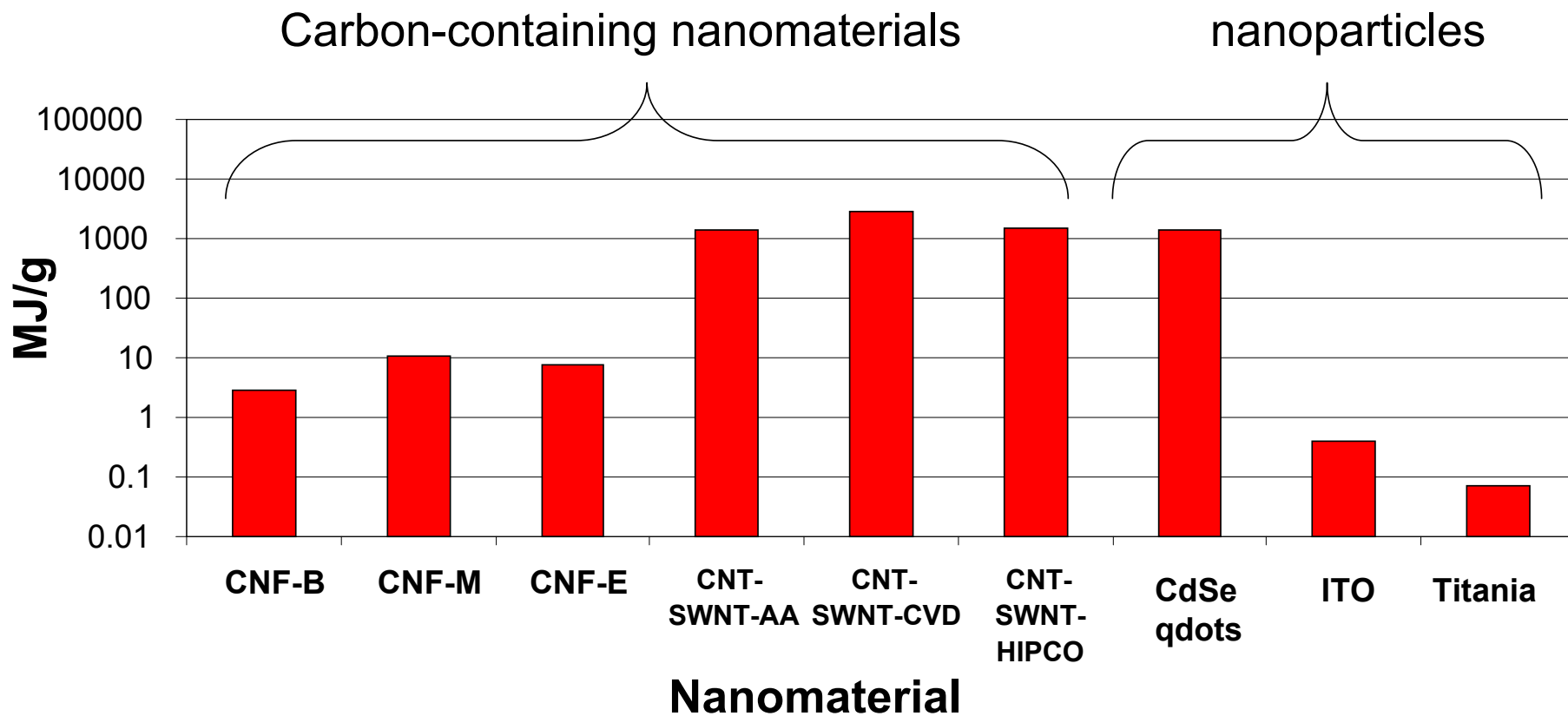


Liquid phase synthesis of CdSe quantum dots (Murray et al. 1993 *J. Am. Chem. Soc.* 1993, 115, 8706-8715)

