

# Nanotechnology



## Is Small Scary?

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June 2010

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**•“Military applications of molecular manufacturing have even greater potential than nuclear weapons to radically change the balance of power.”**

**•Admiral (Ret) David E. Jeremiah,  
former vice chairman of Joint Chiefs of Staff \***

\* “Nanotechnology and Global Security,” (Palo Alto, CA; Fourth Foresight Conference on Molecular Nanotechnology), November 1995.

# Security Puzzles

- Does nanotechnology have unique strategic value?
  - Security, economic, political, &/or scientific
- Disambiguate potential for unique capabilities from enabling previous capabilities
- Perception or ideation vs technical reality
  - “Hope” & “Horror” hype
  - Rhetoric
  - (Pseudo)-technical assessments  
E.g., “*New technologies (at risk for terrorist appropriation) include biotechnology, **nanotechnology, single nucleotide polymorphisms** (SNPs), and **Bose-Einstein condensates**.*”\*
  - Influencing factors: institutional
- International regimes for emerging technologies
  - Adequacy of traditional arms control treaties
  - Value of norms
  - Role of NGOs, transnational actors, industry

\* “WMD Terrorism Research: Where to From Here?” *International Studies Review*, March 2005, vol. 7, p. 140

# Changing Strategic Environment

- Post-Cold War international security environment
- Technology no longer guarantees security
- Globalization and information revolution as drivers
  - Enable spread and accessibility
- Dual-use conundrum
- Changing nature of warfare
  - Asymmetric warfare
  - Interest in unconventional weapons
- Relationship between science and security
- Disruptive technologies

# Evolutionary Approach: 1918 vs 2010



Impregnated suit and various masks



Placing pigeon in cage at trench entrance



Handheld decon unit & decon tank truck

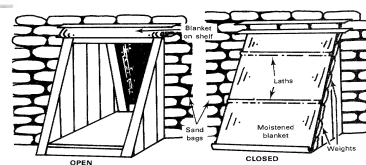


Figure 4. Entrance, gas-proof dugout.

Trench fan and entrance way



Suit, gloves, boots & various masks



Point & "standoff" detection



Handheld decon unit and various applicators including tank trucks



Shelters & filters

# Incremental vs. revolutionary improvements...



Cartoon Courtesy Kathy Sierra,  
Creating Passionate Users

# What is Nanotechnology?

- Nanotechnology is a bundle of diverse capabilities
  - Expectations of synergies between them
- Danger of treating nanotechnology as a *thing*: determinate homogenous entity
- Term creates boundaries around the field and hierarchies within it
- Precision of terms:
  - Nanoscience, Nano-engineering, Nano-engineered materials, Bionanotechnology, & Nanotechnology
- (*Emerging?*) interdisciplinary area of science, engineering, and technology
- Concerned with materials and process at very small dimensions
- 1 nanometer =  $10^{-9}$  m = 1/billionth of a meter

# Examples of Nanoscale Objects

## Things Natural



Dust mite  
200  $\mu\text{m}$

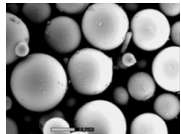


Human hair  
~ 60-120  $\mu\text{m}$  wide

Red blood cells  
(~7-8  $\mu\text{m}$ )



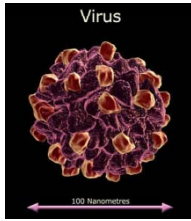
Ant  
~ 5 mm



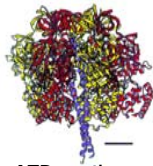
Fly ash  
~ 10-20  $\mu\text{m}$



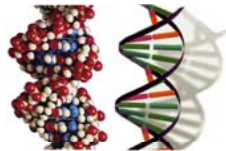
~10 nm diameter



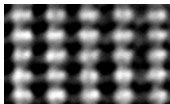
~100 nm



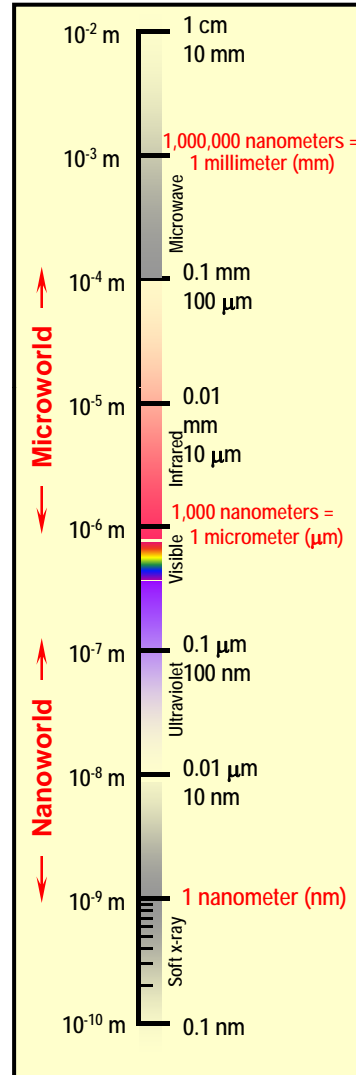
ATP synthase



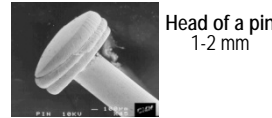
DNA  
~2-1/2 nm diameter



Atoms of silicon  
spacing 0.078 nm

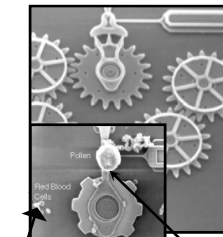


## Things Manmade

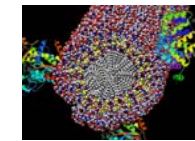


Head of a pin  
1-2 mm

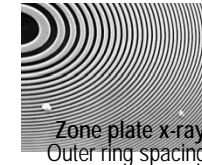
MicroElectroMechanical (MEMS) devices  
10 -100  $\mu\text{m}$  wide



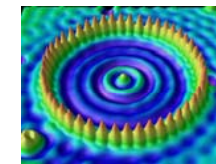
Red blood cells      Pollen grain



Self-assembled, Nature-inspired structure  
Many 10s of nm

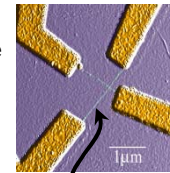


Zone plate x-ray "lens"  
Outer ring spacing ~35 nm

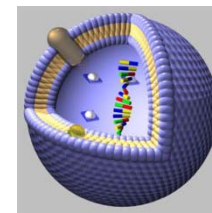


Quantum "corral"  
48 iron atoms  
(14 nm diameter)

Nanotube electrode



Carbon nanotube  
~1.3 nm diameter

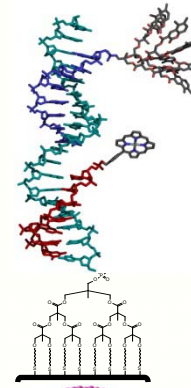


Liposomes  
~15 nm - microns diameter



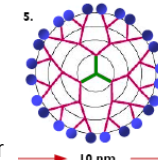
Nanoparticles and nanoshells  
~1-100 nm diameter

The Challenge:  
**Fabricate and combine nanoscale building blocks (natural and manmade) to make useful devices that exploit novel properties and functions because of their small size.**



Inorganic nanoparticles  
~1-100 nm diameters

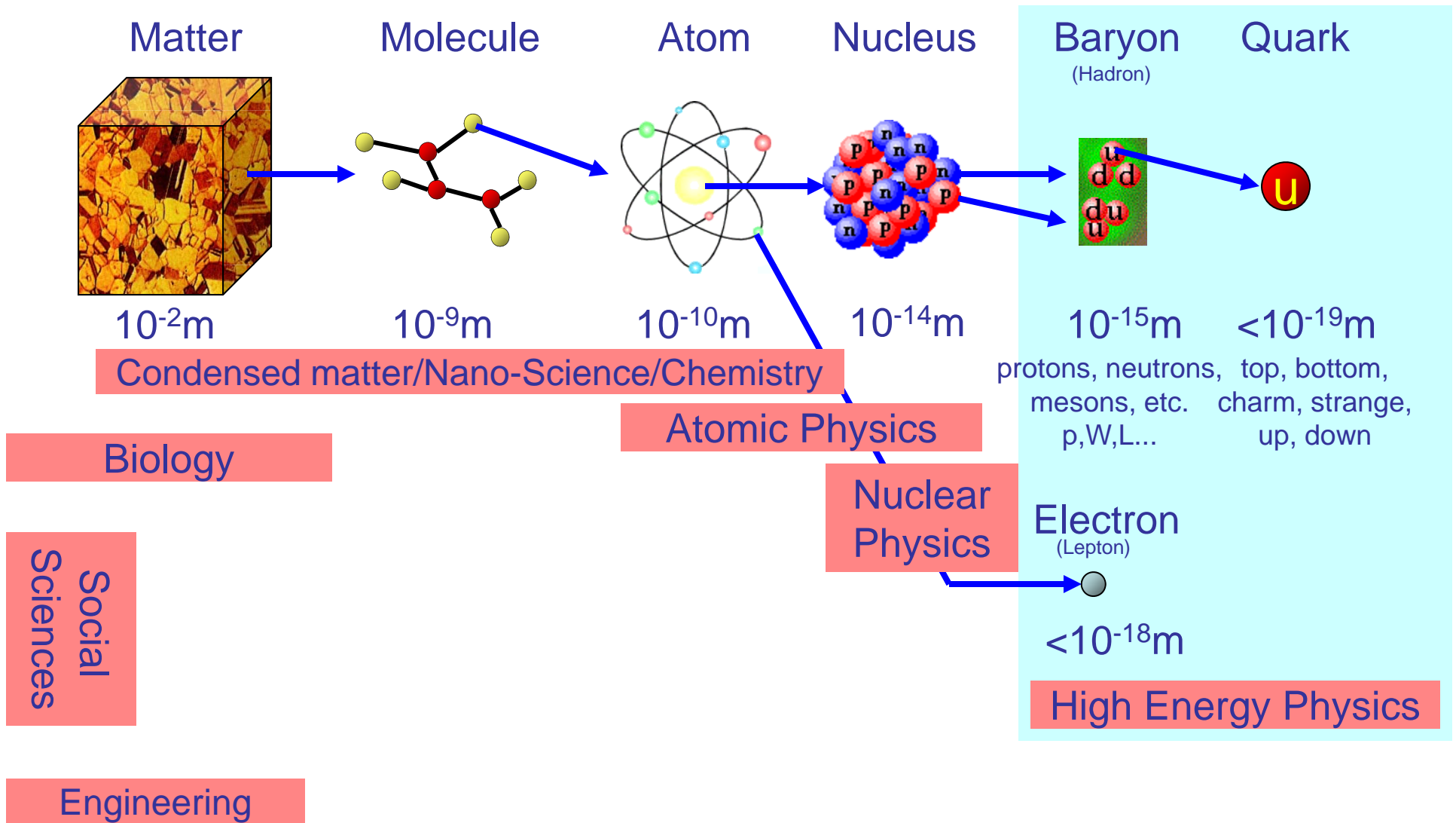
5th generation dendrimer  
~10 nm diameter



