

# Applications of Nanotechnology to Improve Food and Food Supplies



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Future of Food Seminar  
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# Nanotechnology & Foods

- A Brief Introduction -

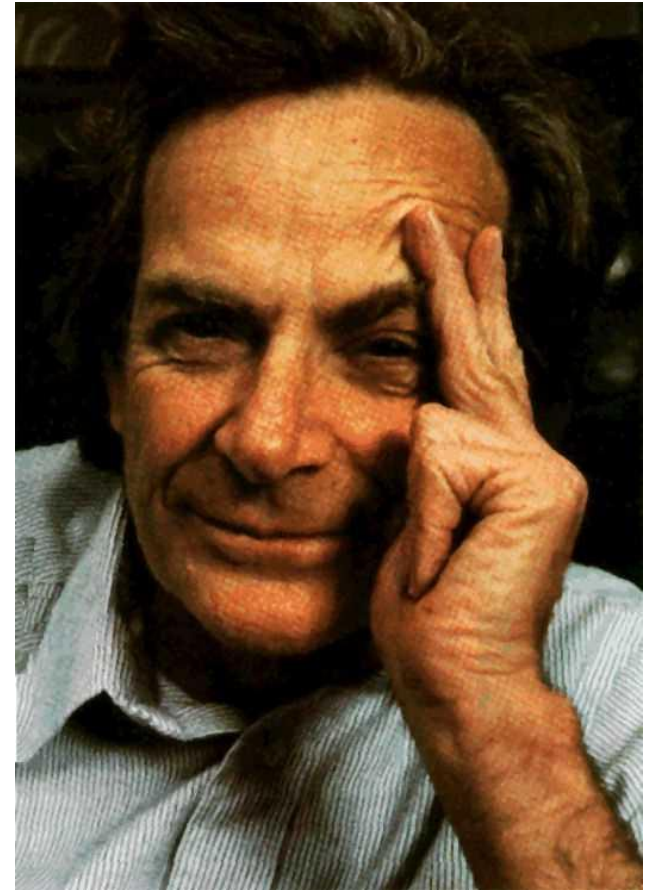
What is the all  
the Fuzz about?

Paradigm Shifts  
in the  
Development of  
Food Systems

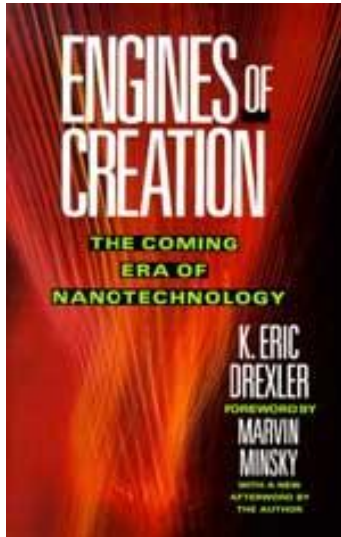


# The Emergence of Nanotechnology

- Birth with Richard P. Feynman, in his visionary presentation titled “There is Plenty of Room at the Bottom” on December 29<sup>th</sup>, 1959.
- Became possible with emergence of new analytical tools in the 80’s
  - Scanning tunneling (STM) and field emission scanning microscopy (STM)
  - Atomic force microscopy (AFM)
- Ability to image, measure, model, control and manipulate matter at dimensions of roughly 1 to 100 nanometers
- Properties governed by **quantum mechanics** rather than Newtonian mechanics → surface/interfacial physics and chemistry are of paramount importance



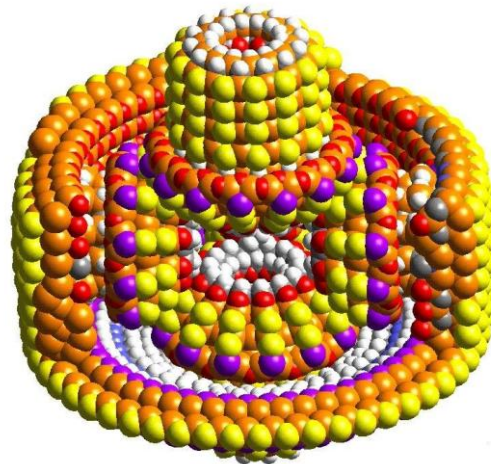
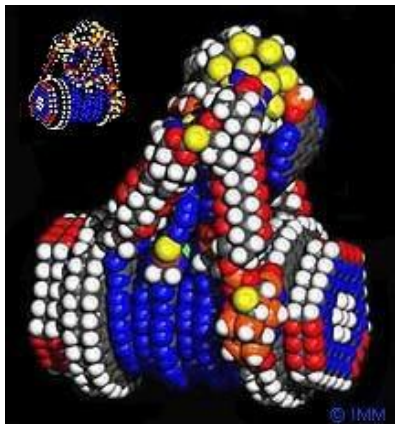
# The Original Vision - Molecular Manufacturing



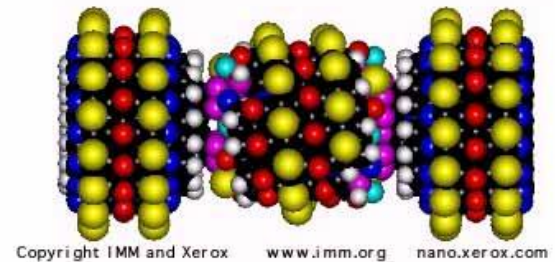
## “Engines of Creation: The Coming Era of Nanotechnology”

Book by K. Eric Drexler, 1986

- “Molecular Assemblers” → Devices capable of precisely positioning atoms and molecules



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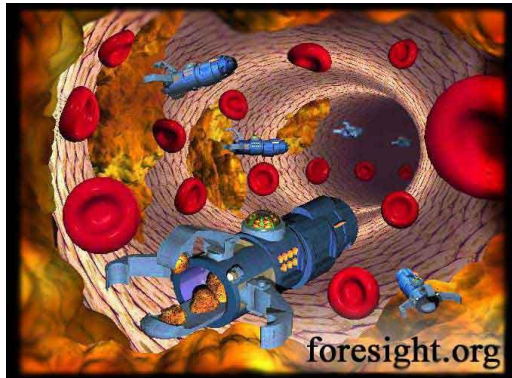
Copyright IMM and Xerox www.imm.org nano.xerox.com



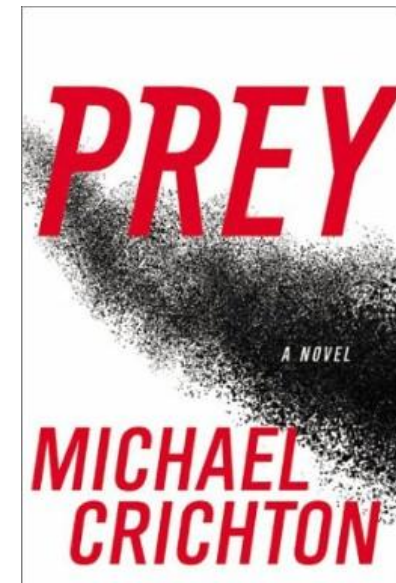
# The True Evolution (not Revolution) of Nanotechnology

- Eclectic derivative of established disciplines:
  - Chemistry, Physics, Interface Science, Microfabrication
  - Discoveries are made on established principles and foundations
- Why add “nano”?
  - Allow researchers to highlight that processes or material structures are designed to use specific properties and behaviors at  $10^{-7}$ - $10^{-9}$  m.
- **What it has evolved into (particularly in Food Science and Technology):**
  - **Conceptual and intellectual framework** that enables the design of more complex macroscopic structures using nanometer length-scale building blocks
  - This does represent a paradigm shift from traditional food manufacturing

# Fiction Fuels Irrational Concerns

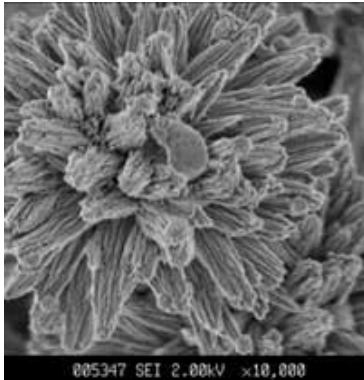


- "Replicating assemblers and thinking machines pose basic threats to people and to life on Earth" - Drexler
- Speculation about the potential dangers of nanotechnology threatens public support – Smalley



# The Reality

## - Everyday Nanotech Products -

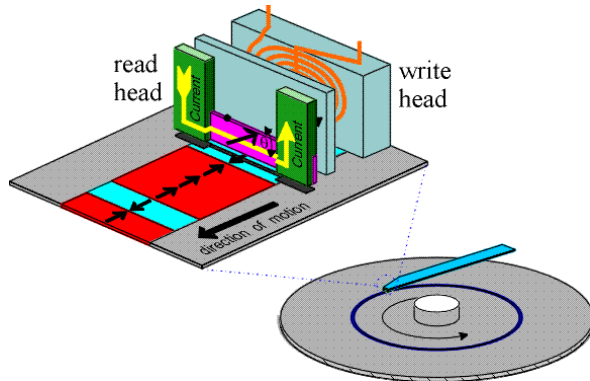
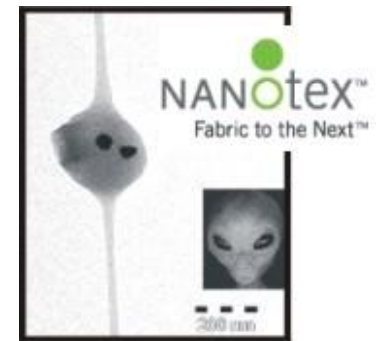


Zeolite catalysts for petrochemical refinery processes



Cosmetics

Stain-resistant Textiles



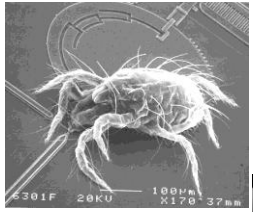
Giant Magnetoresistance for information storage

Reinforced tennis racquets and tennis balls



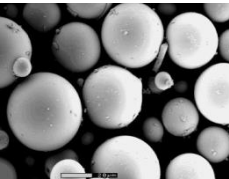
# Natural Objects

**Ant**  
~ 5 mm



**Dust mite**  
~200 μm

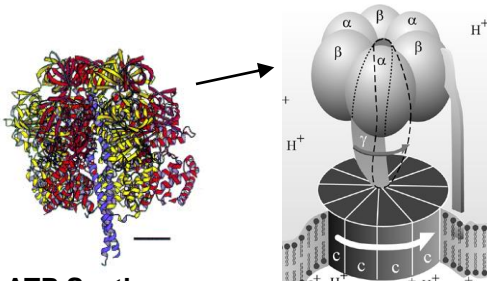
**Fly ash**  
~ 10-20 μm



**Human Hair**  
(~60-120 μm)



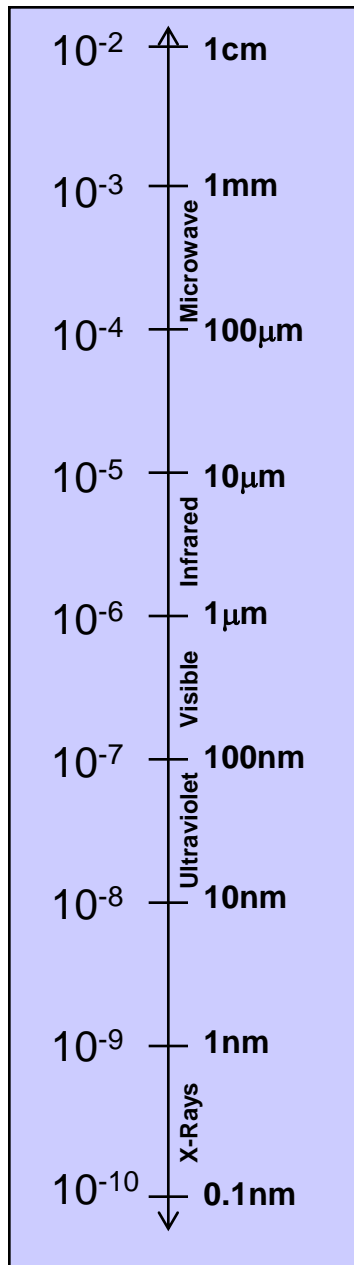
**Red blood cells**  
(~7-8 μm)