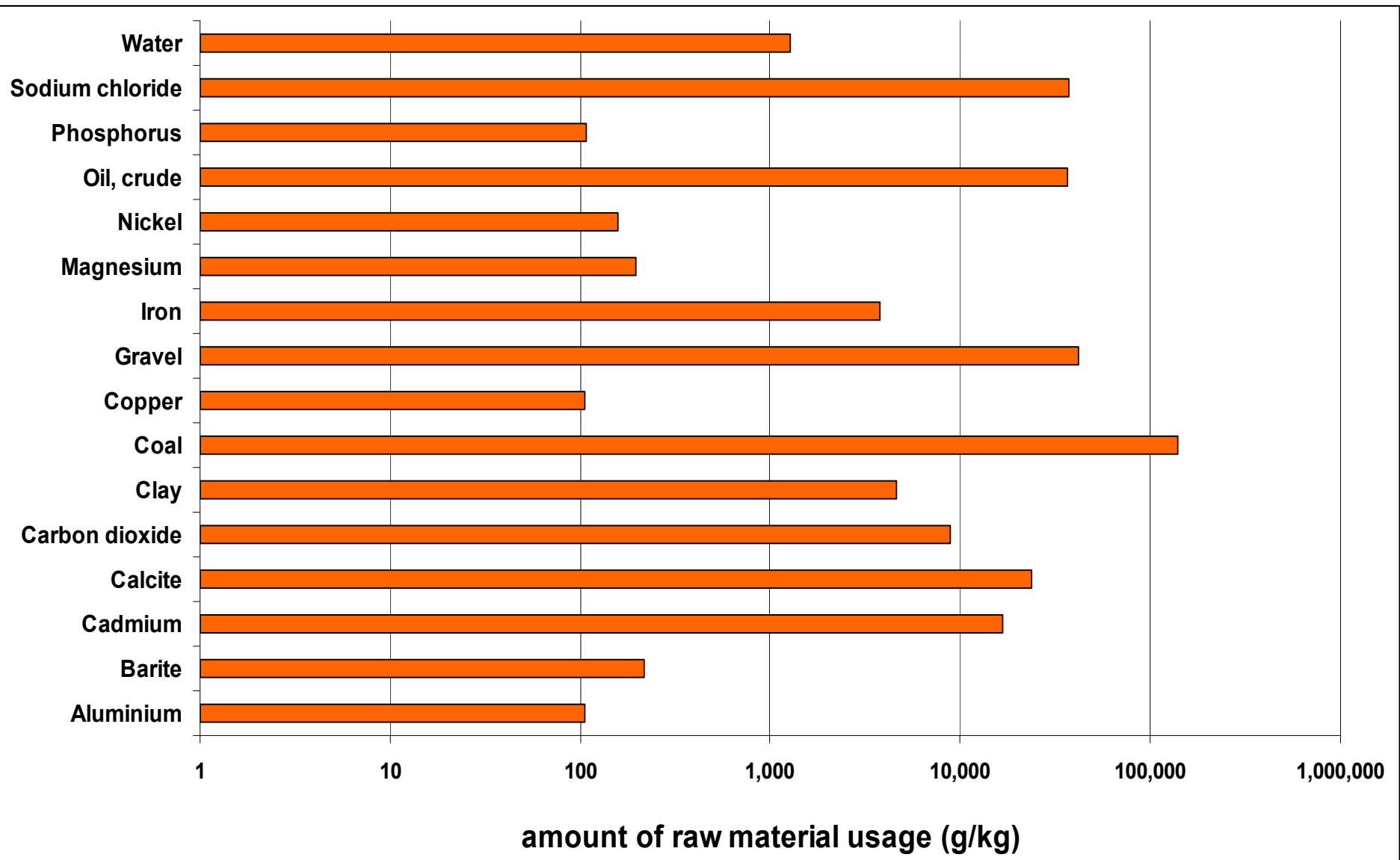


Material flows for the synthesis of CdSe quantum dots using sol-gel.

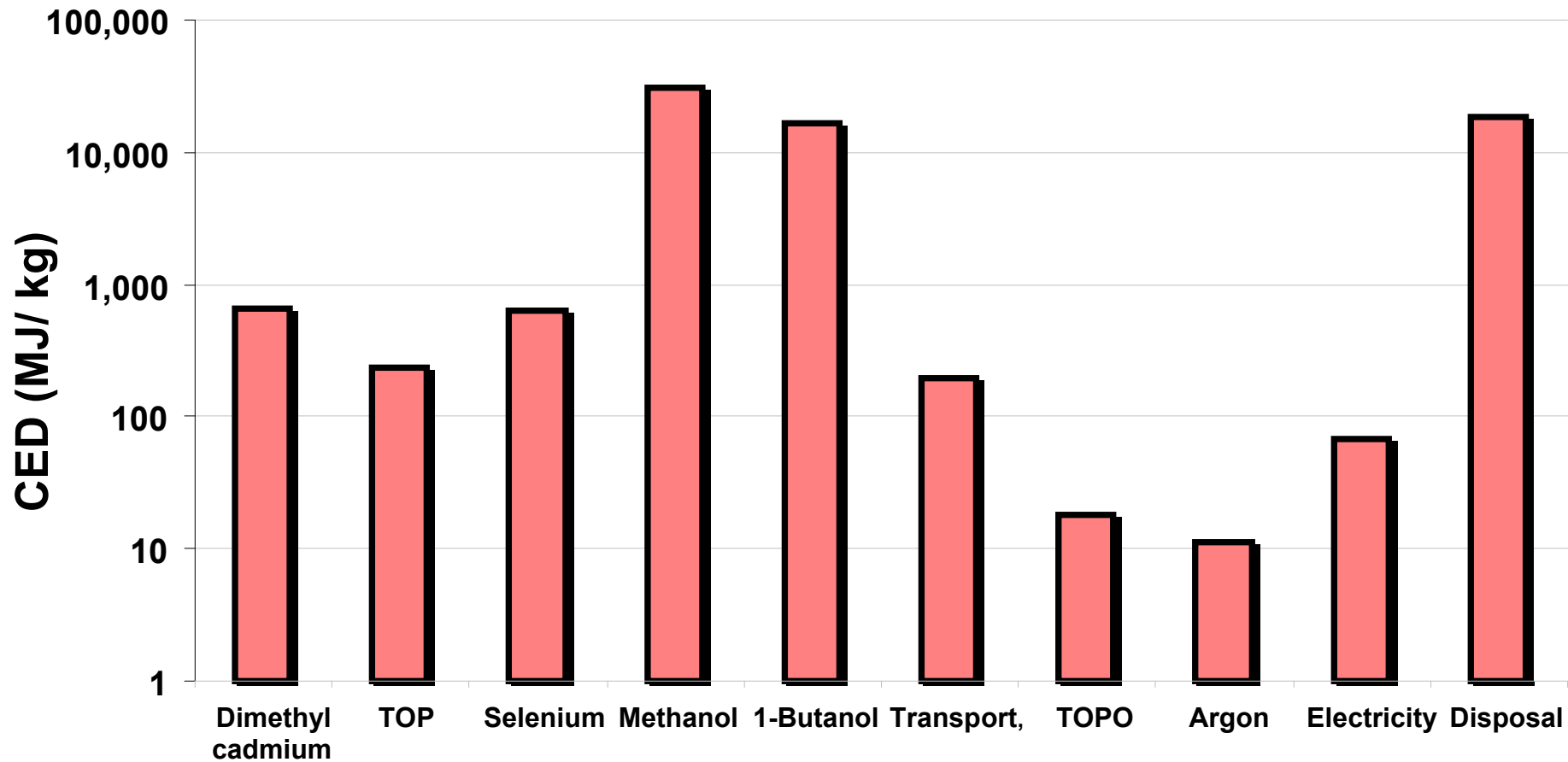
Cumulative energy requirement of nanomaterials