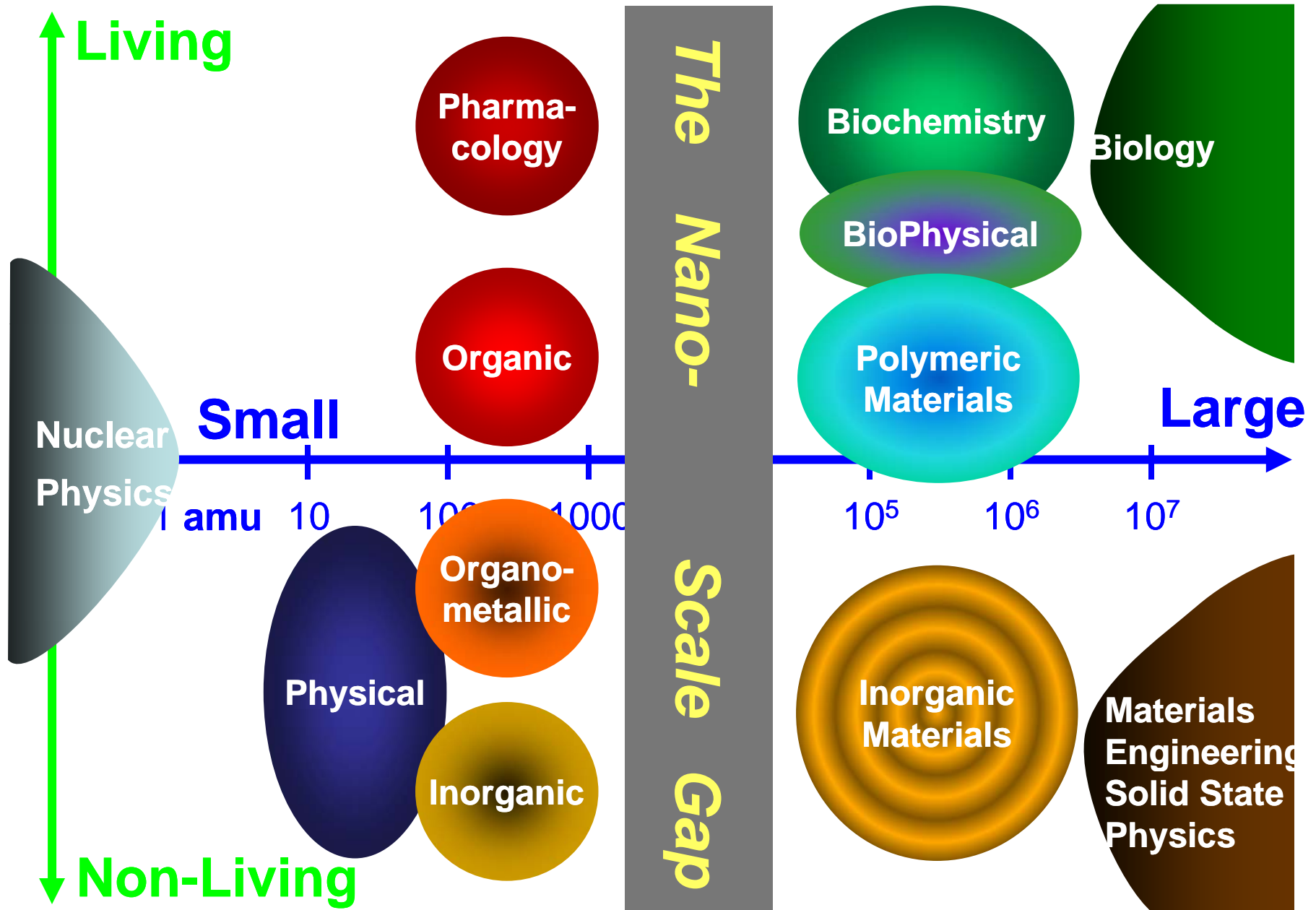
Fullerene  
~1 nm diameter



# Structure of Matter



# What Nanoscience Is



# Feynman: the father of Nanotechnology



Prof. Richard Feynman  
courtesy of Caltech

***‘There’s Plenty of Room at  
the Bottom -  
An Invitation to Enter a New  
Field of Physics’***

December 1959

*“...furthermore, a point that is most important is that it would have an enormous number of technical applications.”*

# Historical Nanotechnology




## The First Nanotechnologists

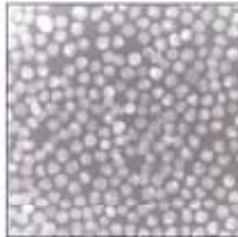
Ancient stained-glass makers knew that by putting varying, tiny amounts of gold and silver in the glass, they could produce the red and yellow found in stained-glass windows. Similarly, today's scientists and engineers have found that it takes only small amounts of a nanoparticle, precisely placed, to change a material's physical properties.

### Gold particles in glass

Size\*: 25 nm  
 Shape: sphere  
 Color reflected:


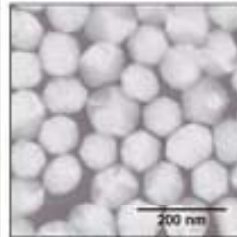


100 nanometers =  
 0.0001 millimeter



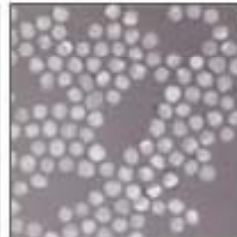
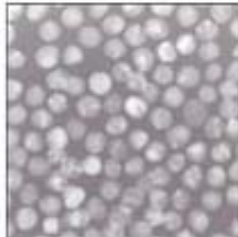
### Silver particles in glass

Size\*: 100 nm  
 Shape: sphere  
 Color reflected:

Had medieval artists been able to control the size and shape of the nanoparticles, they would have been able to use the two metals to produce other colors. Examples:

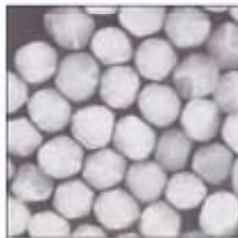
Size\*: 50 nm  
 Shape: sphere  
 Color reflected:

Size\*: 40 nm  
 Shape: sphere  
 Color reflected:



Size\*: 100 nm  
 Shape: sphere  
 Color reflected:

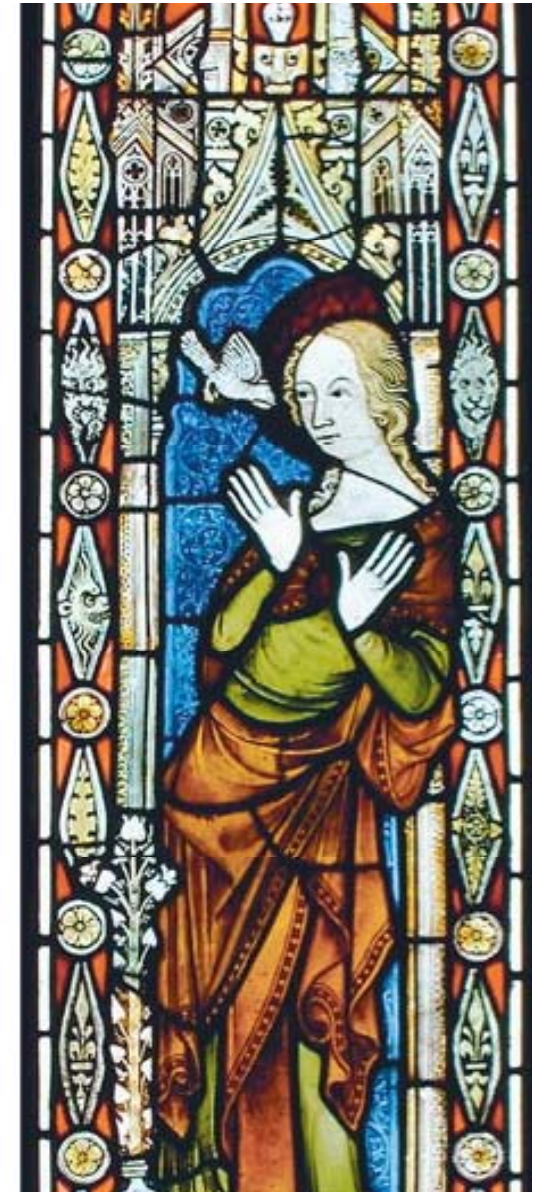



Size\*: 100 nm  
 Shape: prism  
 Color reflected:

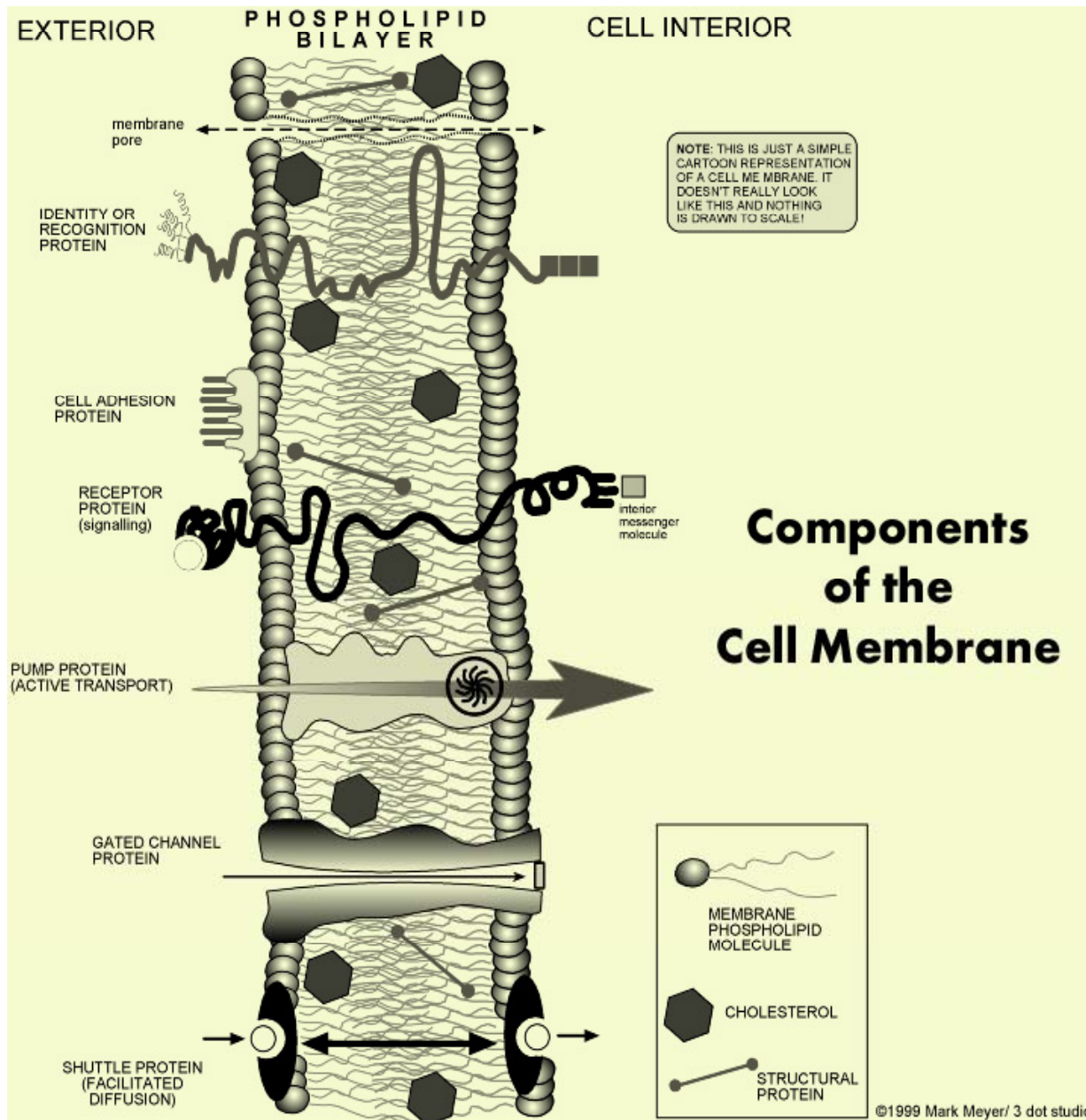


Source: Dr. Chad A. Mirkin, Institute of Nanotechnology, Northwestern University

\*Approximate



# Nature: the original Nanoscientist



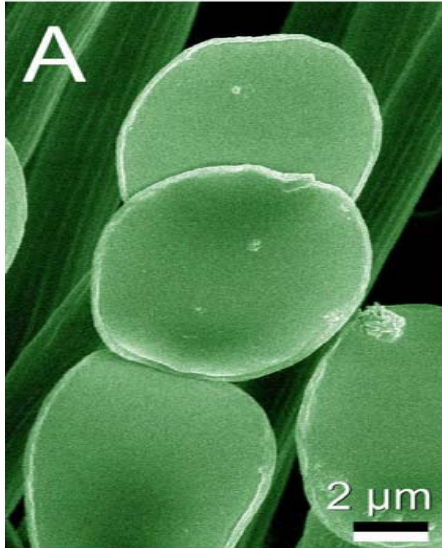
**thickness  
~ 10 nm**

from  
<http://3dotstudio.com/membrane.html>

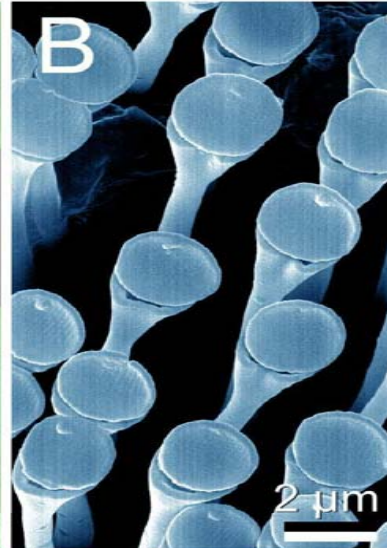
# “Nano-toes”

Beetles, flies, spiders, & geckos have nanostructures that help them stick to walls, ceilings, and what appear to be smooth surfaces.

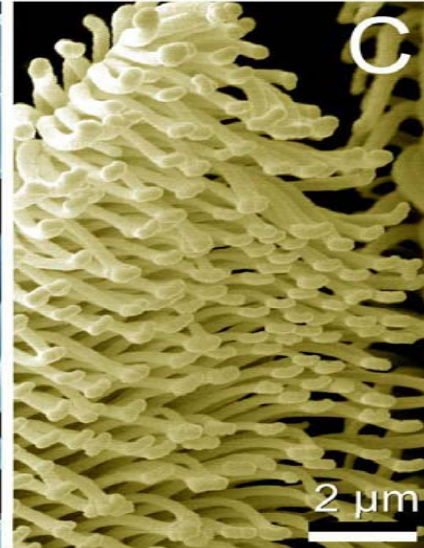
body mass →



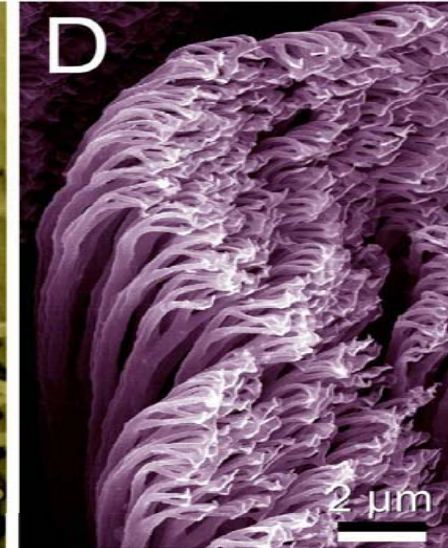
beetle



fly

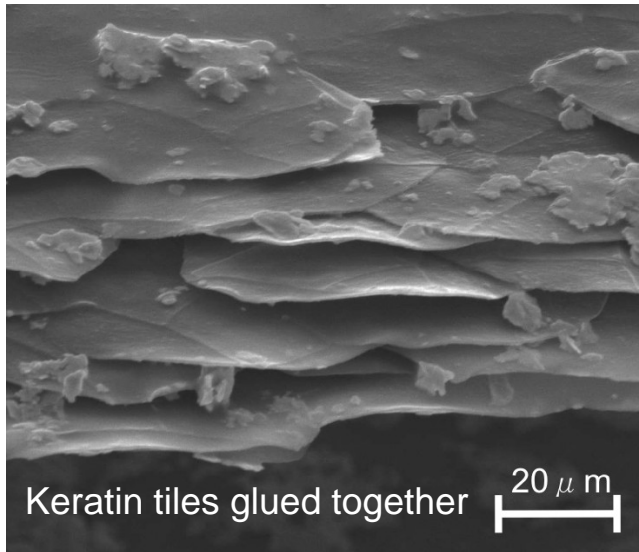


spider



gecko

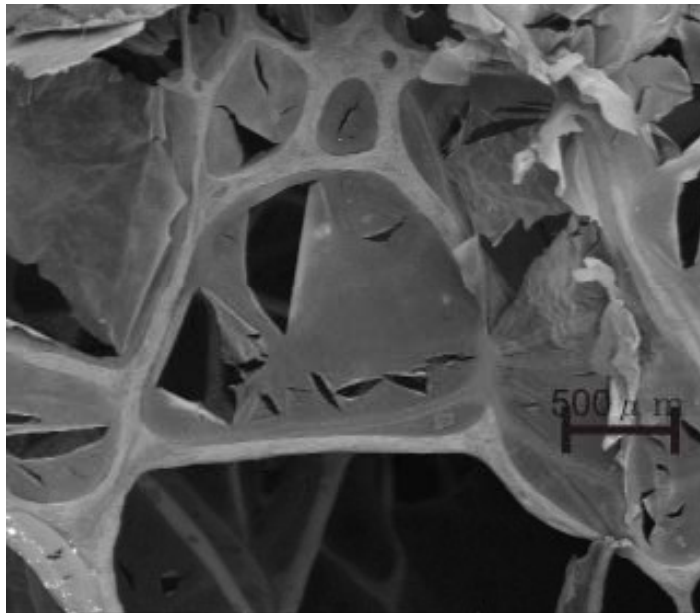
# Toucan Beaks - Strong & Light Nanomaterials



Beak exterior:  
overlapping nanosized  
tiles of keratin  
(same protein that  
makes up hair,  
fingernails, and  
horn)