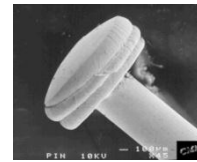
**ATP Synthase**  
~10 nm



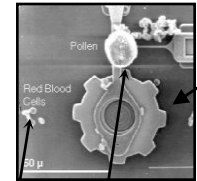
**DNA**  
~2-1/2 nm



# Manufactured Objects

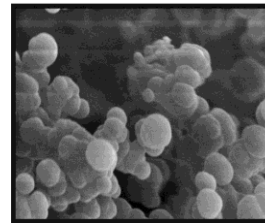


**Head of a pin**  
1-2 mm

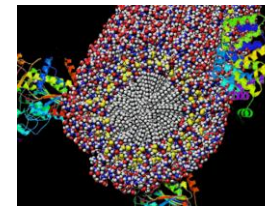


**MicroElectroMechanical (MEMS) devices**  
10 -100 μm wide

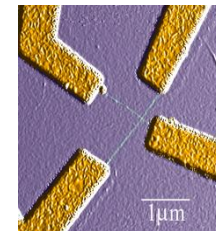
Pollen grain  
Red blood cells



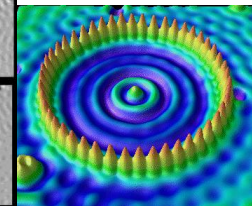
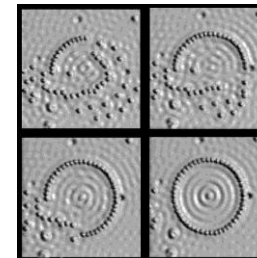
**Globular Protein Aggregate**  
Many 10s of nm



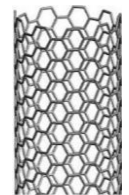
**Self-assembled, structure**  
Many 10s of nm



**Nanotube electrode**



**Nanotech in Nature & in Technology**

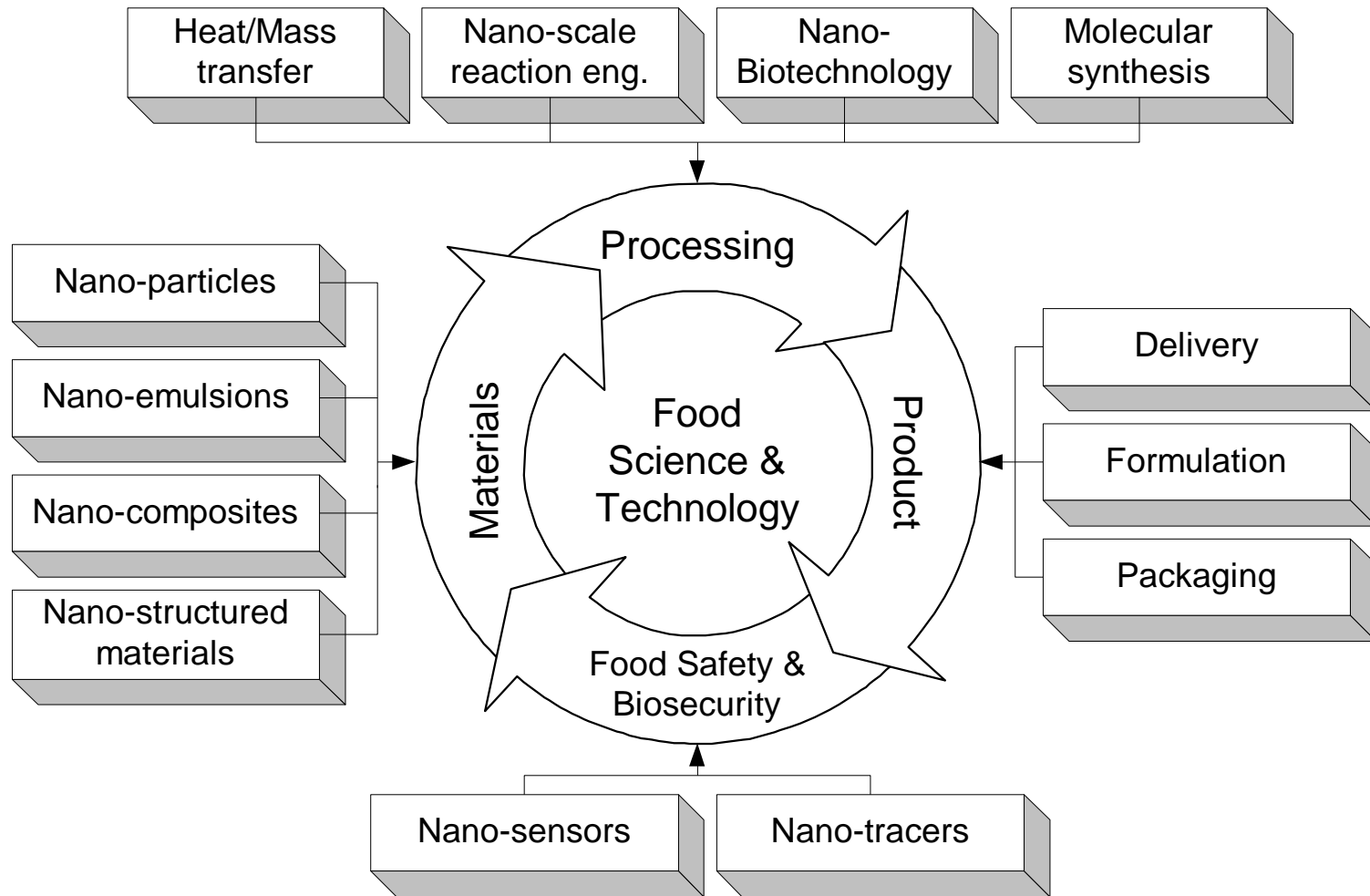


**Carbon nanotube**  
~1.3 nm diameter





# Applications of Nanotechnology In Food Science and Technology



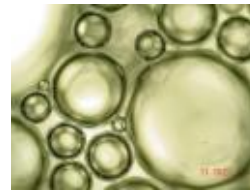


**Agricultural Raw Materials**

**Thermal Treatments  
Shearing/Mixing  
Homogenization  
Extrusion**

**Bulk Processing**

**Paradigm Shift: -  
Fabrication Approaches  
to Nanoscalar Objects -**


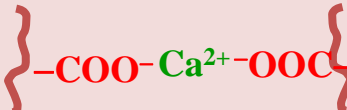


Microstructures


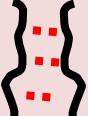
Nanostructures

Food Product



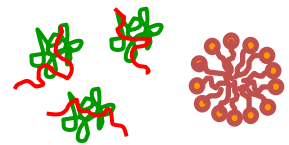
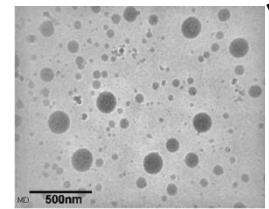
**Covalent Bond**  
**Electrostatic Interactions**  
**Salt Bridging**






**Hydrogen Bonding**  
**Hydrophobic Interactions**  
**VDW Attraction**

**Self Assembly**

**Peptides**  
**Proteins**  
**Oligosaccharides**  
**Polysaccharides**



**Phase Transitions**  
**Network Formation**  
**Phase Separation**



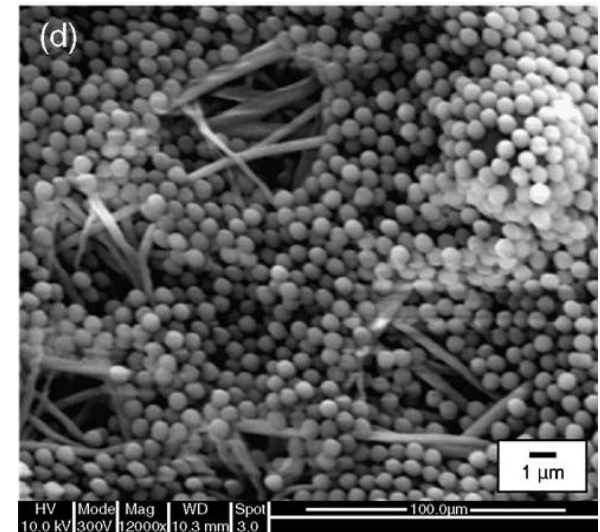
# Food Nanotechnology Applications

Food Safety and Quality  
Food Processing  
Food Packaging  
Ingredient Technologies



# I. Use of Nanotechnology in Processing: Nanofiltration

- Based on fabrication of non-woven filter materials
- Individual fiber sizes vary between 10 – 500 nm
- Extremely high surface-volume ratio – excellent for deep filtration or adsorption
- Production via **ELECTROSPINNING**
- Functionalization of fiber surfaces possible (core-shell spinning, spin-coating, electrostatic deposition)

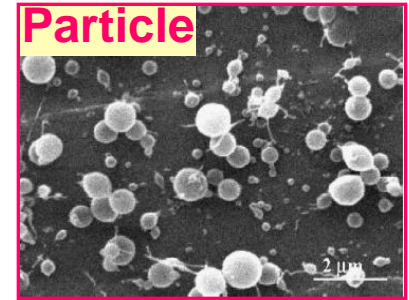
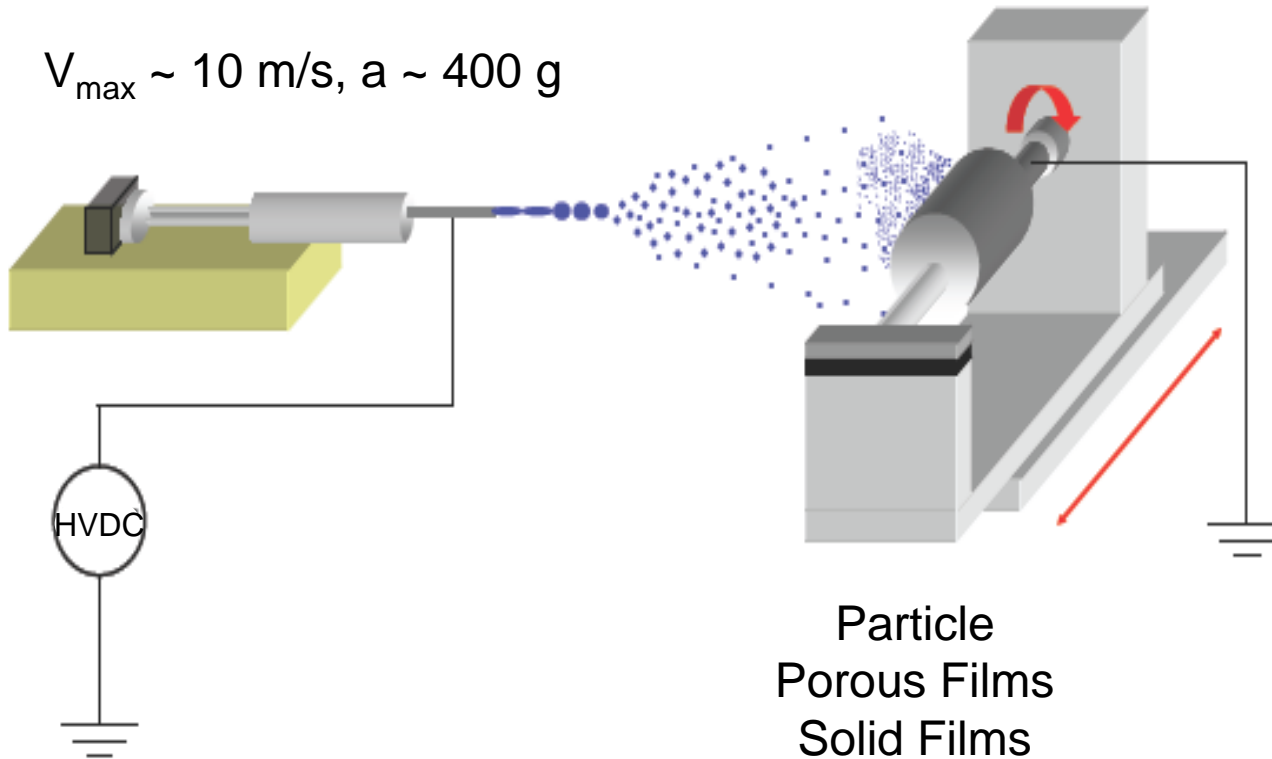