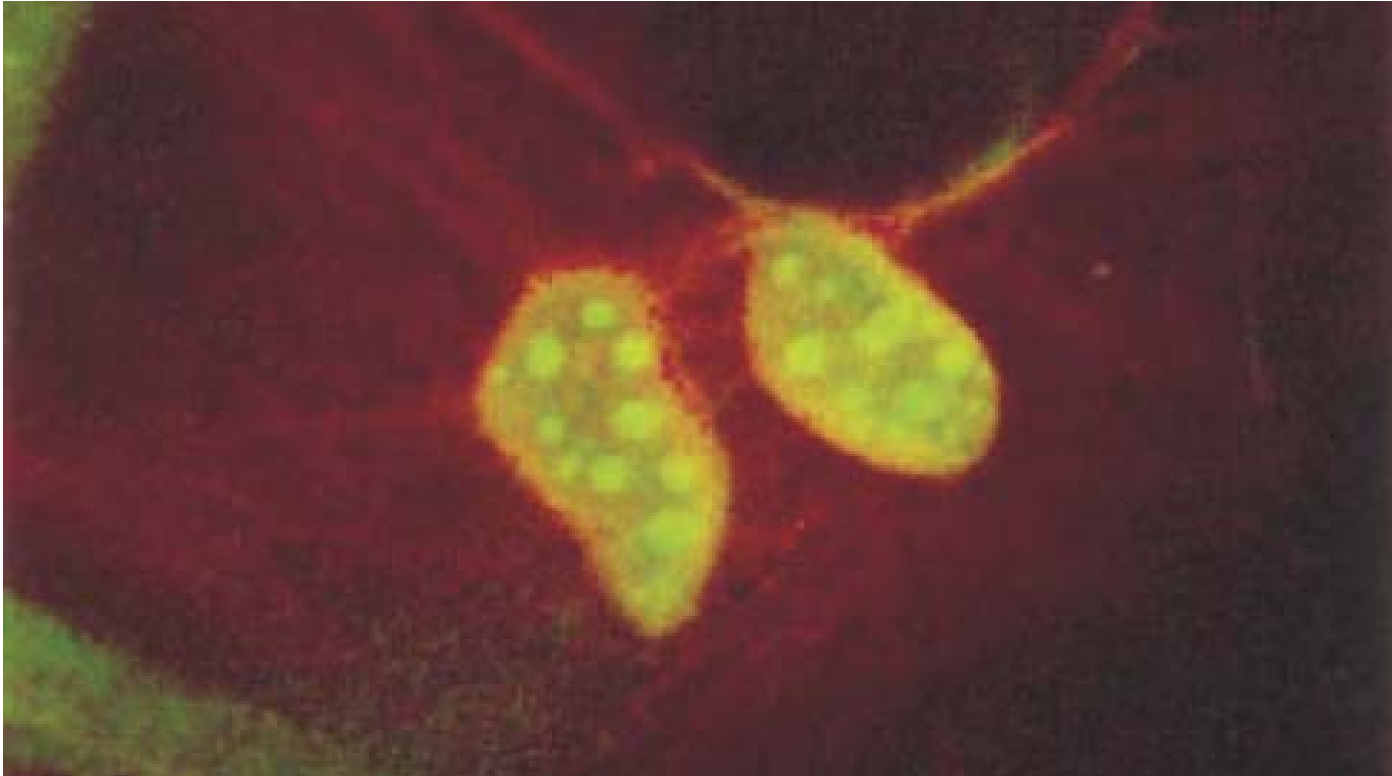
Raw material use for CdSe qdots



Cumulative energy demand CdSe q-dots

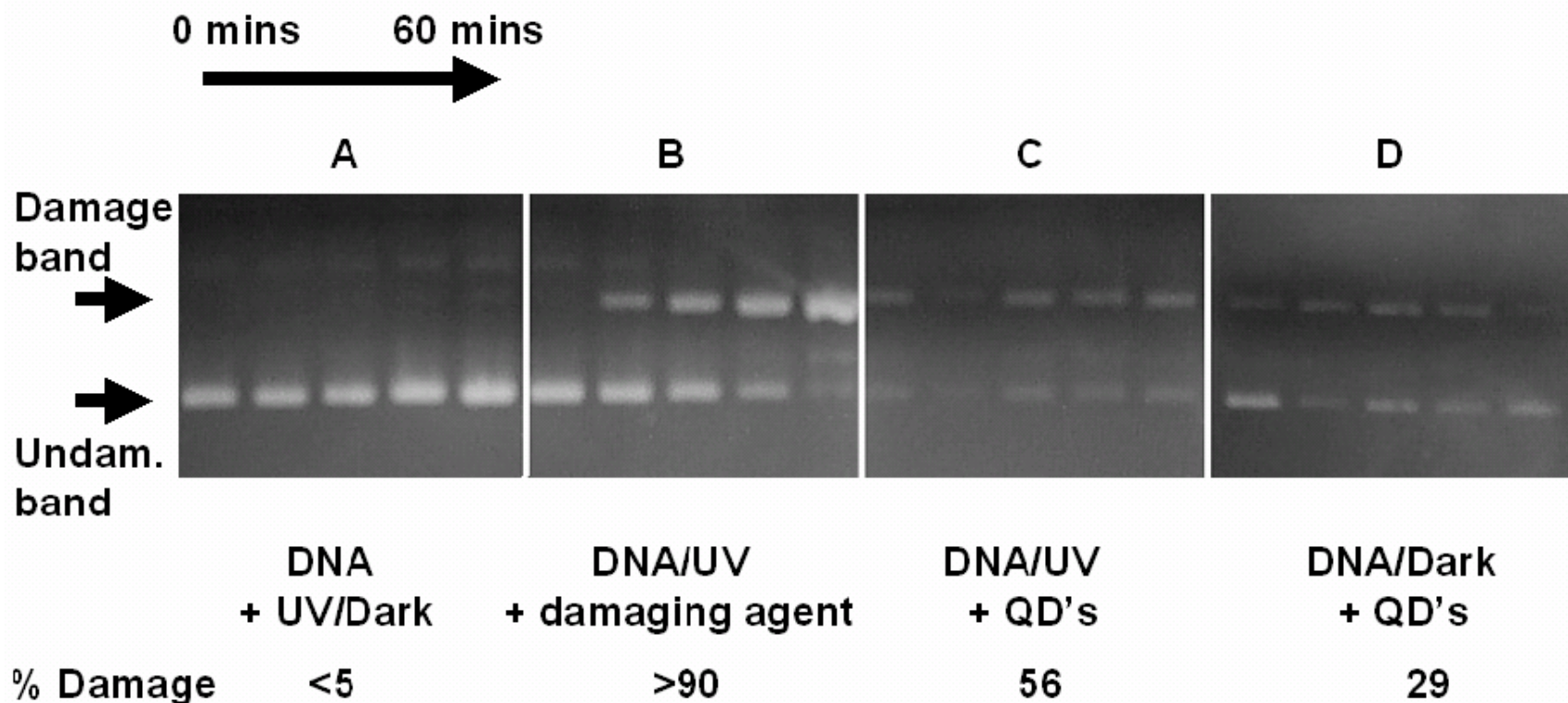


Fibroblast embedded with CdSe QD



(Wang et al. 2005. Bioapplications of
Nanosemiconductors.
Materials Today 8(5): 20-31)