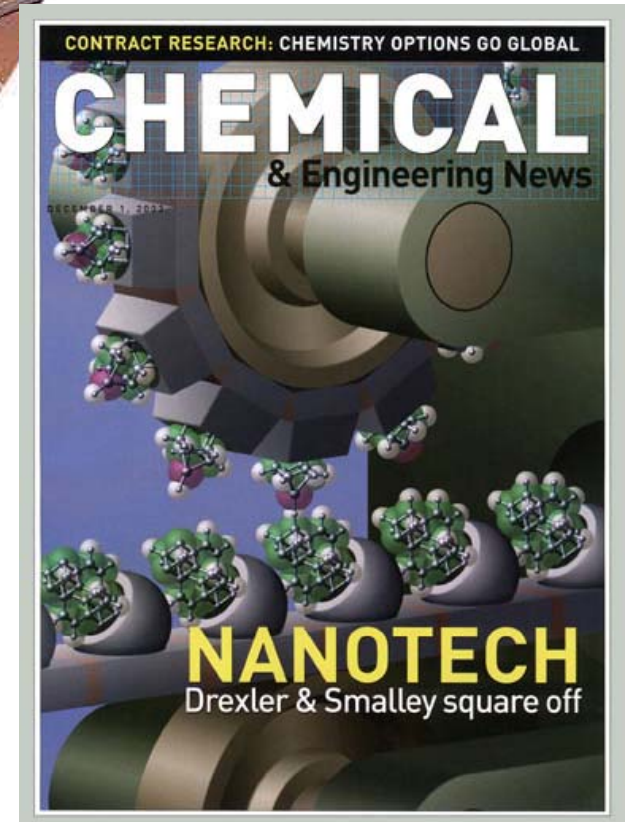
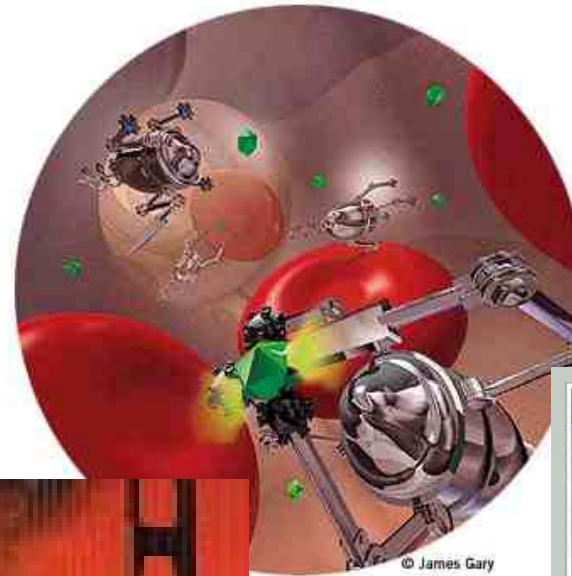
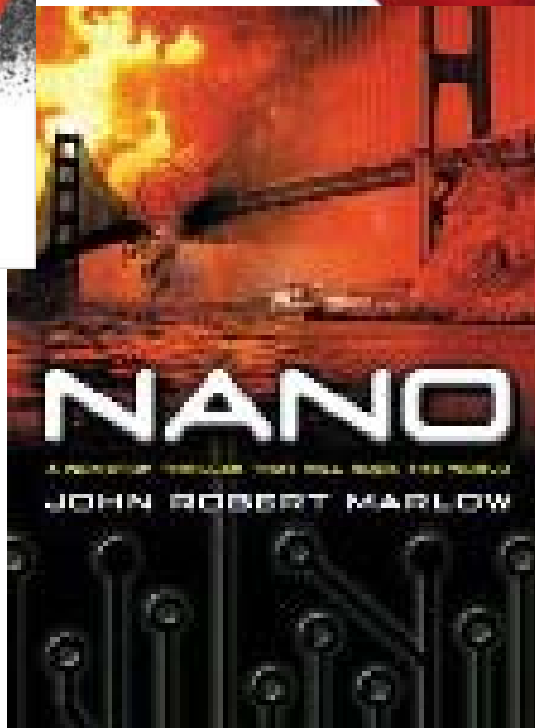
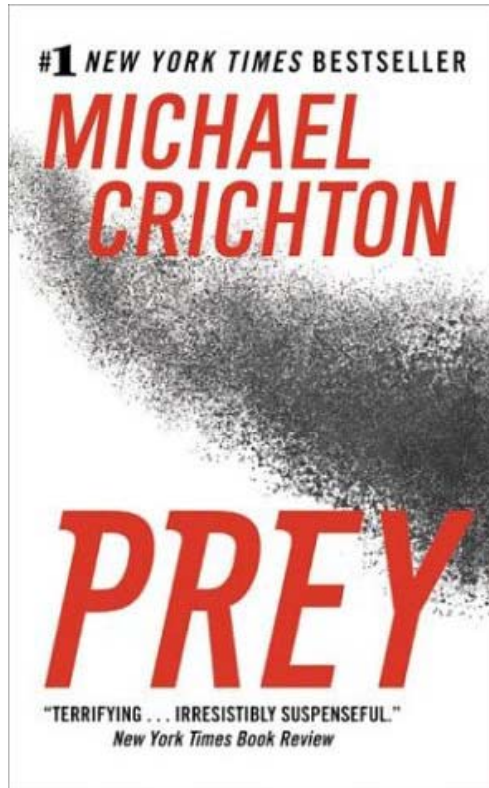
<http://www.nuthatch.birdnature.com/jan1897/toucan.html>



Beak interior:

- rigid foam made of a network of nanosized bony fibers connected by drum-like membranes
- allows the beak to absorb high-energy impacts.

# What Nanoscience Is Not ...





# Today's Nano-Enabled Products

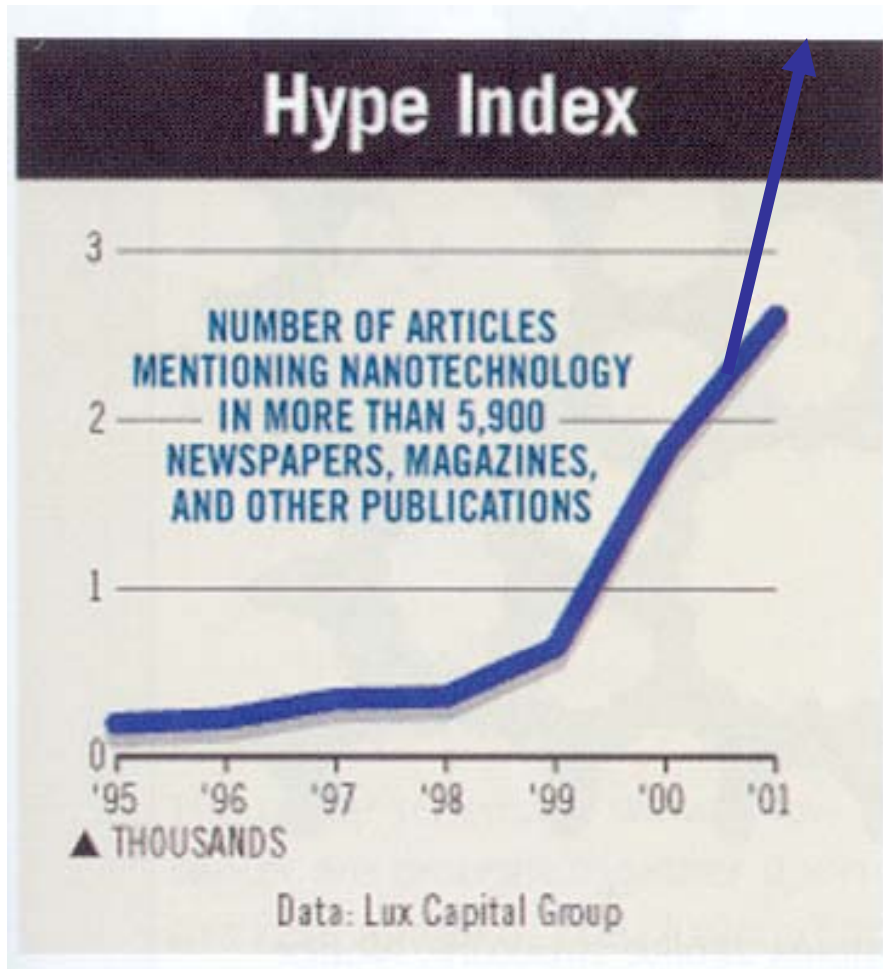
- Step assists on vans and bumpers on cars
- Paints, waxes and coatings to protect against corrosion, scratches and radiation
- Protective and glare-reducing coatings for eyeglasses and cars
- Metal-cutting tools
- Sunscreens and cosmetics
- Longer-lasting tennis balls and longer-distance golf balls
- Light-weight, stronger tennis racquets, skis, and bicycle frames
- Stain-free clothing and mattresses
- Dental-bonding agent
- Burn and wound dressings
- Ink
- Automobile catalytic converters
- Batteries and fuel cells



# State of the Field (or Art)

- Structural nanotechnology (SNT)
  - Current technology
  - Exploiting properties of nanoscale structures
- Molecular nanotechnology (MNT)
  - Future (*far or maybe never?*) technology
  - Designing and manipulating individual molecules
  - Building shapes...machines...products
  - Also known as molecular manufacturing

# Nano-Hype?



**Dilemma or  
opportunity  
or  
both?**

# What Other People Are Saying

“Nanoscale science will give us not dozens, not scores, not hundreds, but thousands of new capabilities in biology, physics, chemistry and computing. Nanotechnology is our country’s future.”

-- Former Speaker of the House Newt Gingrich

# What Other People Are Saying

**“Military applications of molecular manufacturing have even greater potential than nuclear weapons to radically change the balance of power.”**

Admiral (Ret) David E. Jeremiah,  
former vice chairman of Joint Chiefs of Staff \*

\* "Nanotechnology and Global Security," (Palo Alto, CA; Fourth Foresight Conference on Molecular Nanotechnology), 9 November 1995.