Nanoparticle Filtration

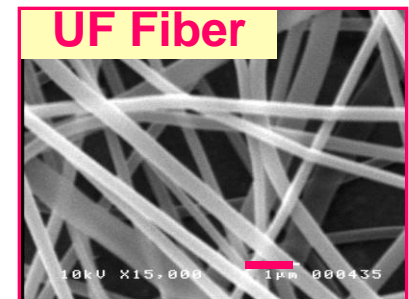


# Electrospraying and Electrospinning

$V_{\max} \sim 10 \text{ m/s}$ ,  $a \sim 400 \text{ g}$

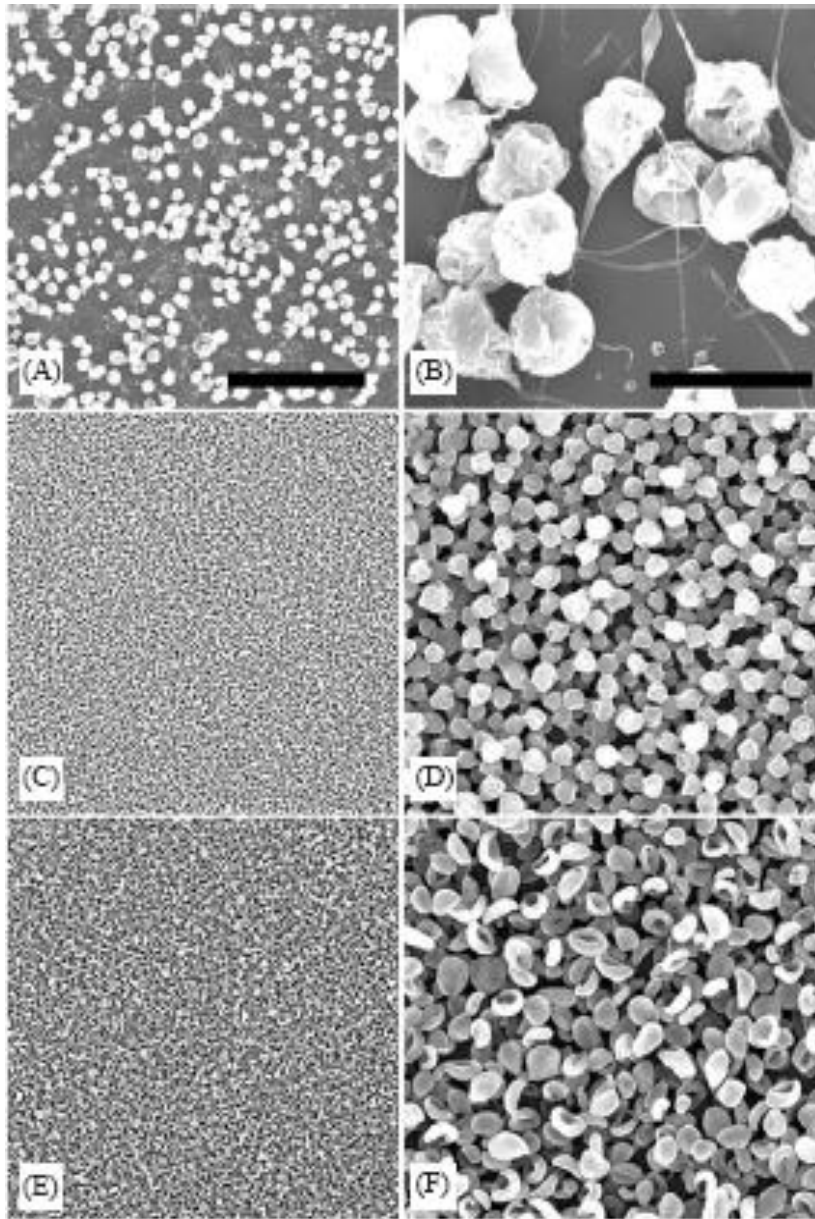


Microfiber



- The polymer solution is being pumped to the capillary → positively charged polymer solution with high charge densities
- At high applied voltages, the electrostatic repulsions is able to overcome the surface tension, resulting in expulsion of a jet (>10kV)

# Electrohydrodynamically Sprayed Nanoparticles

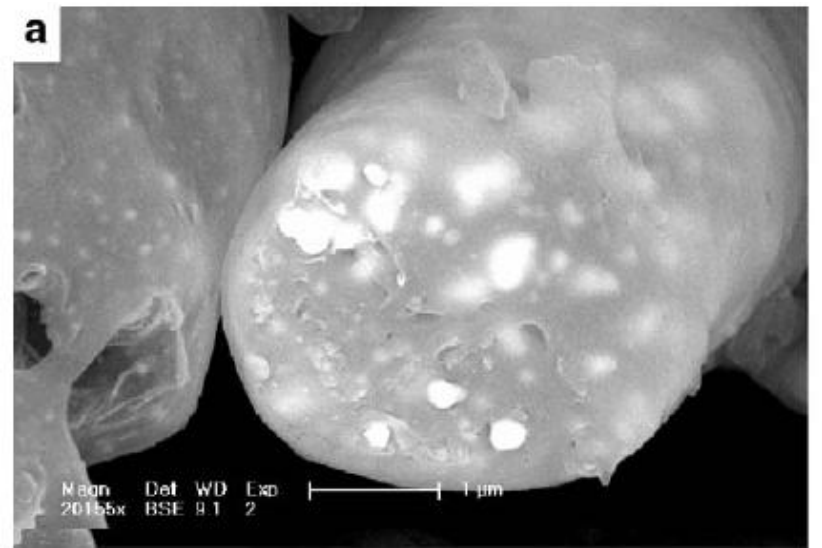
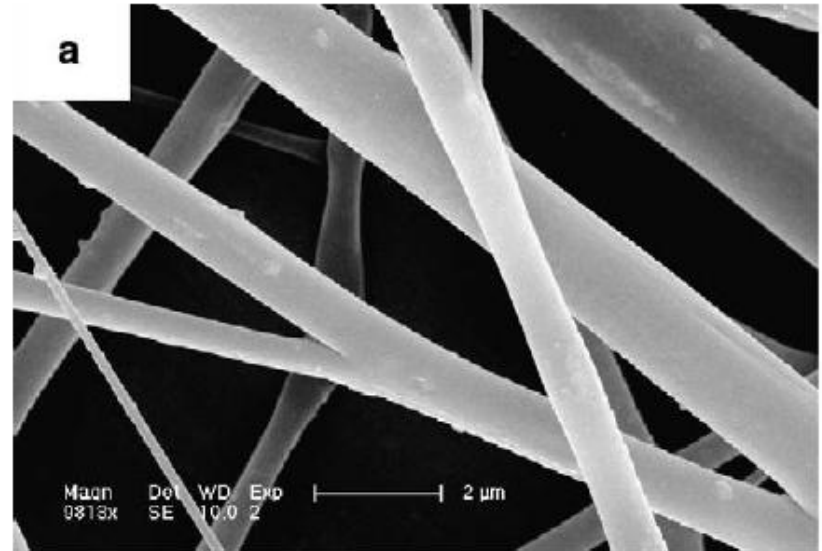
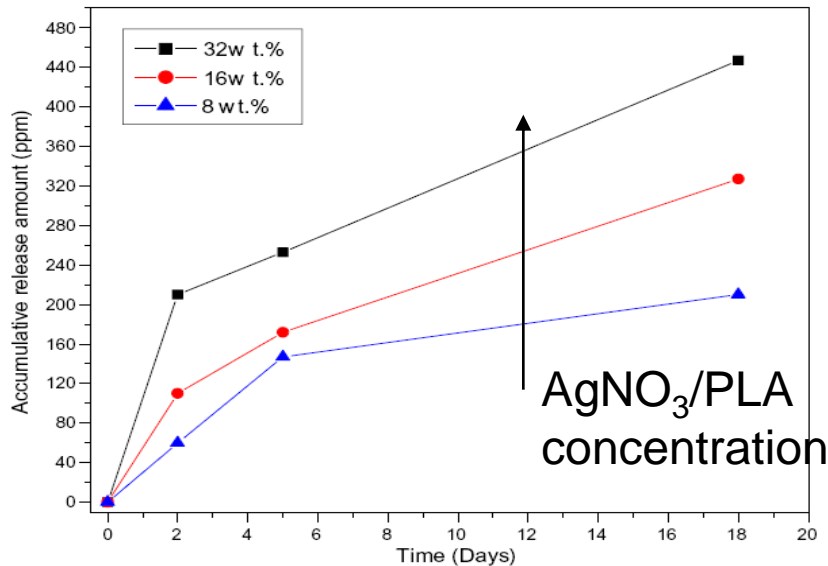


- Uniform particles produced under various conditions
- A & B: Uniform particles ~2.5  $\mu\text{m}$  by spraying 5 wt% PLG in acetone (8 kV)
- C & D, PLG in methylene chloride, 15kV
- E & F, PLG in acetonitrile, 10 kV,
- C,D,E,G approx. 80 – 200 nm in size