DNA damage by CdSe

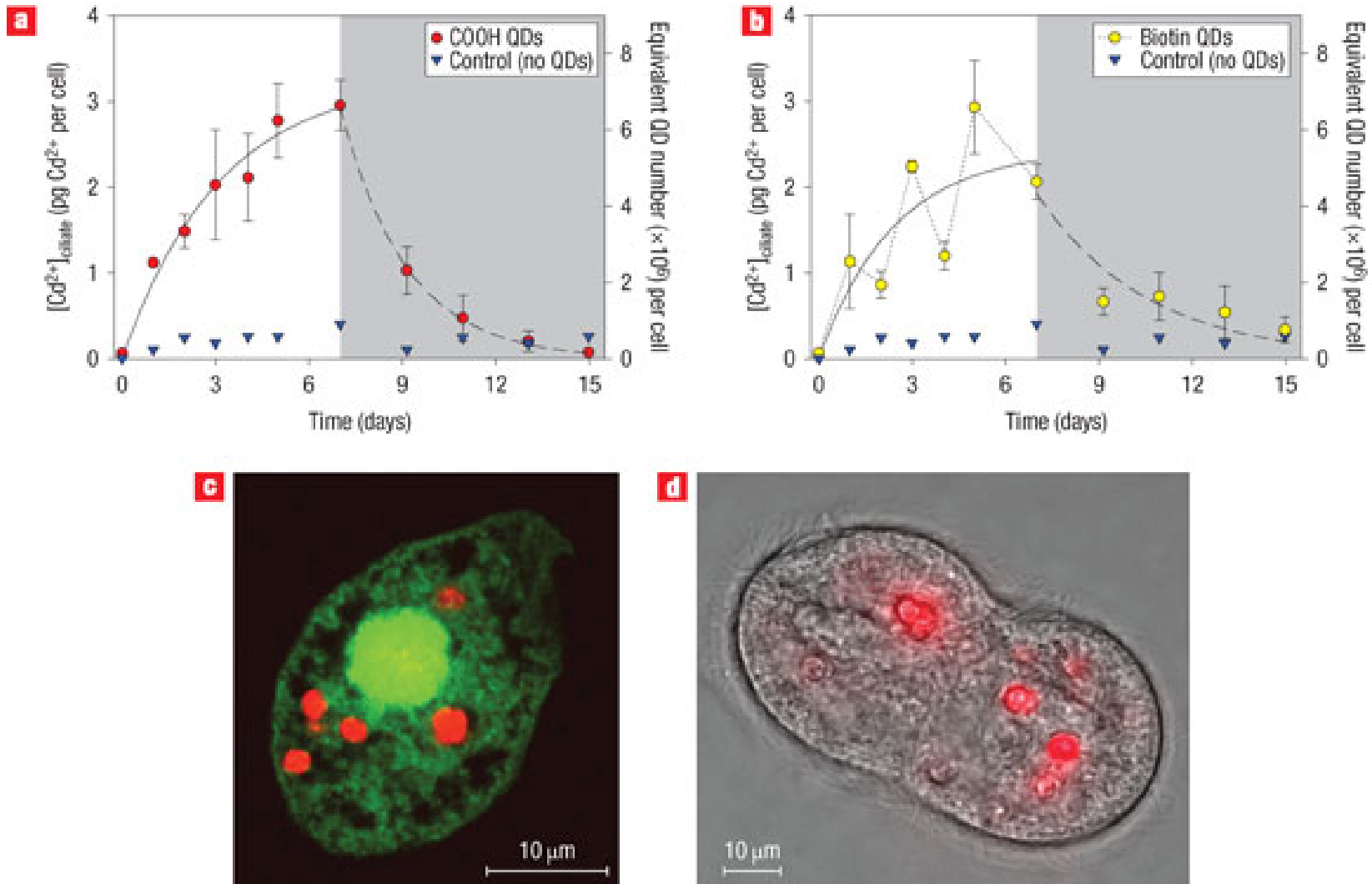


Green, M. and E. Howman

“Semiconductor quantum dots and free radical induced DNA nicking”