# Public Policy Discourse

- Ethics, Legal & Social Issues (ELSI)
  - Health and environmental impacts
    - NSF, EPA, NIOSH, NIH-NIEHS, DOD R&D (~\$38M/year)
    - NNI EHS Research Needs
    - Woodrow Wilson Institute Project on Emerging Nanotechnologies
    - OECD Working Group on Safety of Nanomanufactured Materials
  - Privacy and legal implications
  - Pro-actively avoiding an anti-GMO food backlash
  - Uncontrolled replication (“nano-assemblers”) and artificial intelligence
- **Security is rarely in the dialogue**
  - Could there be an “AQ Khan” of nanotechnology?***
    - Literature: limited & emphasizes “nano-assemblers”
    - How to build a framework to assess analytically?
    - Reconcile with (political science) theories?
      - Balance of Power
      - Offense-Defense
    - Pragmatically, what can be done now to prevent such scenarios?

# A Warfighter's Perspective on Possible Nanotechnology Applications for CBRNE/WMD Operations



**COL Barry Lowe**  
**Chief of Staff**  
**20<sup>th</sup> Support Command (CBRNE)**



- “Individual Protection”
- Applications to make uniform material capable of providing protection against chemical and biological agents, as well as other toxic materials
- Applications to make uniform material “react instantly” to become armor in the event of a bullet or fragment impact
- Applications for prophylaxis against inhalation or ingestion of chemical or biological agents, and toxic materials
- Applications for use as antidotes

# nanotechnology

for Chemical and  
Biological Defense 2030

January 30 - February 1, 2007

## CBIRF Perspective

**TECHNOLOGY**  
**An Operators Perspective**  
CDR Mike Penny  
Senior Medical Officer



## What Do They Think of Technology?

Requires too much training

Requires too much maintenance

Too delicate

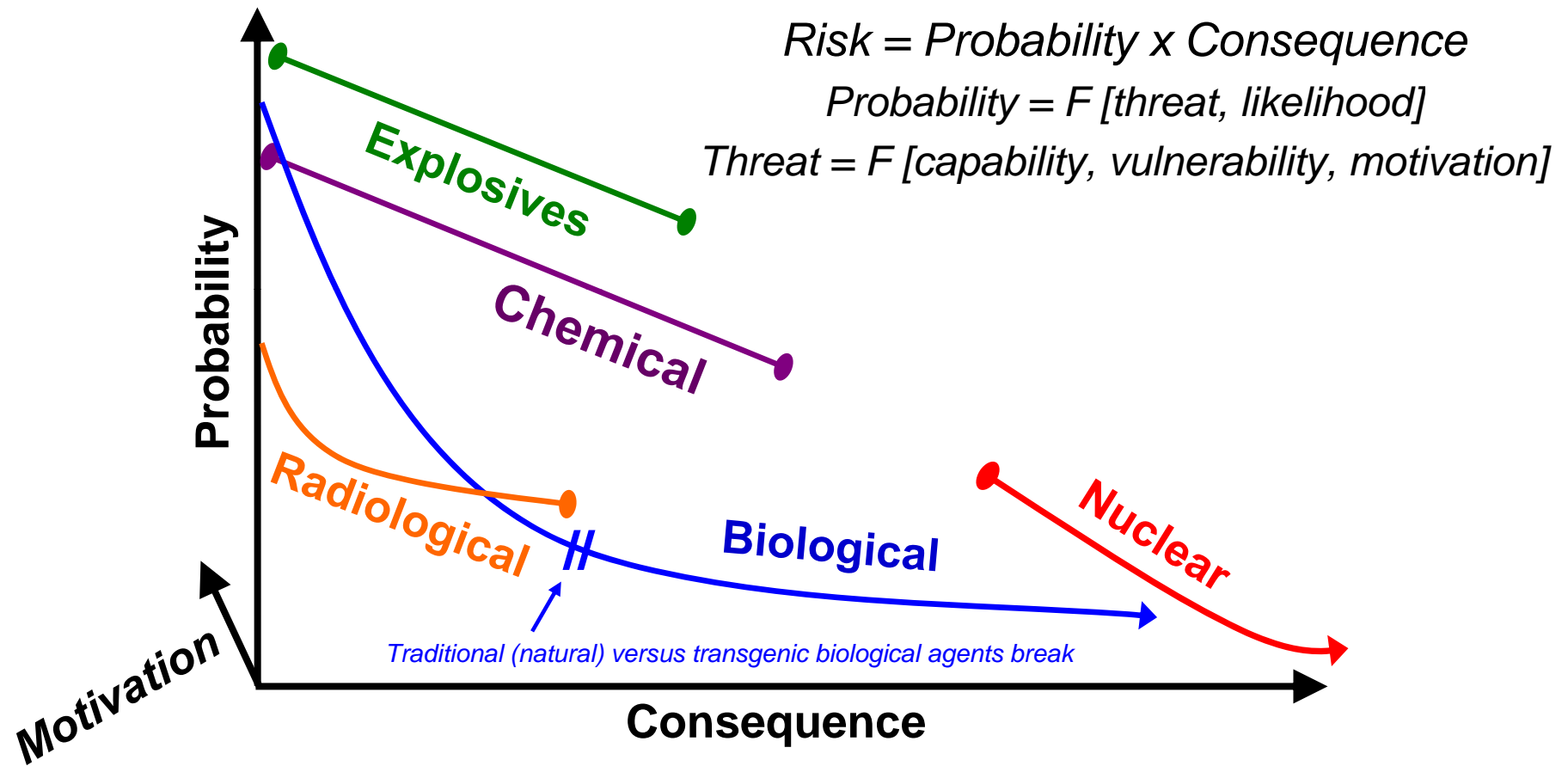
Too expensive

Then... it lets you down when you need it the most





# WMD Terrorism Risk Assessment



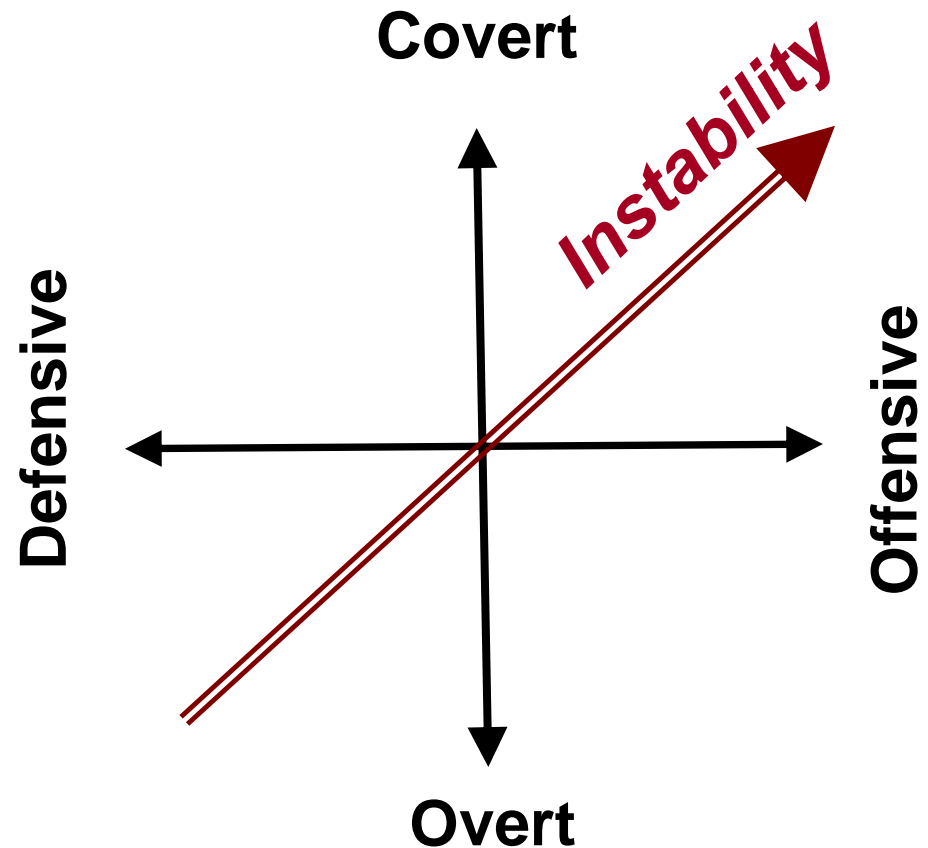
Where to place nanotech weapons?

Probability is very low.

Consequence is potentially very large but also hard to gauge meaningfully.

# Analytical Frameworks for Assessing Strategic Significance of Technology

- Offense-Defense Theory
- 4GW



**These are all**

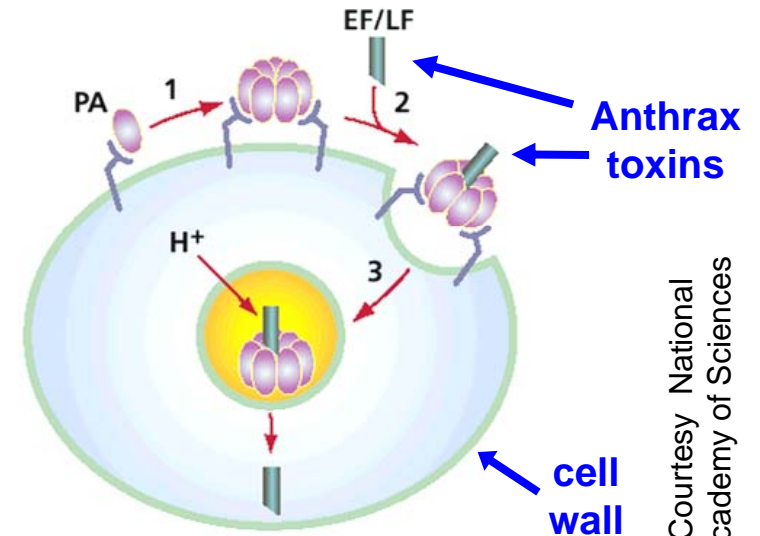
**Notional**

**Scenarios**

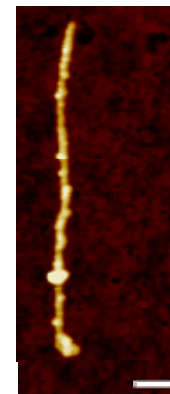
*that means not real, intellectual  
thought experiments, etc*