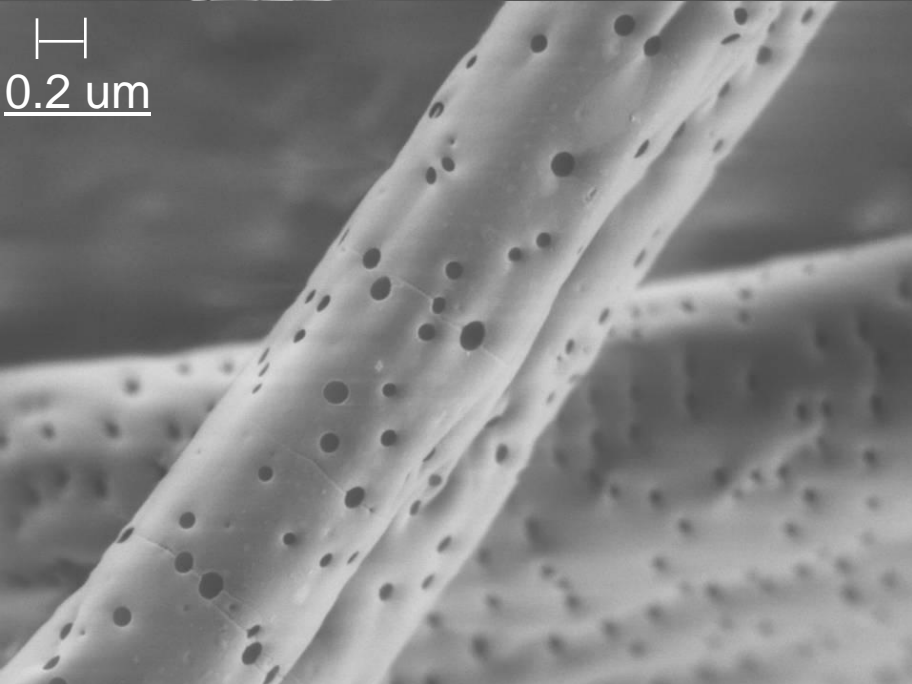
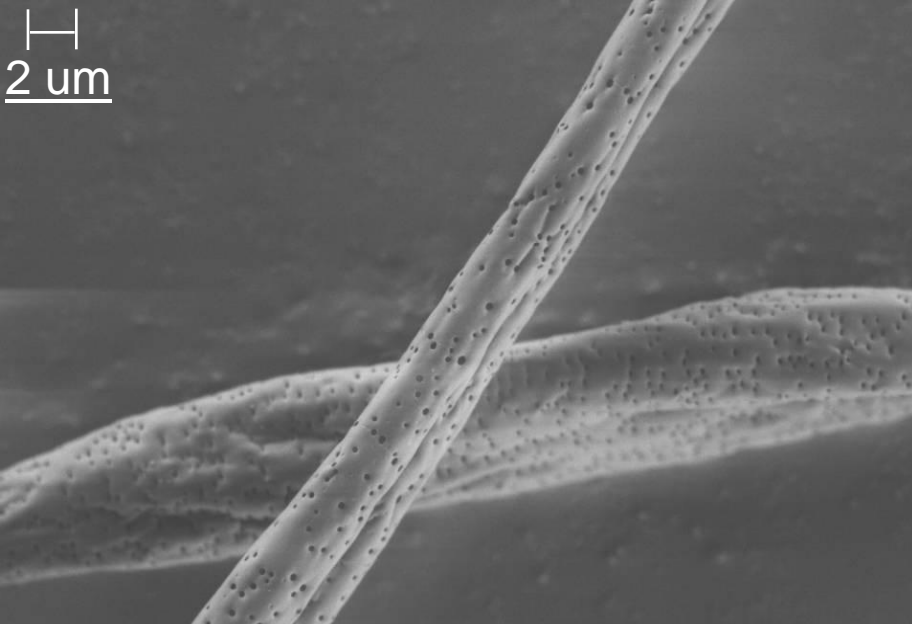
Berkland et al, 2004

# Silver Containing Fibers

- Biodegradable PLA fibers, containing silver nanoparticles
- High antimicrobial activity due to silver ion release



Xu et al, European Polymer Journal, 2006.

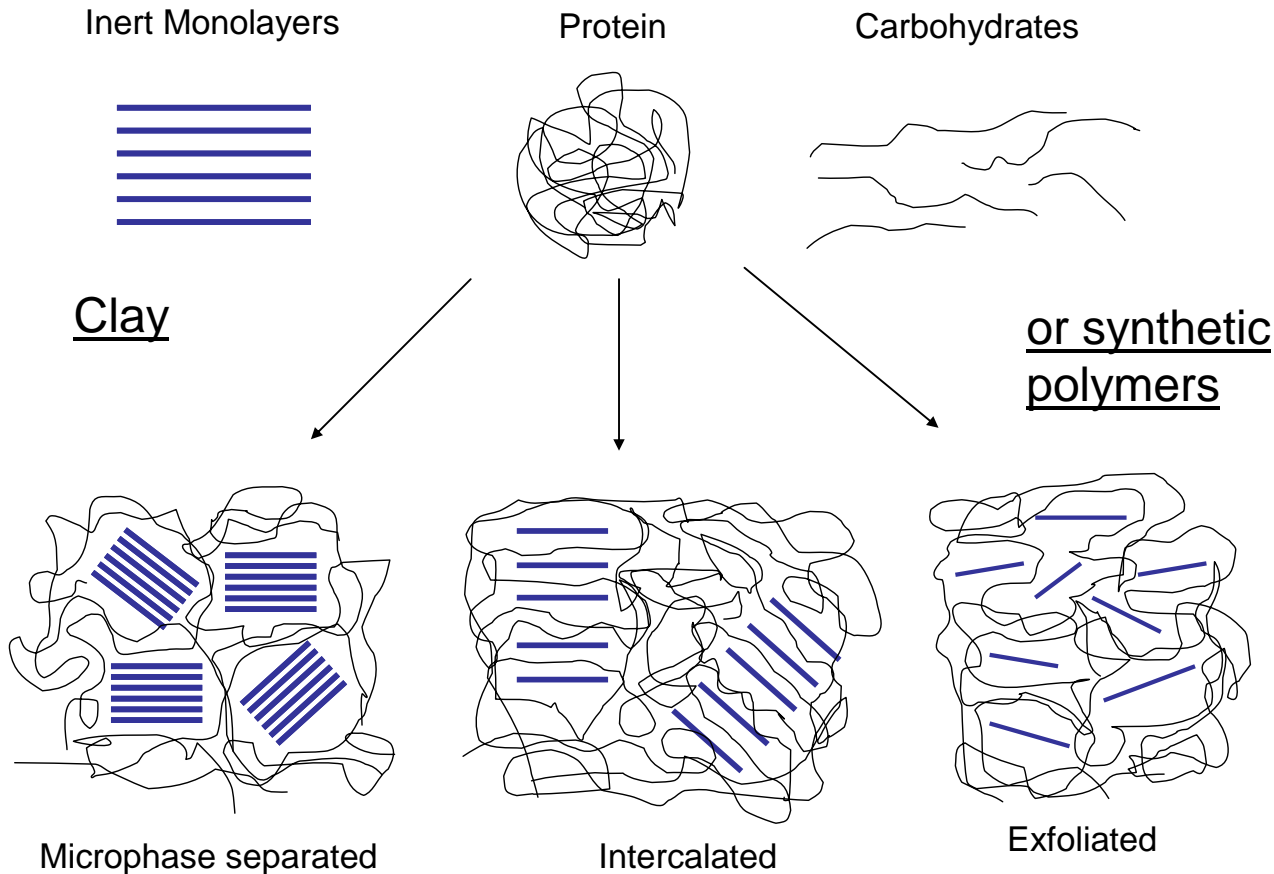


# Porous Nanofibers

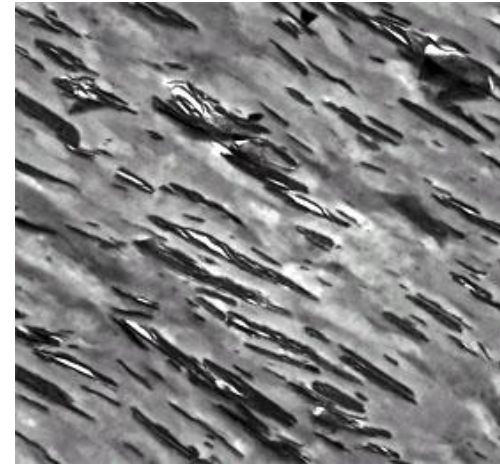
- Example: Polystyrene (collaboration with University of Tennessee)
- Under appropriate processing conditions, production of porous fibers possible
- Ideal materials for catalysis due to extremely high surface-volume ration and good mass transport
- Enzyme Immobilization



## II. Use of Nanostructures in Packaging: Nanoclay Composites



- Torturous Path
- Reduced O<sub>2</sub> and H<sub>2</sub>O transmission
- Microwavable
- Increased mechanical strength

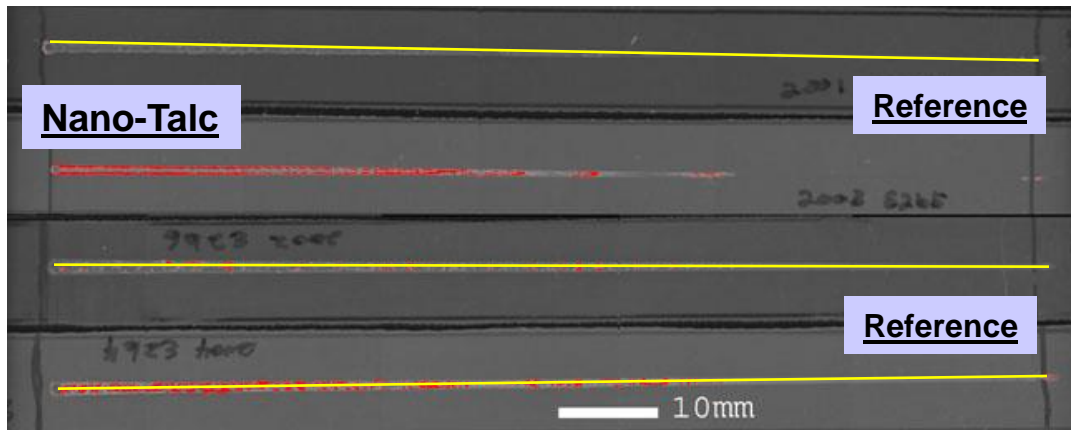


# Performance of Exfoliated Nanocomposite Packages

- Increased resistance to scratch and tear
- Increased resistance to high-temperature exposure – materials can be retorted
- *Difficulty:* chemical bonding of clay/particles to polymer matrix

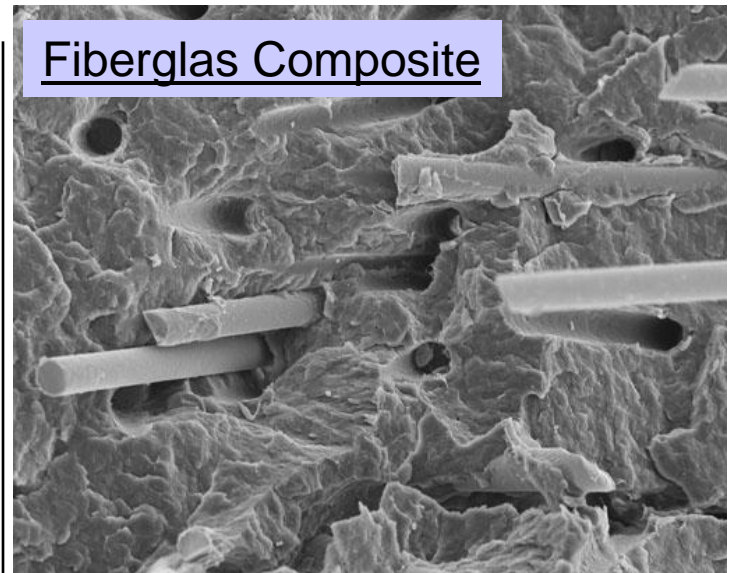
Scratch Test - Linear Load Increase at 100 mm/s