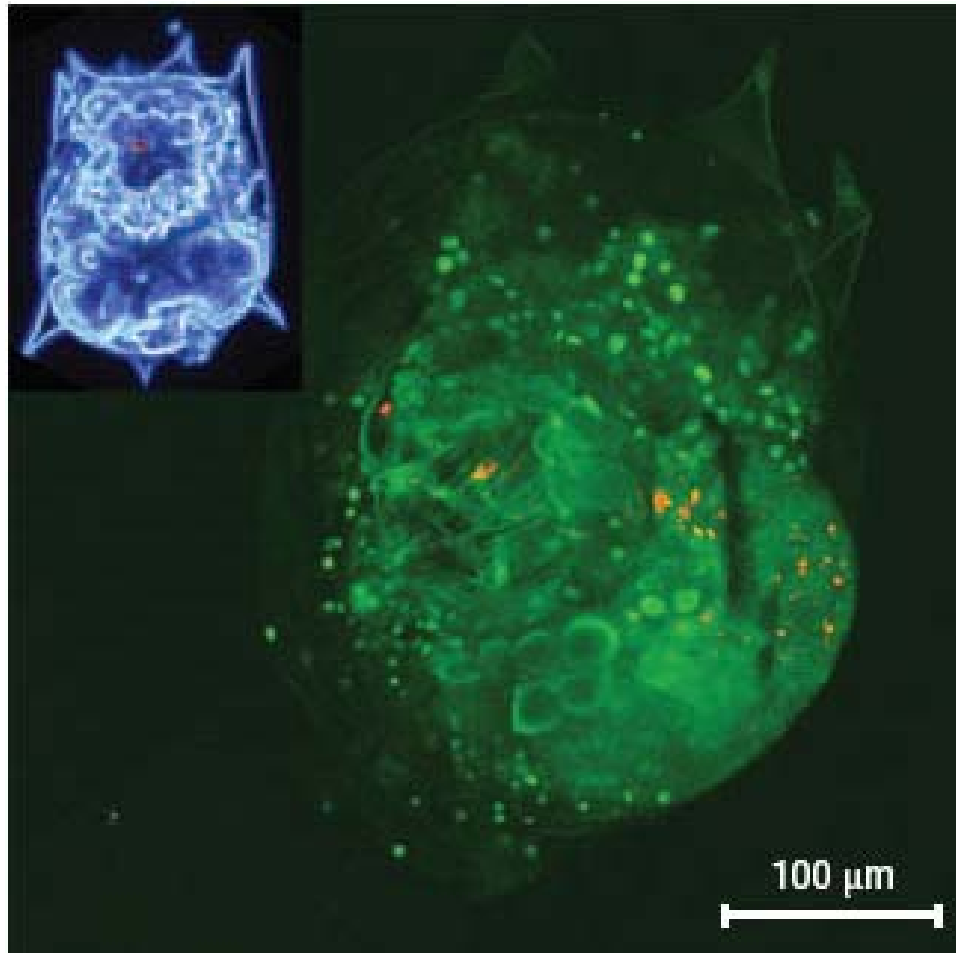
Chem. Commun., 2005, 121 - 123

Uptake and depuration of QDs by *T. pyriformis*



Holbrook, RD et al. "Trophic transfer of nanoparticles in a simplified invertebrate food web" NATURE NANOTECHNOLOGY 3(6): 352-355 (2008)

Trophic transfer of qds from ciliate to rotifier



Holbrook, RD et al. "Trophic transfer of nanoparticles in a simplified invertebrate food web" *NATURE NANOTECHNOLOGY* 3(6): 352-355 (2008)