# Circumventing Vaccines

- Biothrax (AVA) & BioShield-funded recombinant vaccines based on protective antigen (PA)
- PA necessary to endocytose toxic proteins (*the lethal and edema factors (EF & LF)*) to cytosol
- Functionalized single-walled carbon nanotubes (*f*-SWNTs)
  - cross mammalian cell walls & release *biologically active “cargos”* - proteins, peptides, DNA, RNA, small molecules
- Motivated by medical applications drug delivery & gene therapy



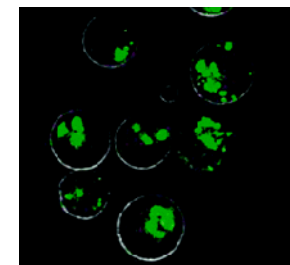
Courtesy National Academy of Sciences



100 nm

AFM image of SWNT + Staphylococcal Protein A (SpA)

*f*-SWNTs inside human cells



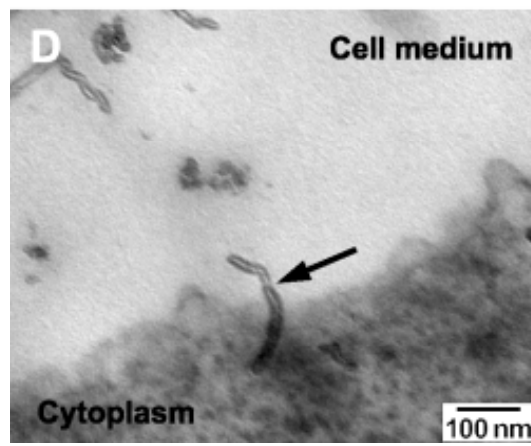
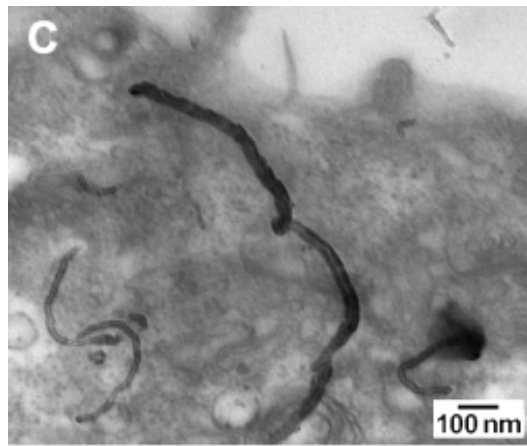
Courtesy Hongjie Dai, Stanford

# Toxin Delivery

## ***Applicable to other BW agents, e.g., Botulinum toxin***

- Difficult to produce in large quantities via traditional microbiological methods (*Commercial Botox requires 30-275 vials to achieve one LD<sub>50</sub>, strain-dependent*)
- Current transgenic methods can only produce light chain (LC) of toxin from *E. coli* or yeast
- Heavy chain (HC) necessary for toxin to cross cell wall
- *LC + carbons nanotubes could circumvent technical difficulties*

Courtesy Alberto Bianco, CNRS

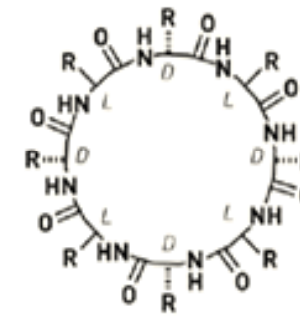
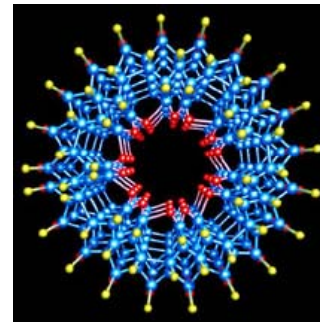


C) Human HeLa cells treated with functionalized multi-walled carbon nanotubes (f-MWNTs) to deliver DNA into cells.

D) A multi-walled carbon nanotube crossing the cell membrane.

# New or Bio-Vesicants

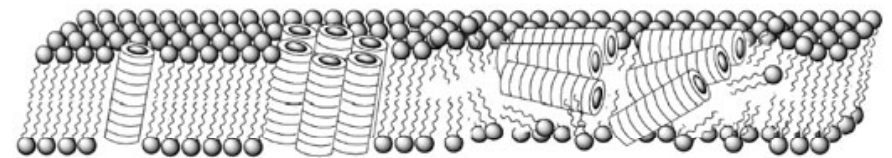
- Supramolecular Peptide Nanotubes (SPN)
  - lyse cell walls
  - rupture phospholipid layer
- Easier, cheaper and uses technology more widespread than Wimmer's illustrious 'synthetic polio' experiment
- Potentially more environmentally robust than mustard agents
- Motivated by emergence of antibiotic resistant bacteria goal to disrupt bacterial cell walls



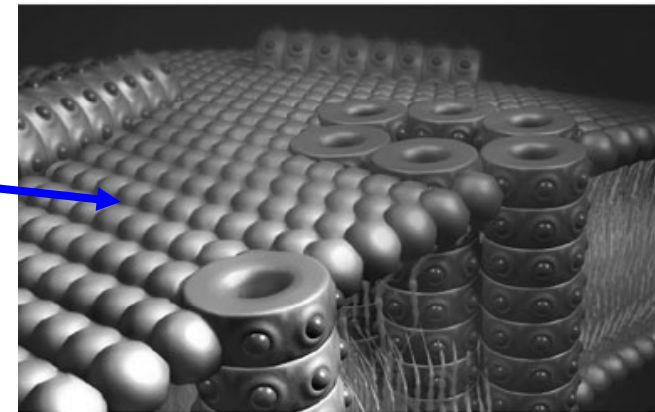
Self-assembly →



Courtesy Nature Magazine



Cell wall  
or skin  
(lipid  
bilayer)



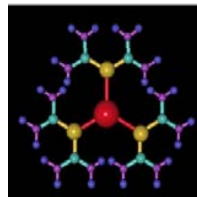
Courtesy Reza Ghadiri,  
Scripps Institute

# Nanotoxicity: Range of Novelty

- Some classes of nanoparticles not actually new
  - Liposomes
  - Ultrafine (<100 nm) particles
- Toxicology of more familiar materials is better understood
  - Ultrafine “associated with exacerbations of airway disease” and implicated in enhanced inflammation
- Carbon nanotubes (CNTs) – highly unusual aspect ratio and material properties
  - Focus of many early nanotoxicity studies
  - Not top candidate for medical applications



liposome



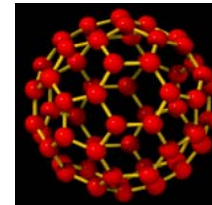
dendrimer



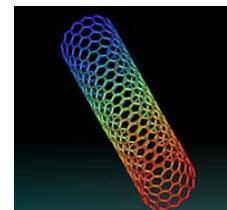
gold & silver nanoparticles



nanoshell



fullerene



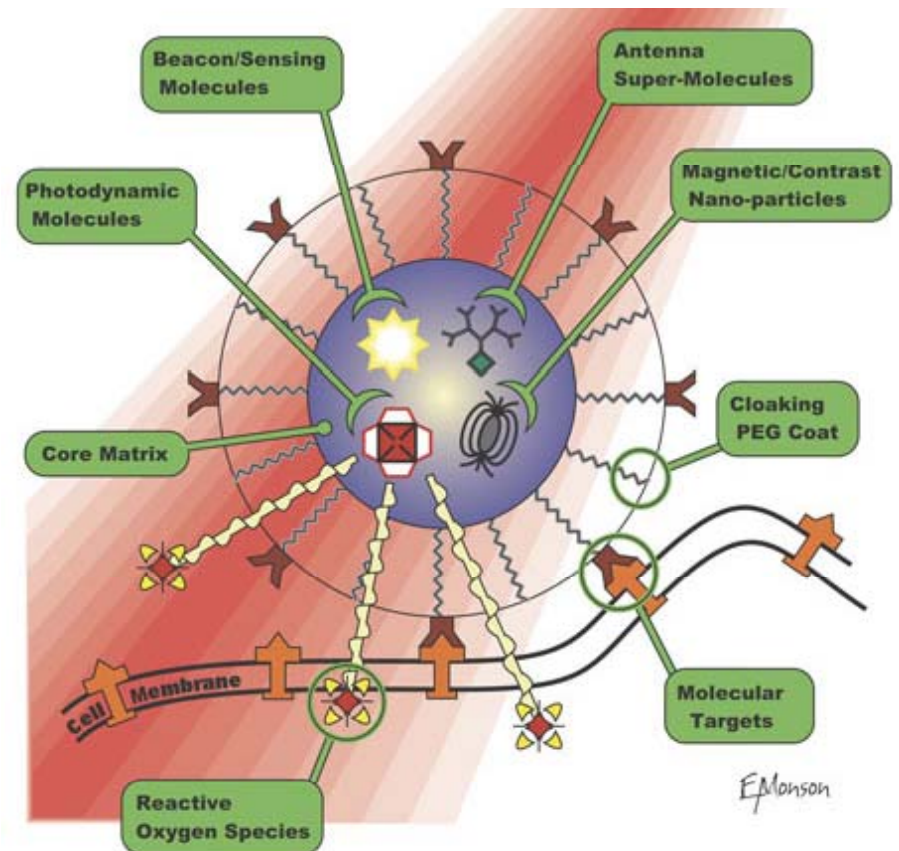
Carbon nanotube or other nanowire (GaN)