50N ← ————— → 5N



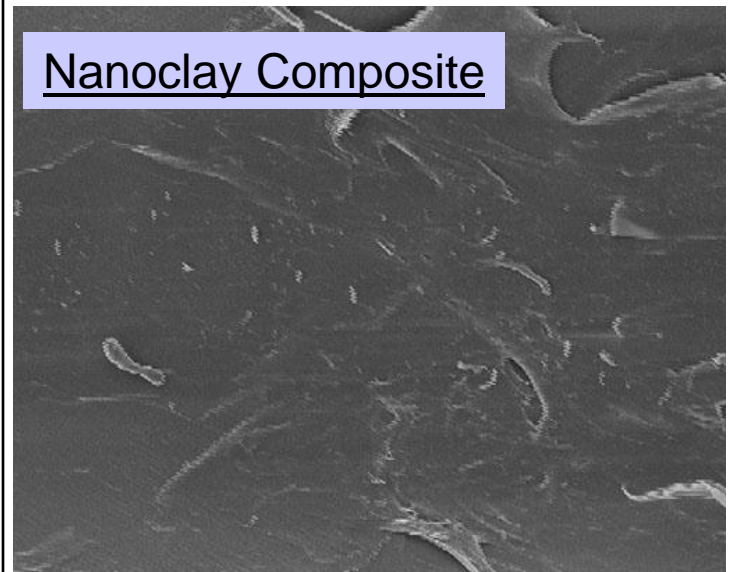
Scratch Direction ←

Fiberglass Composite



Surface after extensive stress testing

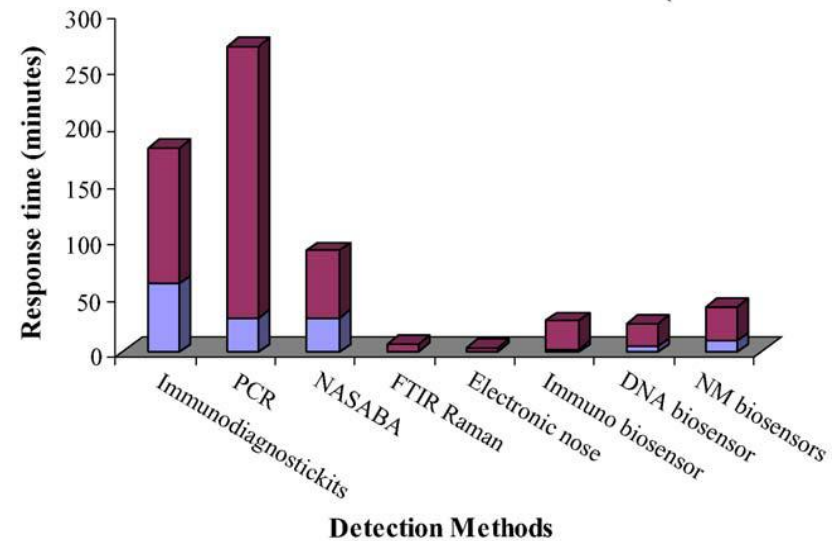
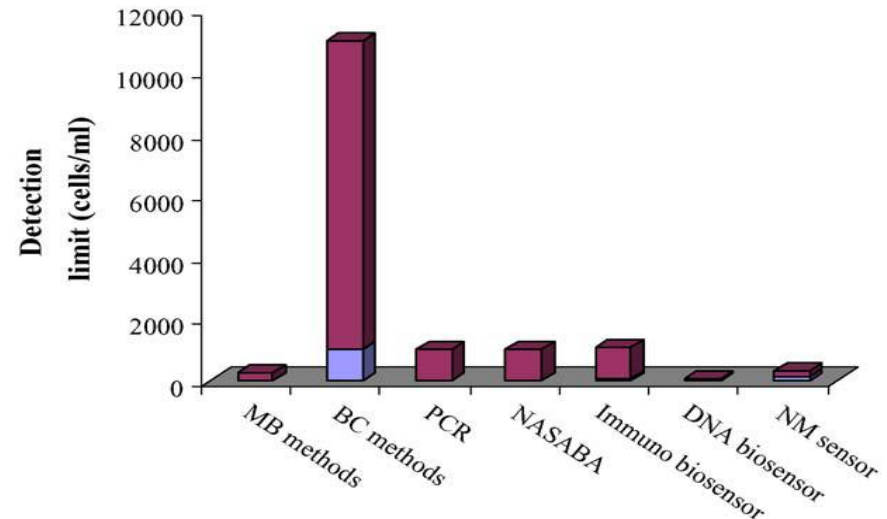
Nanoclay Composite



Courtesy Texas A&M, Mat. Science

# III. Use of Nanotech in Food Safety: Biomolecular Sensors for Food Pathogens

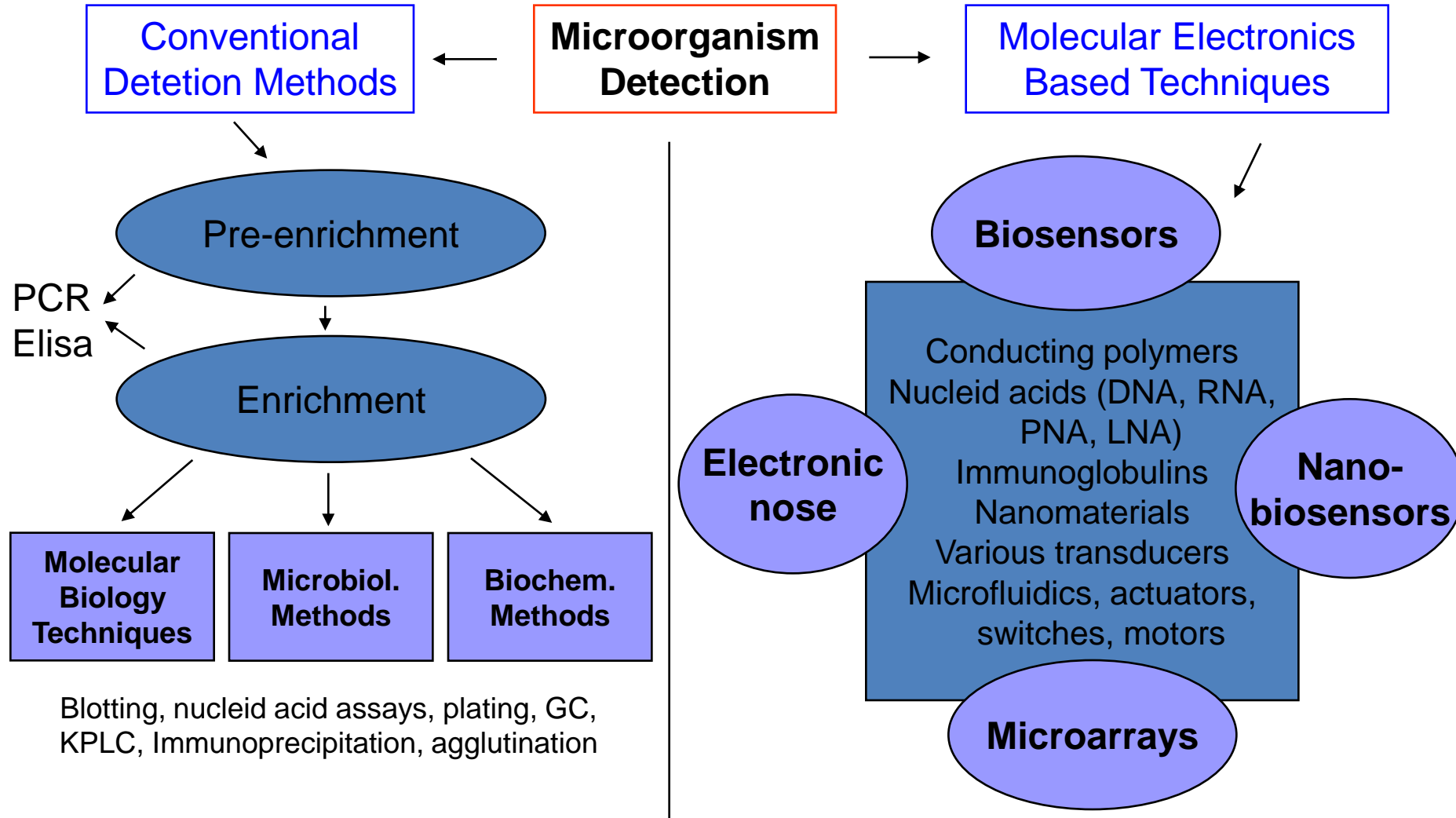
- Application of new materials:
  - Carbon, Au, Zn
  - Quantum Dots
  - Nanocomposites
  - Conducting polymers
  - Langmuir-Blodgett films
  - Self-assembled monolayers
  - Microfluidics
  - Molecular switches and gates
- Advantages:
  - Smaller size
  - Quicker response time (seconds to minutes)
  - Reusability
  - Portability
  - Multi-analyte detection
  - High sensitivity → 10 cells/0.1ml,  $10^{-2}$  cfu/ml,  $10^{-14}$ M oligos



# Pathogen Sensor Overview

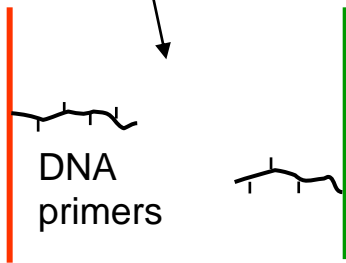
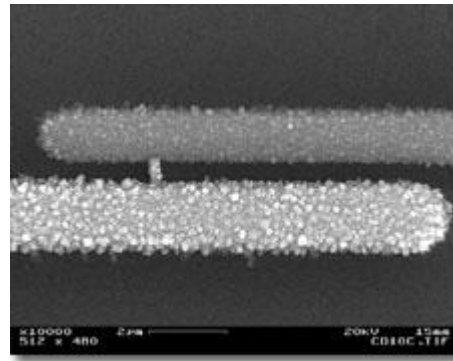
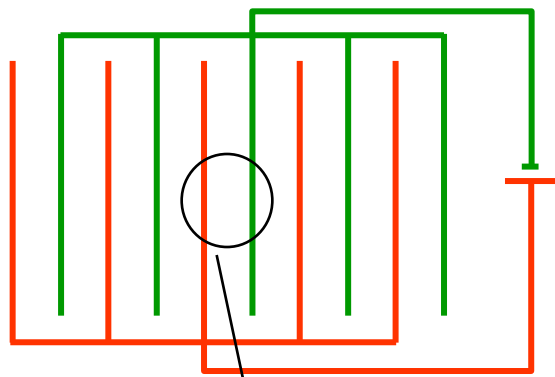
Hours to days