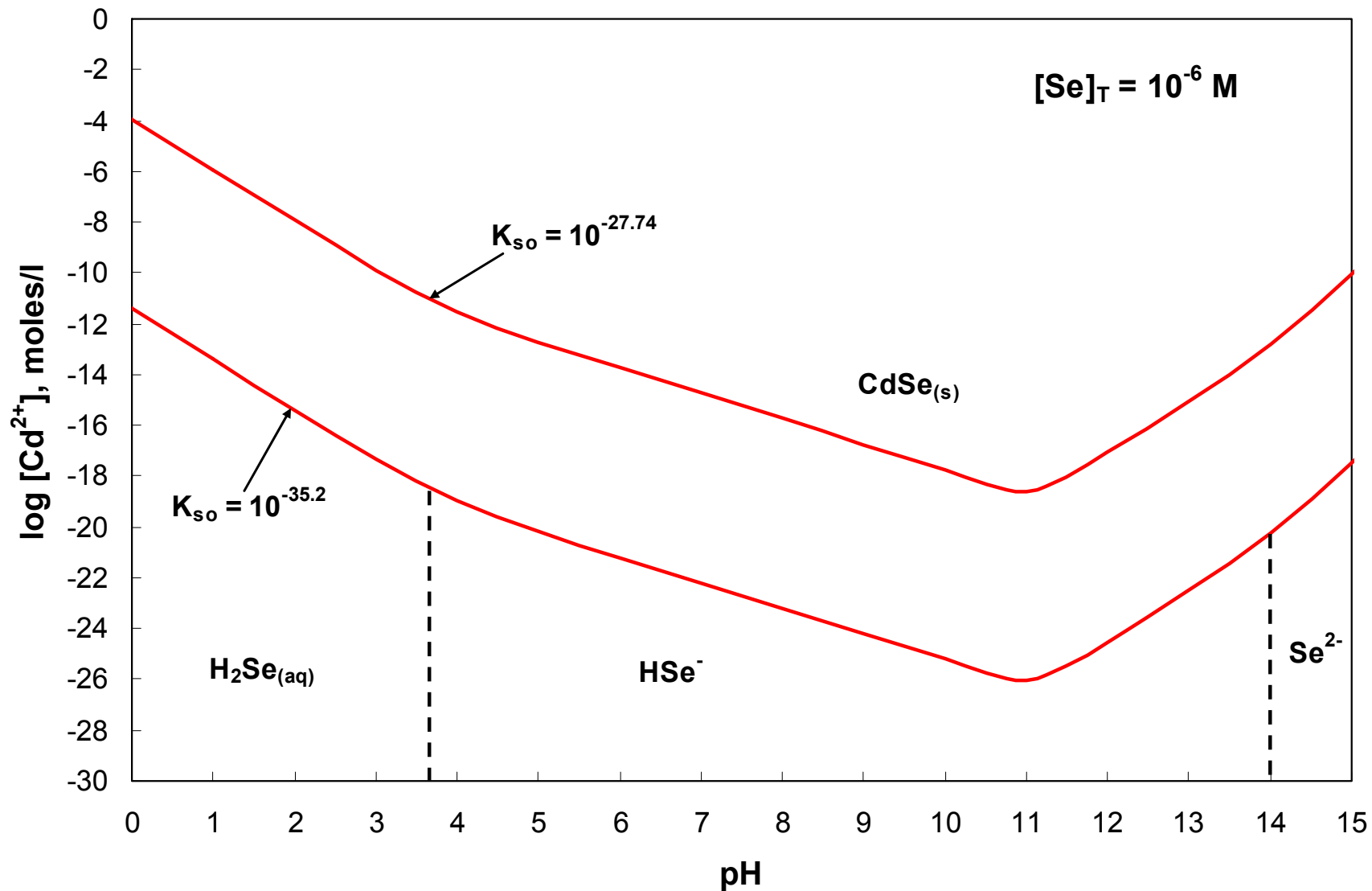
Aqueous solubility search

Sulfides, most oxides: abundant

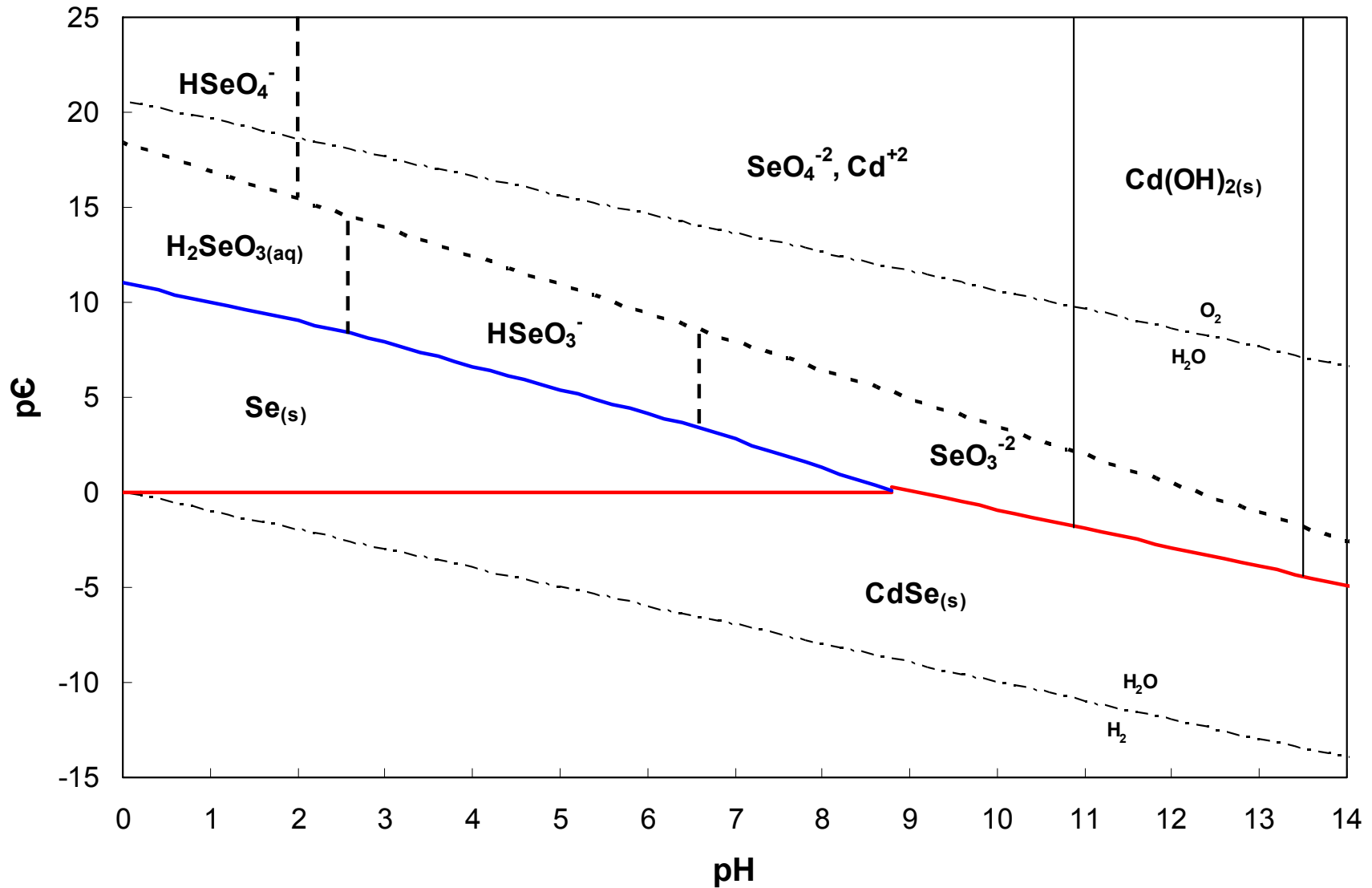
Binary selenides, tellurides: some

Nitrides, phosphides, arsenides,
stibnides, tertiary, quaternary, doped,
magnetic: none