# Controlled Agent Distribution

## Advectus's Nanocure™

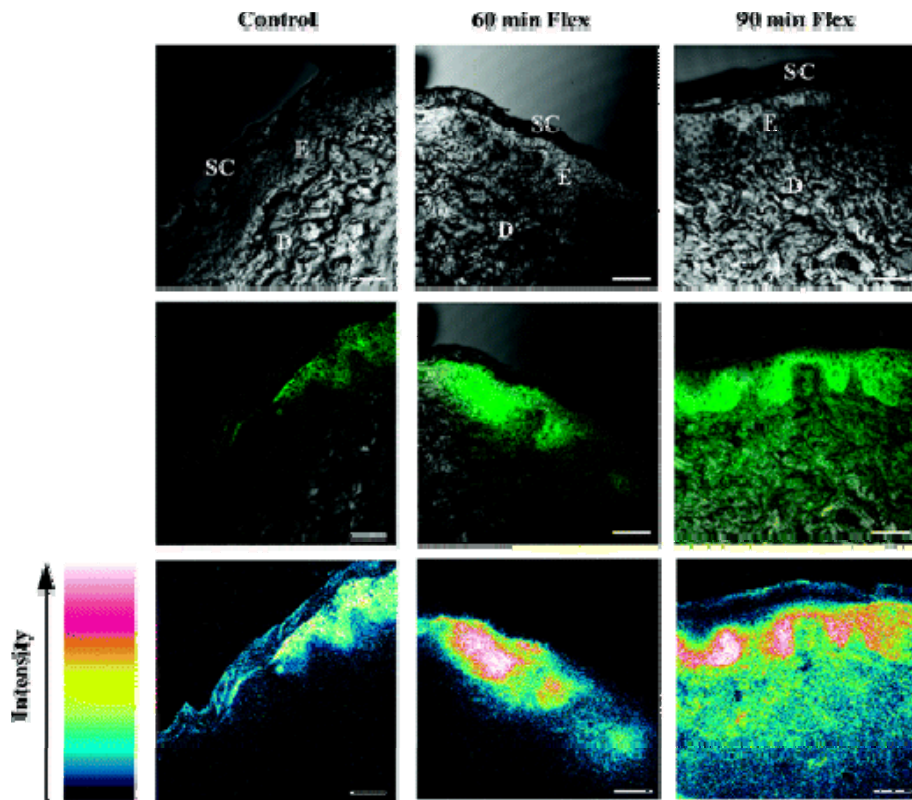
- Nanoparticle-based formulation for the delivery of approved chemotherapeutic (doxorubicin) that does not cross the blood-brain barrier
- Polymer nanoparticle coated with chemotherapeutic and emulsifying saccharide layer (polysorbate-80)
- Outer layer attracts lipoproteins that camouflage particles
- Blood-brain barrier treats the particles as if they were low-density lipoproteins (LDL) - cholesterol
- LDL receptors in the brain transport the Nanocure particles through the blood-brain barrier
- Nanoparticles break down, allowing the diffusion of doxorubicin into the brain tissue





# Penetration of Bio-Nano Conjugates

Courtesy Nancy Monteiro-Riviere, NCSU

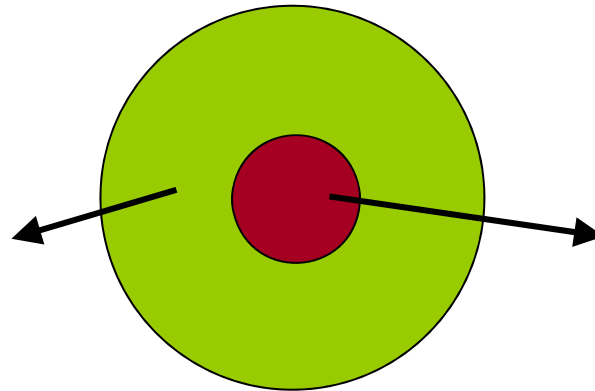


Uptake of fullerene-lysine-FITC complex through intact stratum corneum (SC) and underlying epidermal (E) and dermal layers (D). Scale bar = 50µm

- Fullerenes conjugated to cationic peptide show substantial uptake through skin
- Mechanically stressed skin shows increased penetration
- Skin observed to be surprisingly permeable to nanomaterials (fullerenes & quantum dots) with diverse physicochemical properties
- Motivated by transdermal drug delivery applications & nanoparticle safety assessments

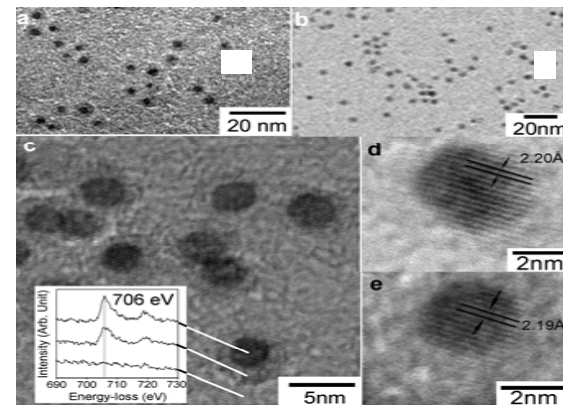
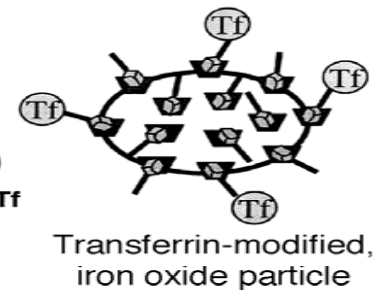
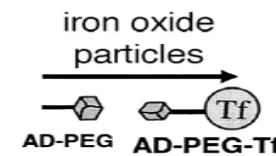
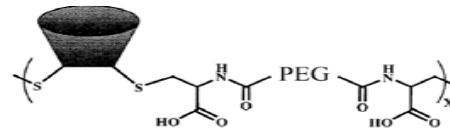
# “Brain Fry”

*Stealth coat – defeats detection and optimizes aerosolization*



*NP that heats up A LOT upon absorption of EM – maybe from a cell phone*

- Coated Fe<sub>2</sub>O<sub>3</sub> nanoparticles
- Pass the blood brain barrier
- EM-activatable
- Unique combination of people, materials, & facilities:
  - Expertise in nanoparticle production (especially biological apps),
  - Directed energy experts who may have worked on ablation therapies,
  - Engineers who have experience in battlefield delivery of EM radiation,
  - Vets to oversee animal testing,
  - Aerosol expert- someone who specializes in aerosol drug delivery.
- Current research motivated by need for targeted chemotherapeutics and diagnostic imaging



**Platinum-iron oxide core-shell nanoparticles**

Courtesy Hong Yang,  
University of Rochester

# Molecular Assemblers, aka “nanobots”

- Self-replicating machines and products built from molecular, “the bottom up”
  - **Currently more Sci-Fi than Science**  
**Fact**, e.g., *Star Trek* & *Crichton’s Prey*
    - “Blue/Grey sky” outlook: autonomous behavior & grey goo phenomenon
    - *Caveats: The Laws of Thermodynamics & limitations of behavior at low Reynolds Number will still apply*
  - Supramolecular chemistry is “version 0.2” of molecular assemblers.
- Molecular Manufacturing Proponents point to commercially available 3-D printers
  - rapid model prototyping of models from computer-aided design (CAD) programs
- Tissue engineering applications:
  - Organ/bio-printing
  - Combined with synthetic biology???

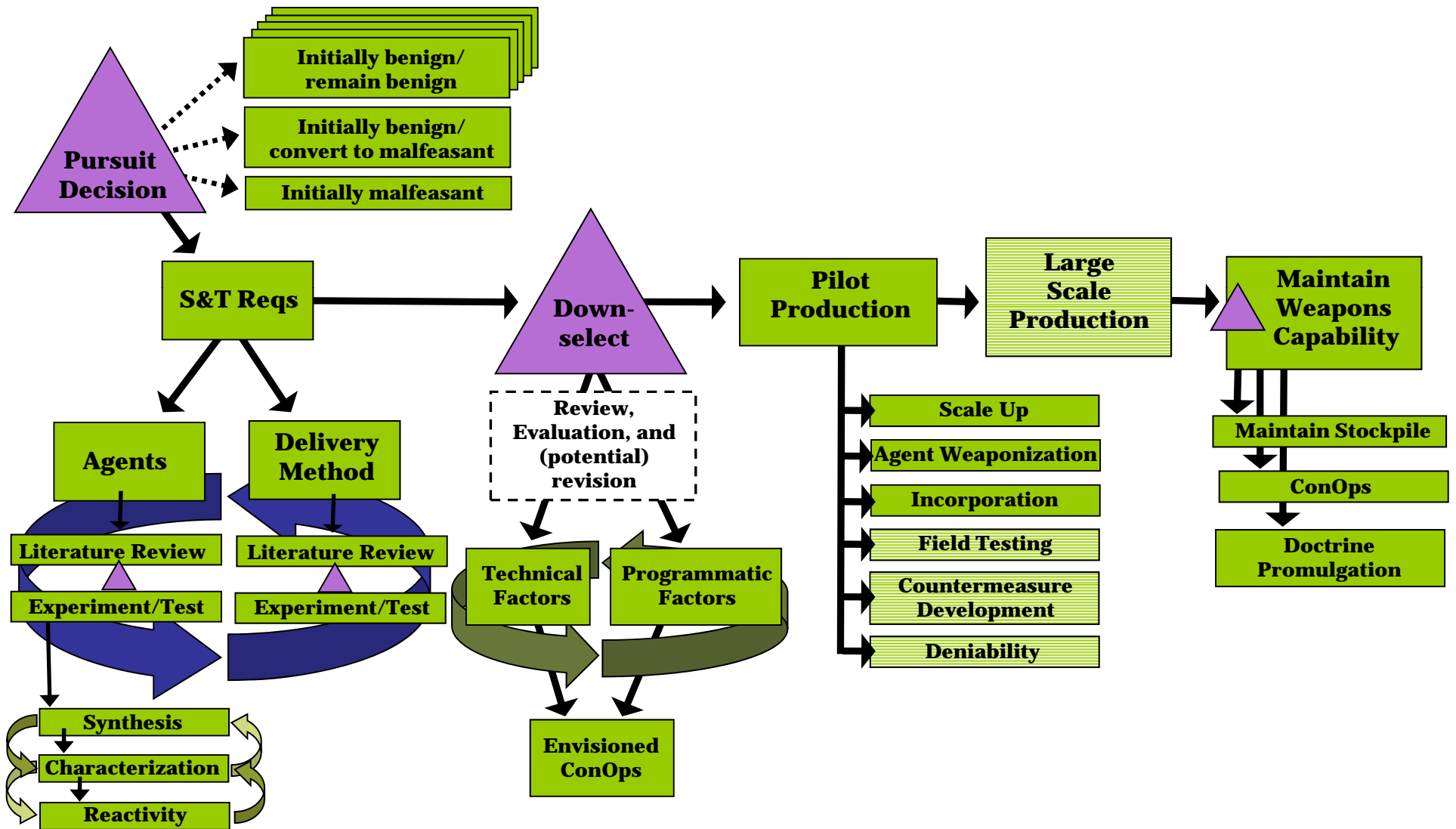


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**The Science is Real, the Scenarios are Notional!**