Seconds to minutes

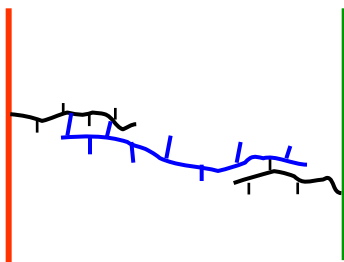




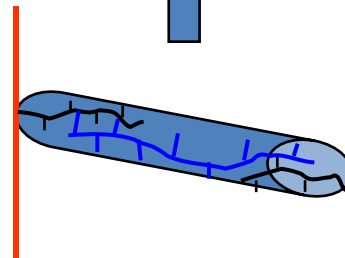
# Example: Single DNA Detection



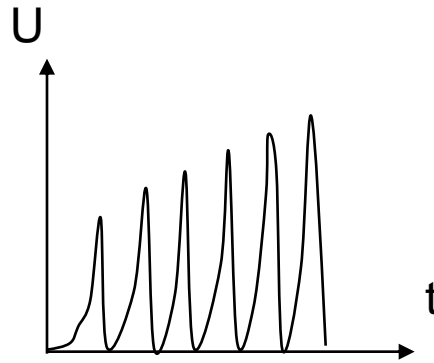
+ DNA sample



Metalization

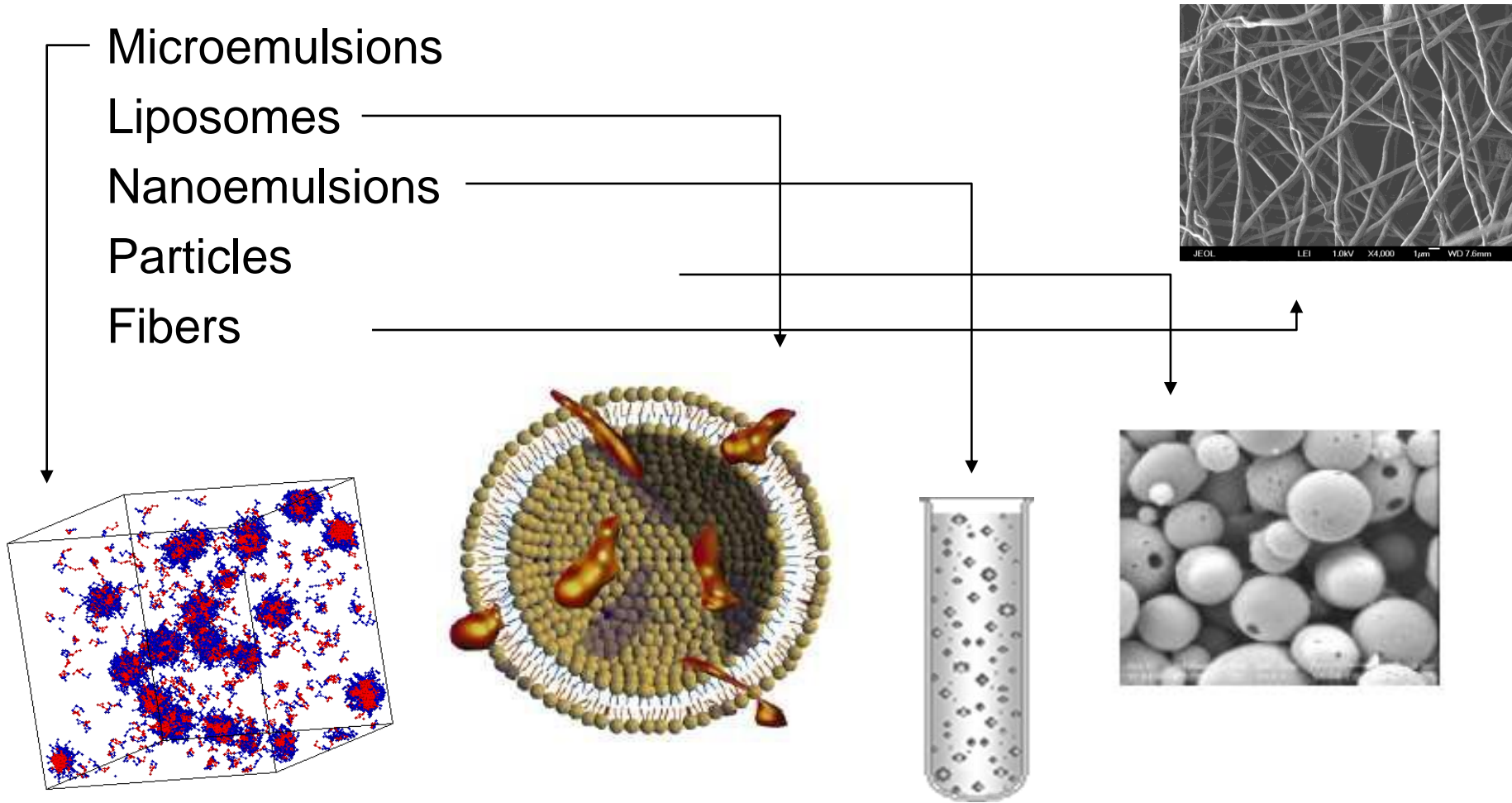


Decreased Resistance



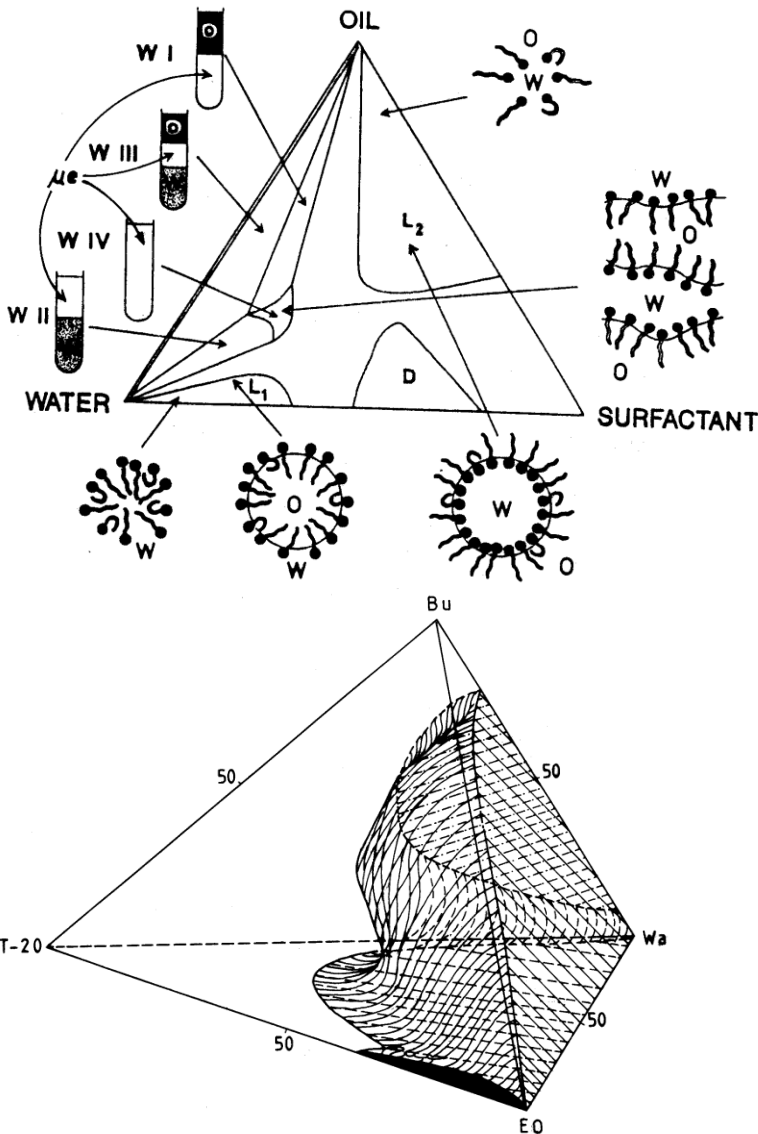
- Simple Test Kit Based on single DNA binding to primers
- DNA us coated with a conducting metal
- Resistance greatly decreases as bound & coated DNA can transmit electrons
- With increasing amperage, connection is severed → individual event
- Allows counting of DNA

# IV. Functional Ingredients From Nanostructures



# A. Microemulsions

- Microemulsions are 'thermodynamically stable'. In contrast to emulsions.
- They are isotropic solutions that are typically transparent
- Like emulsions, their stability can be influenced by addition of salt, other additives, temperature or pressure.
- Microemulsions can be prepared from milky emulsions by addition of short chain alkanols or by addition of oil to a mixed surfactant system.
- As such they are three or four component systems
  - Water/amphiphile/oil
  - Water/surfactant/co-surfactant/oil



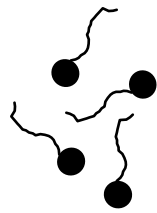
**Example of a ternary phase diagram of water-oil-surfactant mixtures**

Current Science, 2001, Vol. 80, pp.990-1002

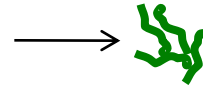
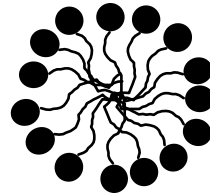
# Development of Microemulsions

1999-2003

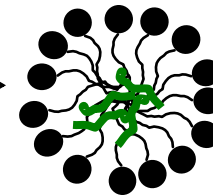
Nonionic  
Surfactant



Simple Micelle



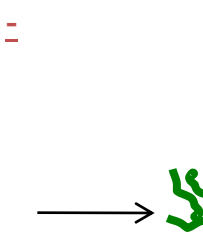
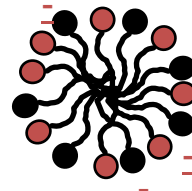
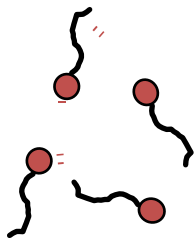
Lipid  
Antimicrobial



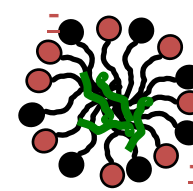
Simple Antimicrobial  
Microemulsion

2003-2006

Anionic  
Surfactant

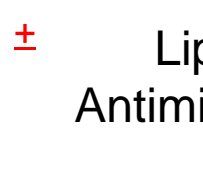
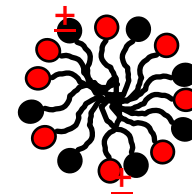
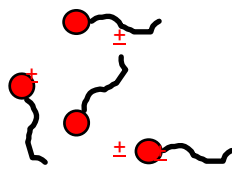


Lipid  
Antimicrobial

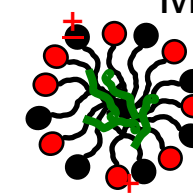


Binary  
Microemulsions

Cationic  
Surfactant



Lipid  
Antimicrobial



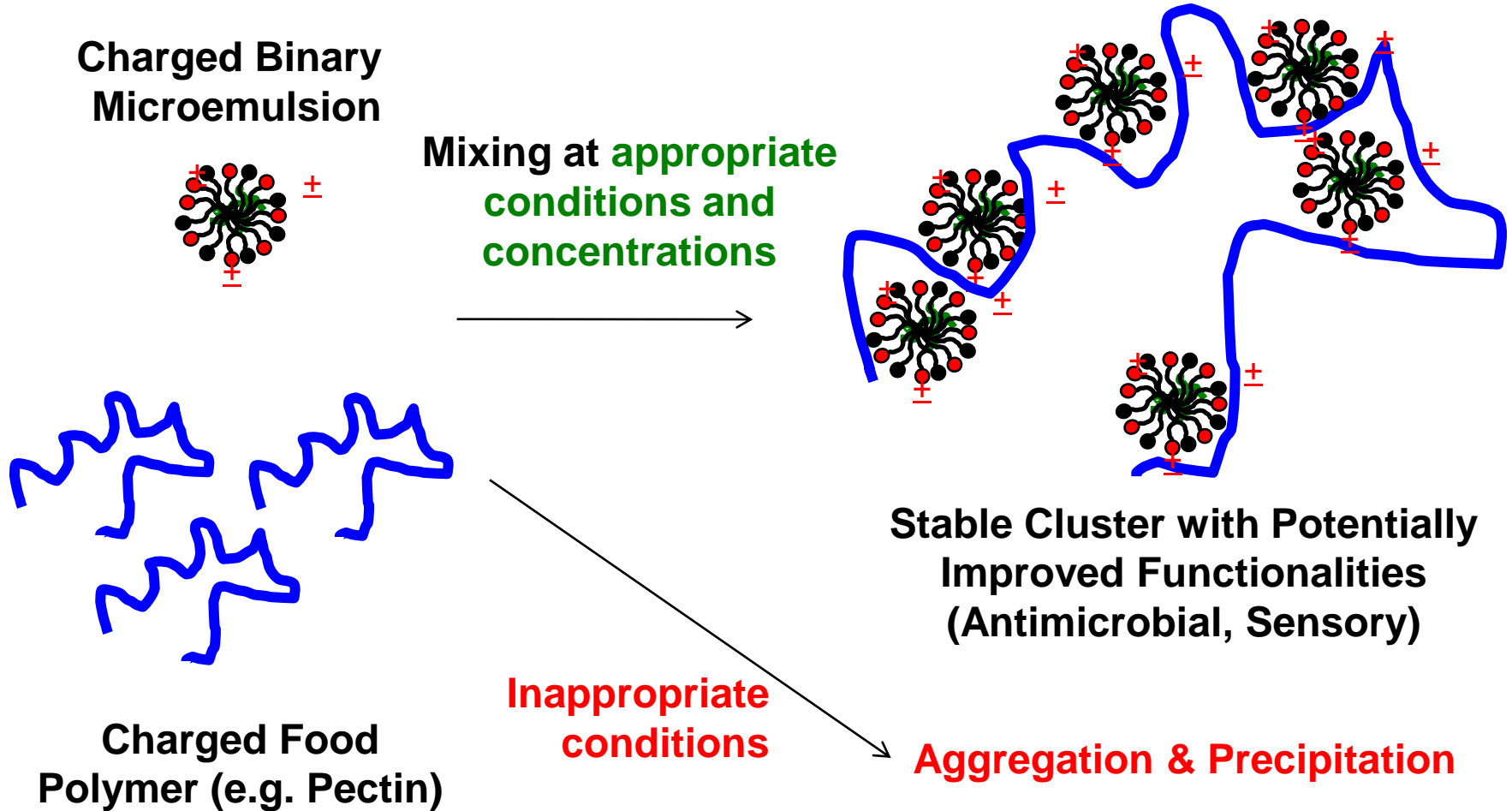
Binary Micelle  
(may already be antimicrobial)