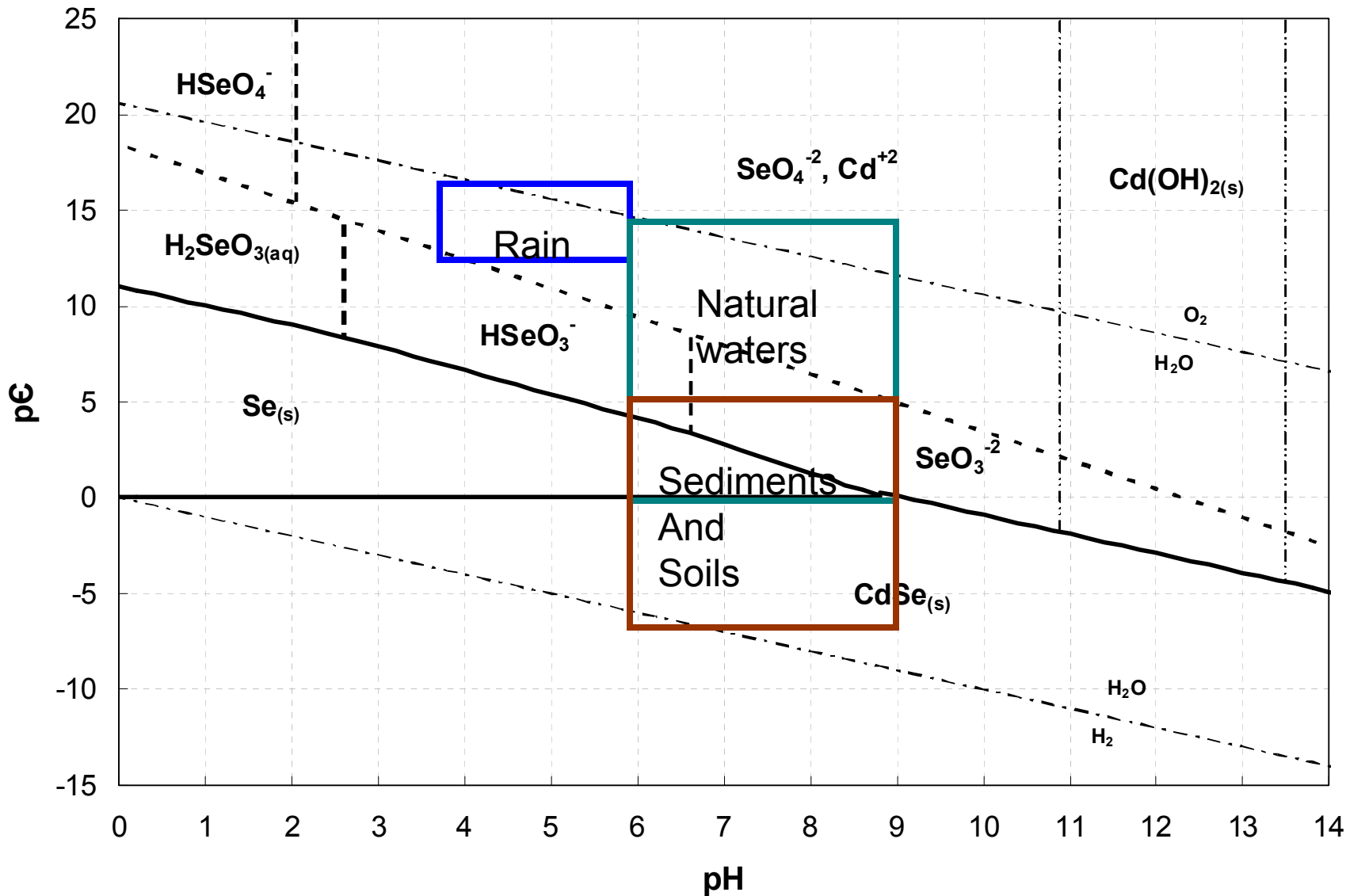
Solubility of CdSe in water



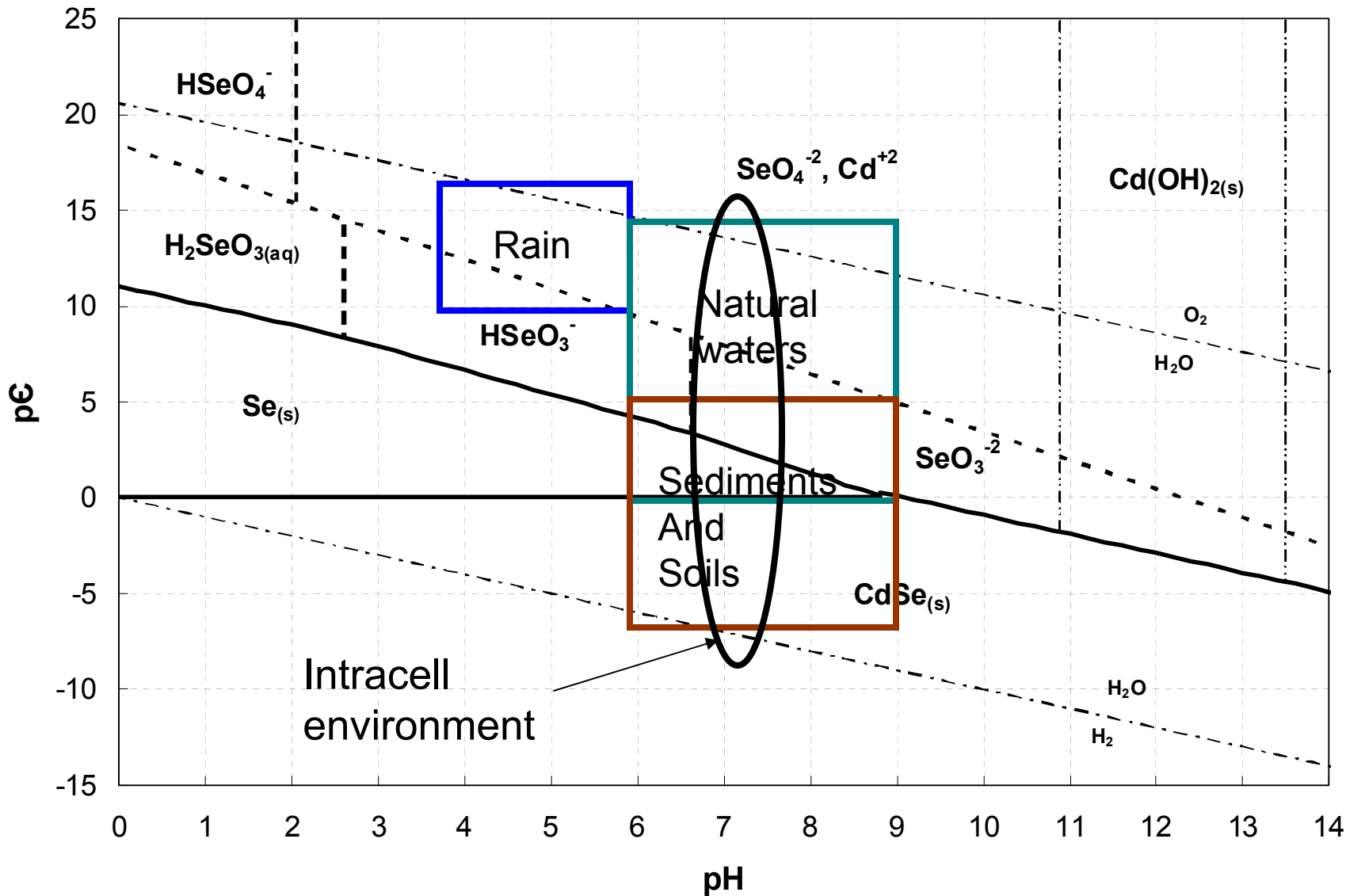
$p\epsilon$ -pH diagram for CdSe



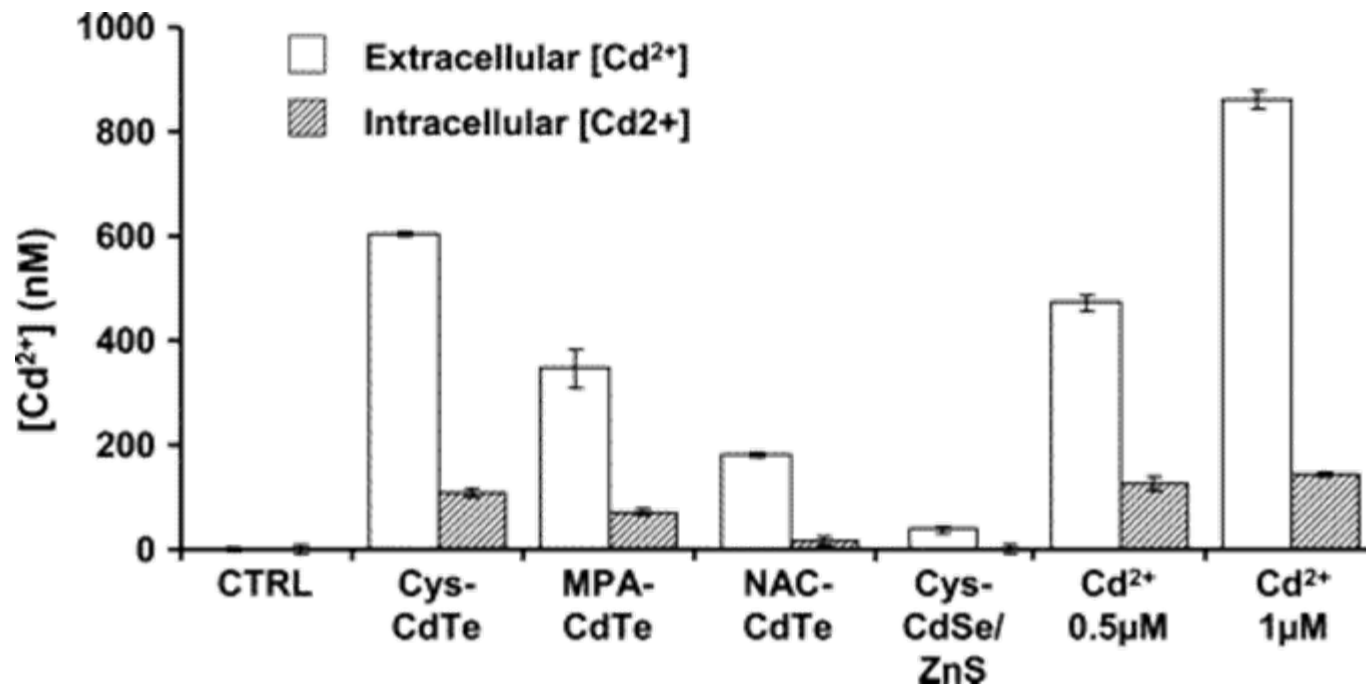
CdSe in aquatic environments



CdSe in aquatic environments

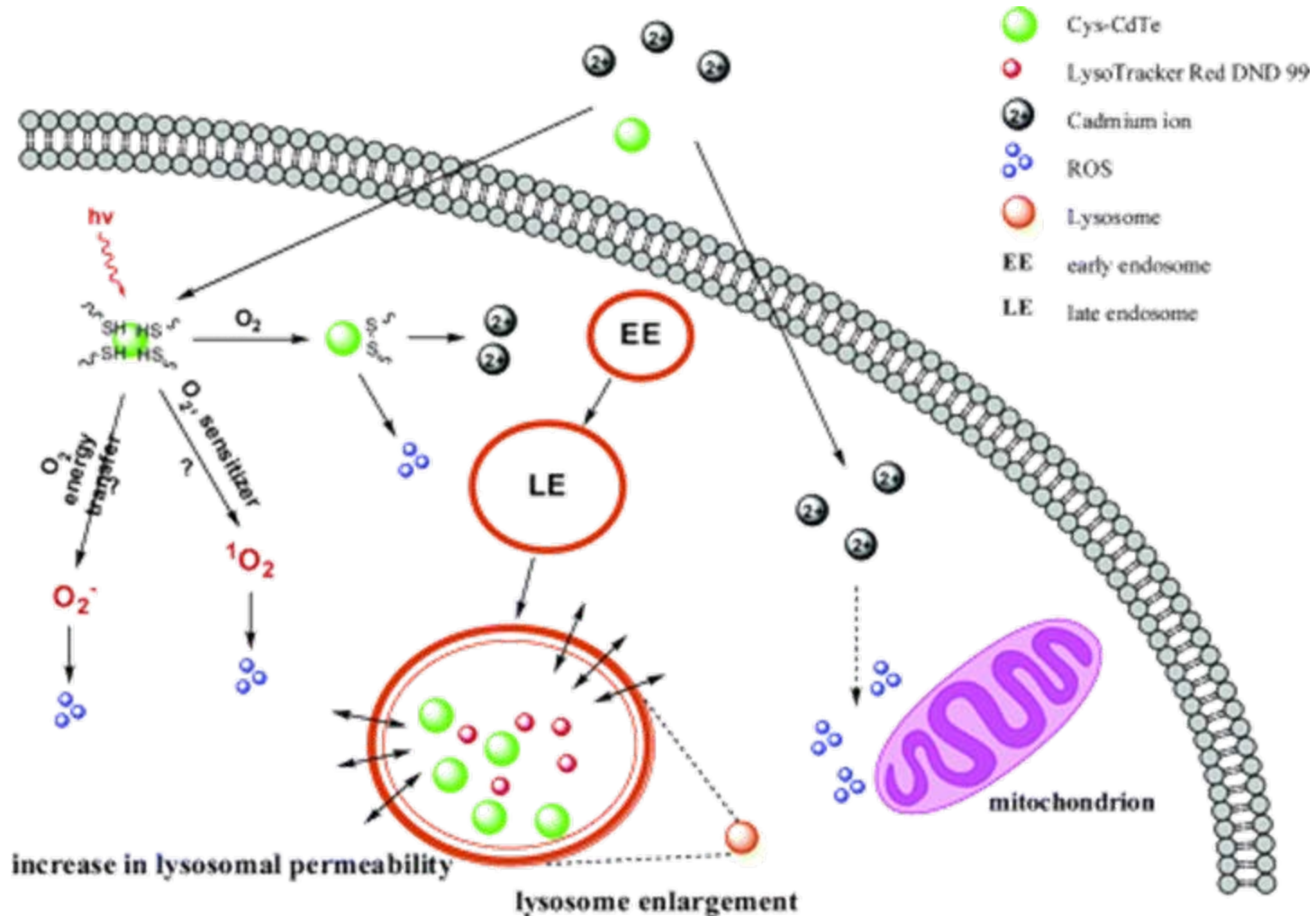


Live Cell Exposure to CdTe Quantum Dots



Cho, S.J. et al. "Intra- and extracellular Cd²⁺ concentrations in MCF-7 cells incubated for 24 h with various QD samples and with CdCl₂ solutions" *Langmuir*, **23** (4), 1974 -1980, (2007)

Mechanism of toxicity



Schematic representation of the mechanistic pathways implicated in the cytotoxicity of CdTe QDs in live cells, highlighting the salient changes in cellular morphology, the chemical species involved, and the chemical reactions that can lead to ROS and free Cd²⁺ ion release (Cho et al. (2007)).

Concluding remarks

- The ability to make and control very small structured materials has very large implications for human health, comfort and convenience, and economic well-being
- In comparison to basic nanoscience and the fabrication of nanostructures, our understanding of environmental and life cycle behaviors of nanomanufacturing, nanomaterials, and nano-containing products exhibit exceptional lags
- Even so, it is clear that there will be a suite of significant waste management problems
- There is a need for greater application of environmental systems thinking, and development of holistic policies for nanotechnology