# Notional General Nanotech Decision Pathway



▲ = major decision points

■ = major steps/activities

▨ = optional steps/activities

# Characterizing Emerging Technologies

- Disambiguate potential for unique capabilities from enabling previous capabilities
- Perception or ideation vs technical reality
  - “Hype” & “Horror”
  - Danger of (Pseudo)-Technical Assessments
    - Not understanding the underlying science
    - Presuming that anything with a science-sounding name is inherently dangerous
    - E.g., “*New technologies (at risk for terrorist appropriation) include biotechnology, **nanotechnology, single nucleotide polymorphisms** (SNPs), and **Bose-Einstein condensates**.*”\*
- Fundamental interdisciplinarity

\* “WMD Terrorism Research: Where to From Here?” *International Studies Review*, March 2005, vol. 7, p. 140

# Global Overview

## European Union

~\$2.5B/y since 2008

## Japan

~\$800M - \$1B/y since 2004

## ROK

~\$200M/y since 2003

## Southeast Asia

Singapore Nanyang Technological University (NTU)

“NanoFrontier” >\$200M/y

Malaysia

Taiwan ~\$600M over 6 years

## China

Estimated ~\$250M per year (PPP) 2000-2005

Estimated \$1.5-1.8B/y (PPP) 2007-2009

## Russia

~\$5B 2008-2012 for research and infrastructure modernization

“nano-enabled thermobaric bomb”

## Iran

Majles Rep “America cannot tolerate Iran’s success in scientific fields such as **nanotechnology** and **nuclear technology**,” Dec 2005

## •US

21<sup>st</sup> Century Nanotech Act  
(2003-2008) \$3.7B/5years

NNI, US federal nanotech  
(2000) \$710M

(2011 PBR) \$1.7B

DOD (2009 budget) \$464M

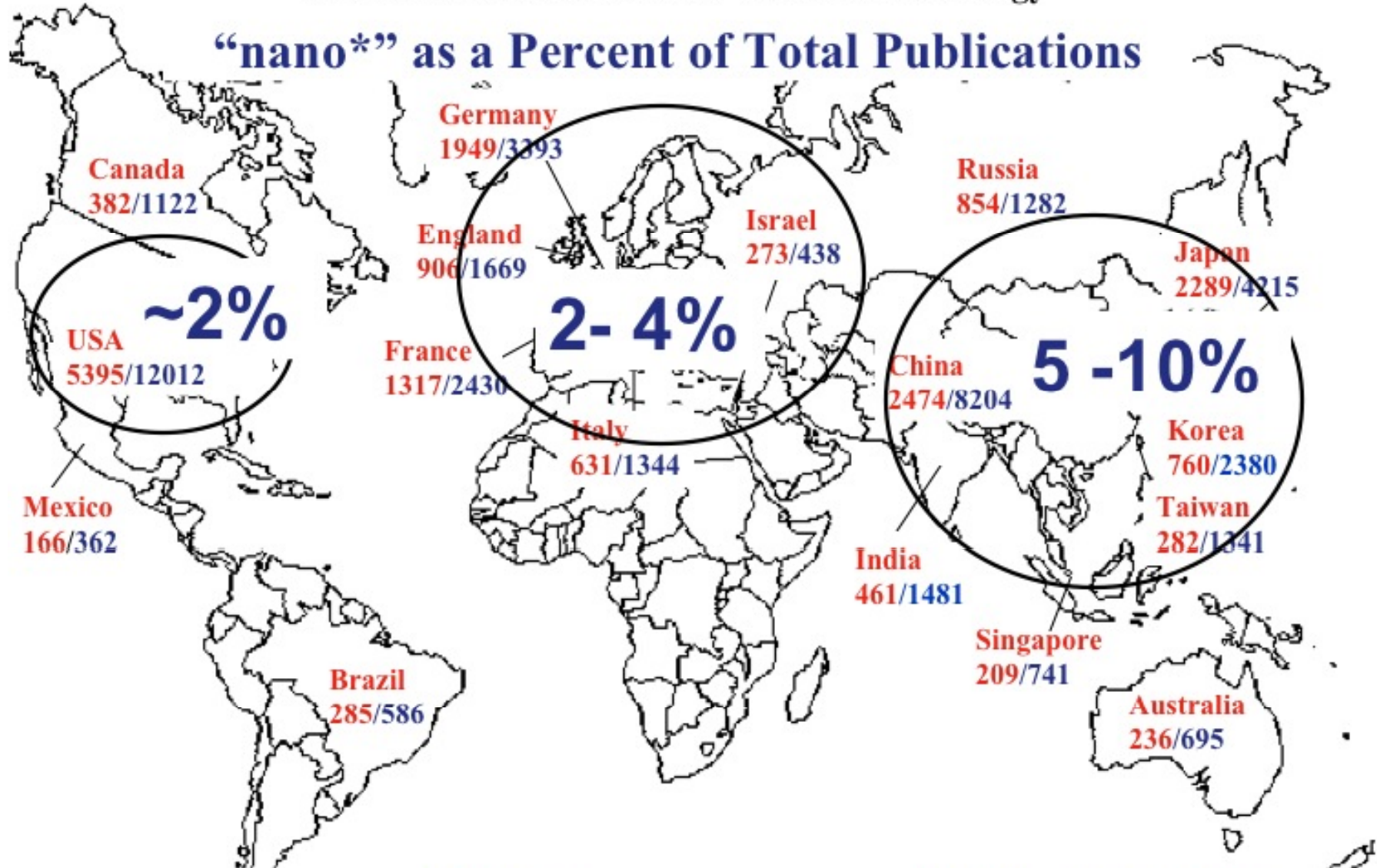
(2011 PBR) \$349M

## •Significant private investment

“guestimation” of \$2T sales by 2015

## Global Race Toward Nano-enabled Technology

### “nano\*” as a Percent of Total Publications



Worldwide CY2002/06/08 Publication Counts – 18,539 / 43,225 / 57860



# U.S. Overview

## Federal

- 21st Century Nanotech Act (2003-2008) \$3.7B/5years (*planned*)
- NNI (2001-08) \$8.3B (*actual*)
- US federal nanotech  
(2000) \$710M  
(2011 PBR) \$1.7B

### **NNI Strategic Plan (Dec 07)**

- *Early Detection of Life Threatening Diseases*
- *Engineered Nanoscale Materials*
- *Nanobiotechnology*
- *Nanotechnology-Based Water Purification & Testing*
- *Information Processing & Advanced Electronics*
- *Predictive Toxicology*
- *Societal Dimensions of Nanotechnology*

## DOD

**2009 \$431M PBR**

**\$464 appropriated**

**2011 \$349M PBR**

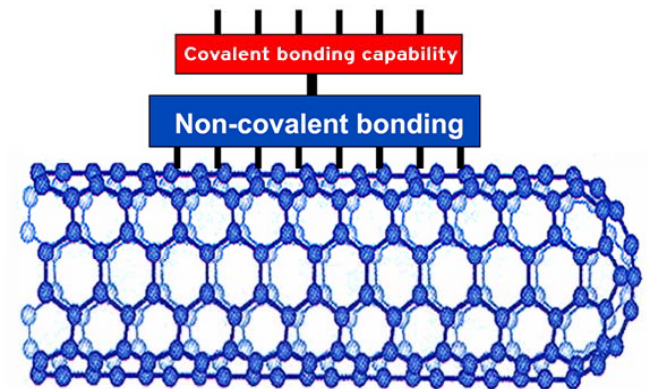
- DARPA
- Air Force: electronics, computing, communication, sensors (AFOSR)
- Army: energetics, ballistic protective materials, power/energy (ARO)
- Navy: electronics, materials, sensors (ONR)
- CBDP: passive defense
- DDR&E
- MDA
- OSD Emerging Contaminants Working Group

# International Security Regimes

- Biological Weapons Convention (BWC)
- Chemical Weapons Convention (CWC)
- Export Controls

## Case Study: Zyvex

- Richardson, Texas \$10M revenues in 2005
- Nanoworks – nano tools, electron microscopes & photovoltaic applications
- Kentara™ – CNT dispersions in resins
- Current market
  - CNT-reinforced mountain bikes
  - Easton baseball bats
- Required to submit ITAR licenses for CNT-product exports to China
- In response, founder suggests may relocate to SE Asia



# Key Security Factors

- Deniability & Lack of Transparency
  - Most of the dual-use concerns raised regarding biotechnology risks are *potentially* applicable to malfeasant co-option of nanotechnology \*
  - Except, biological agents require damp environments with moderate temperatures, moderate pressures and ambient oxygen
  - \* *Nano-engineered materials do not replicate*
  - Lack of explicit norms
  - Lack of explicit category for international arms control regimes
- Vulnerability Perception
  - Perceived lack or limitation defensive countermeasures, e.g., limitations of stand-off biological (& to a lesser extent, chemical) detection
- International prestige
- No single discipline on which to focus
  - Chemistry to electrical engineering
  - Materials science to molecular biology
- Overwhelmingly, a state-based proliferation concern
  - Secondarily, rogue scientist scenario
- Intent must be balanced with capability
  - Offensive versus defensive not transparent
- Globalization
  - Private sector is major player global, e.g., sale or transfer of technology