2006-now

**May be DOUBLE !!!**



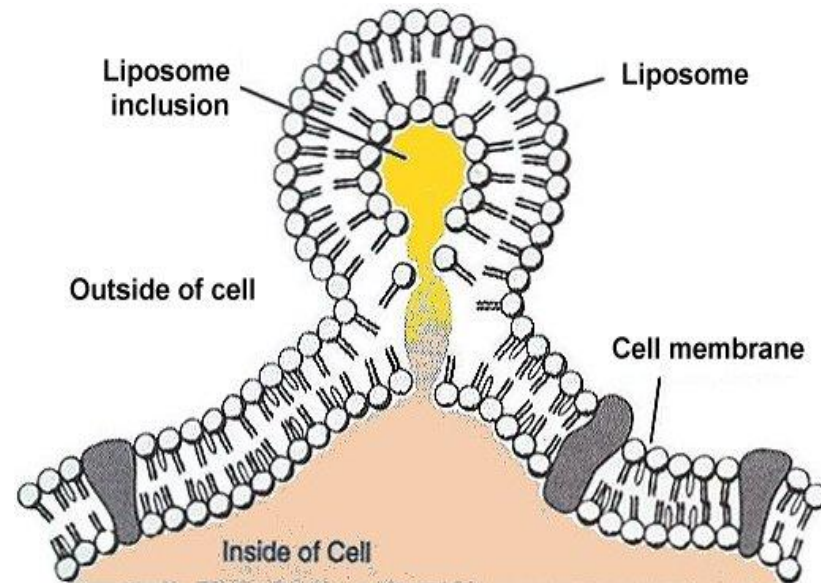
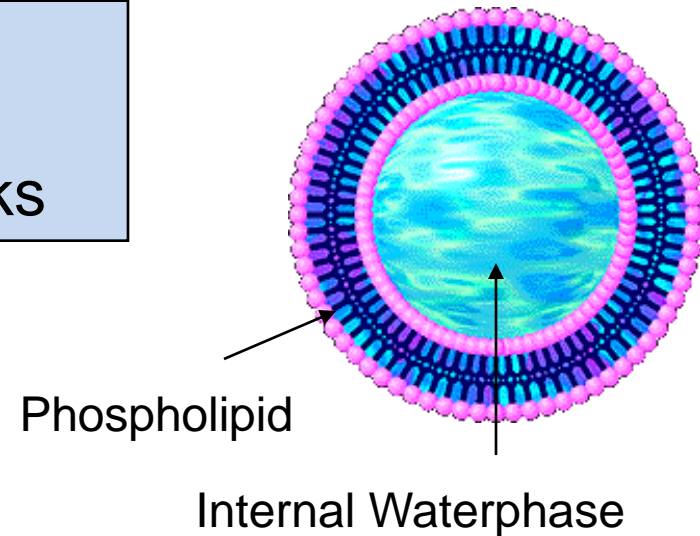
# On the Horizon: Formation of Microemulsion – Polymer Clusters



# B. Liposomes:

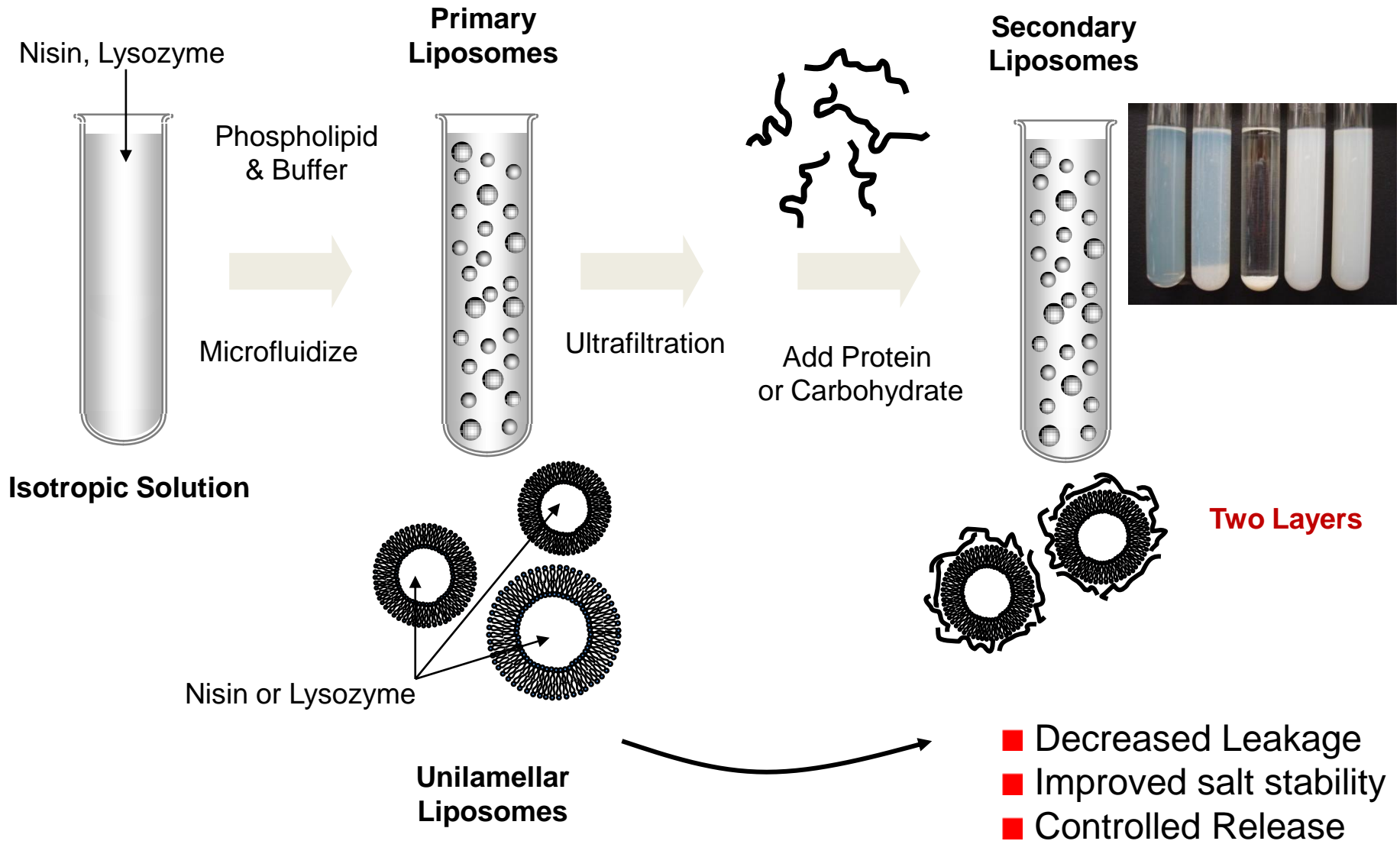
## Using Polar Lipids as Building Blocks

- Spherical membrane structure (bilayer)
- Base materials (phospholipids) widely available in nature
- Materials digestible
- Good interactions with cell membranes
- Internal pH und electrolyte concentrations adjustable
- Suitable for both lipophilic and hydrophilic compounds



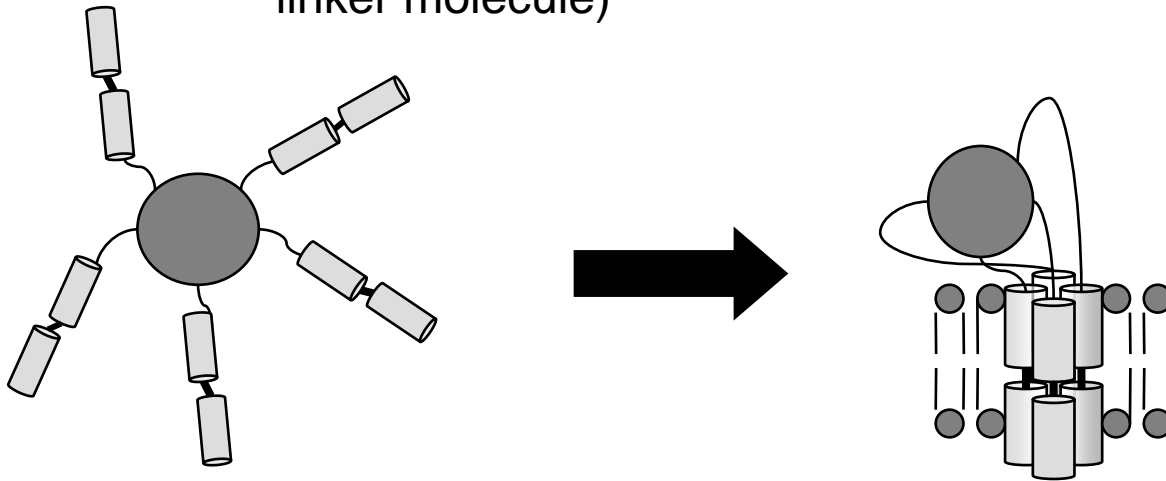
Acceptance of liposome into cell

# Double-Layered Liposomes

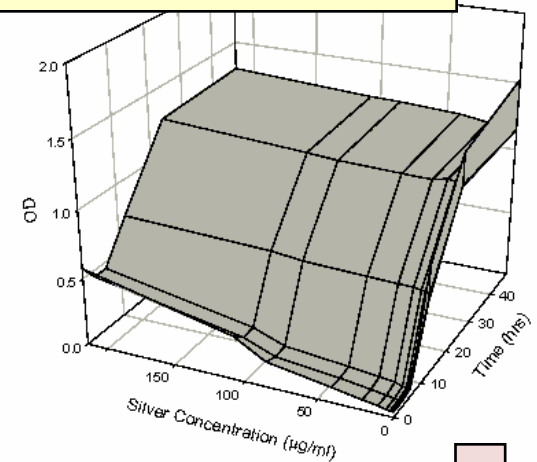


# C. Biopolymeric Nanoparticles as Ingredients

- Biopolymer Nanoparticles
  - Solid Particles with diameters < 100 nm
  - Basis of modern anti-cancer drug delivery systems
  - Extremely high bioactivity
  - Als carrier of antimicrobial components:
    - As part of the particle matrix structure
    - Adsorbed at the surface (direct oder via linker molecule)

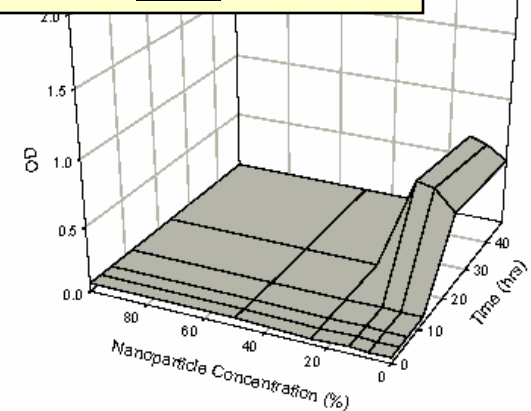


Activity against *E. coli* O157:H7 without nisin



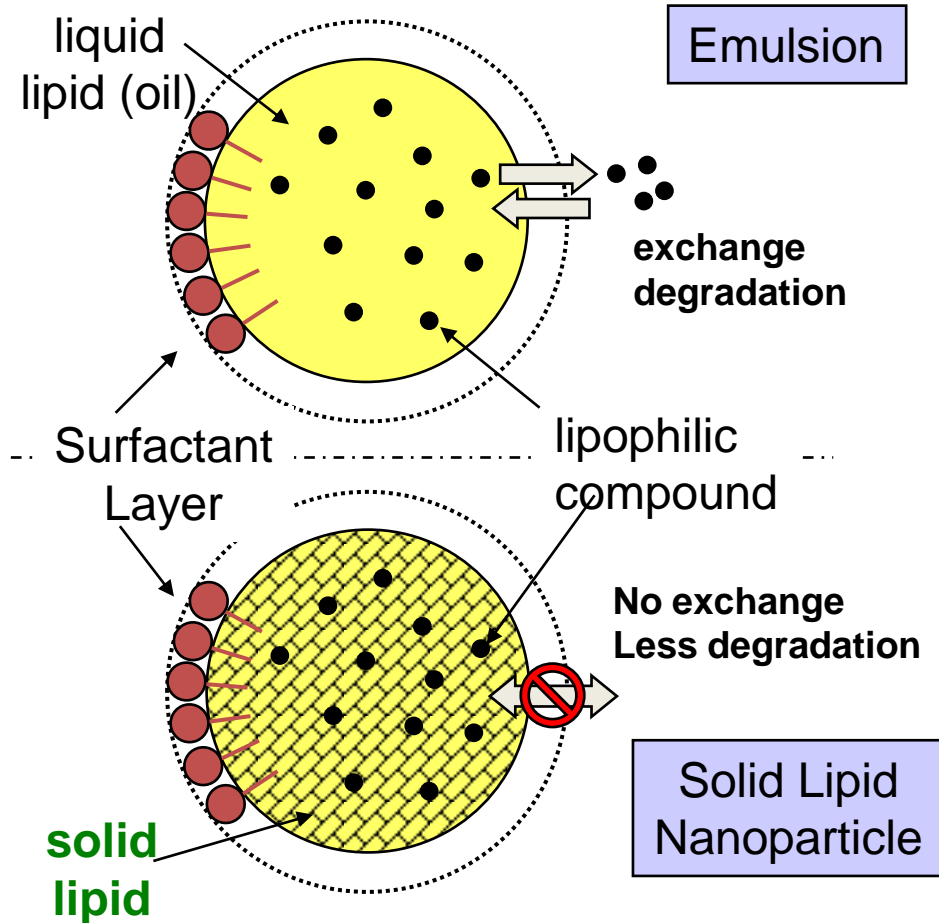
Addition of nisin

Activity against *E. coli* O157:H7 with nisin



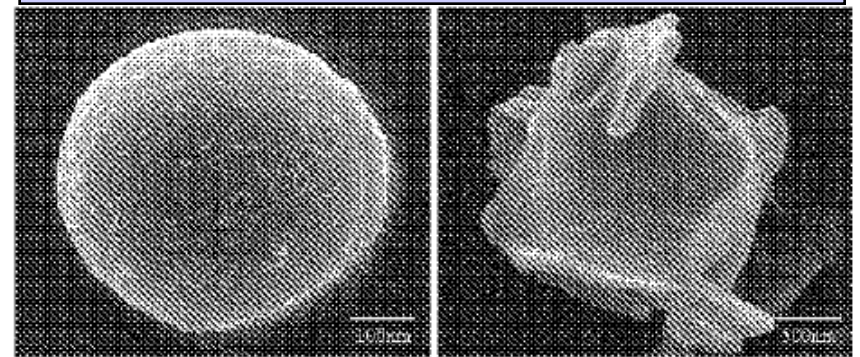


# D. "Solid Lipid Nanoparticles" (SLN)



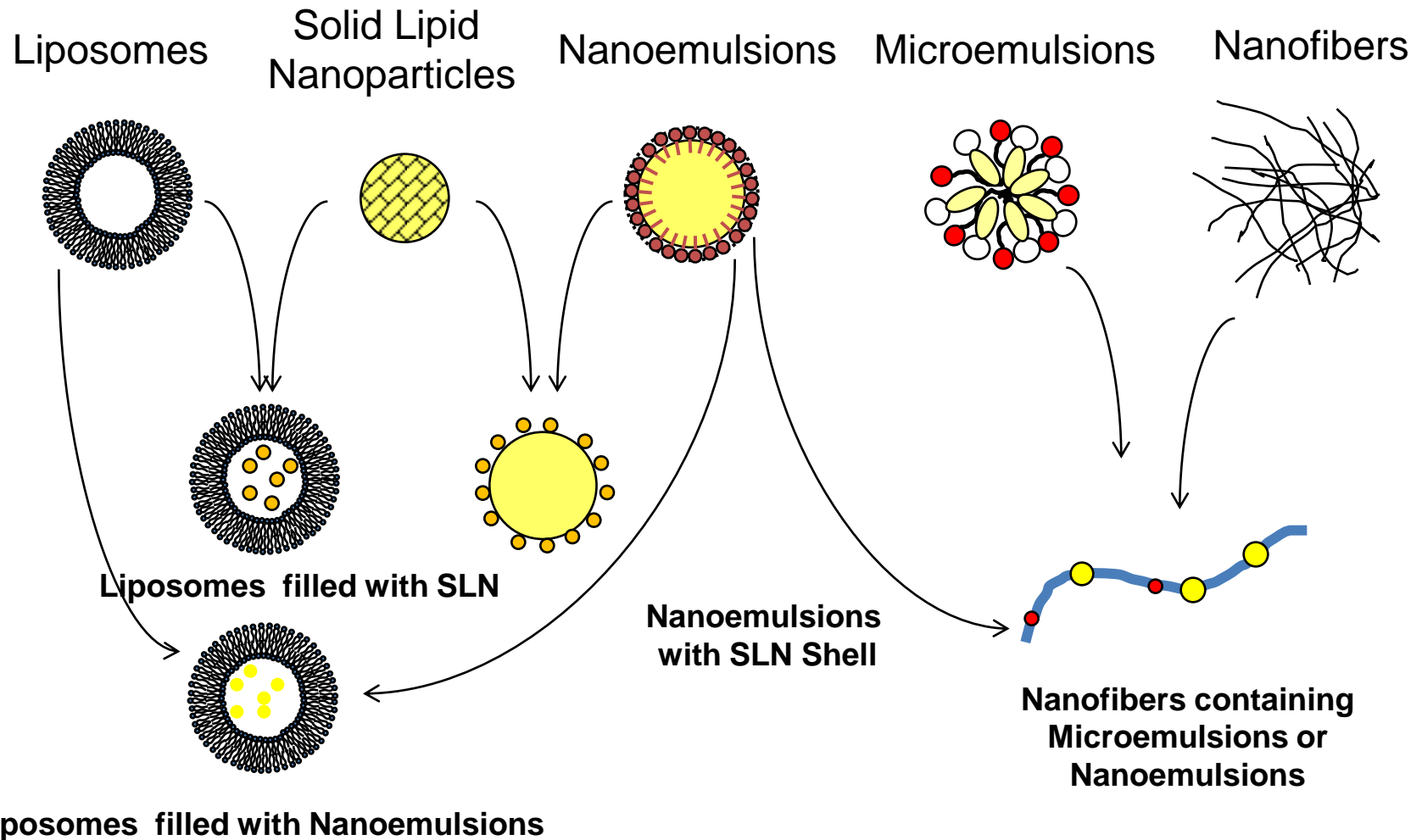
- Liquid lipid in emulsion is replaced by high melting point lipid
- Glycerides or waxes suitable
- Typical medium size ranges from 50 - 500 nm
- At small sizes, crystal structures become dependent on surfactant and size
- Highly effective carrier systems for susceptible bioactive ingredients

**TEM of SLN Preparation after 1 year storage**

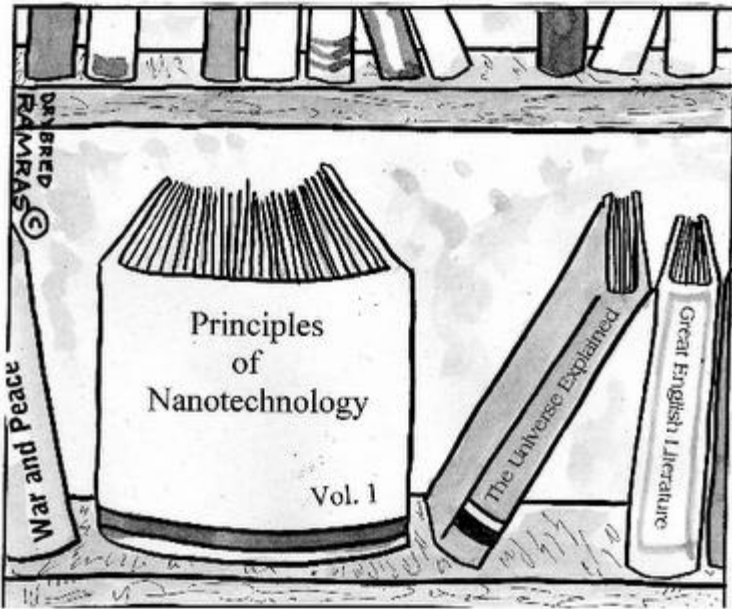


Dubes et al, European Journal of Pharmaceutics and Biopharmaceutics, 2003, Vol. 55, 279-282

# The Future of the Science: Playing Lego with Molecules - Composite Nanostructures -



# Implications for Stakeholders



How does this impact the consumer and what issues will we, the stakeholders, have to wrestle with?

# Implications for A World of Diminishing Resources & the Developing World



- Material production involves little labor and requires less energy due to the better use of natural processes → self-assembly or „assisted“ assembly
- Improved utilization of previously underutilized resources and materials to achieve known or new functionalities
- The skill/art lies in the initial design and construction of the functional structure, and less so in the actual process.
- BUT: thermal fluctuations can introduce some randomness at very small lengthscales



# Can Nanotechnology Bridge Consumer Demands and Diminishing Resources ?

- **Diminishing Resources:**

- **Energy Savings:** Nanofabrication processes can require less energy consumption than traditional processes → substantial energy savings
- **Waste Creation & Sustainability:** Material may be more effectively used and previously not utilized materials (due to performance issues) may be functionalized to be of use (e.g. wider use of cellulose based renewable materials).
- **Water Usage & Purification:** Improved methods for water purification, but probably little impact on overall usage

- **Consumer Demand:**

- **Healthier Foods:** Nanoencapsulation will be a key tool to include bioactive ingredients in foods, new structures may also simulate performance of “less healthy” ingredients (e.g. fat reduction, replacement)
- **Safer Foods:** Food safety may be enhanced through better detection methods (see later)



**Nanotechnology offers a technological approach to address rising consumer demand while having diminishing resources !**

# The Big Issue Though .....

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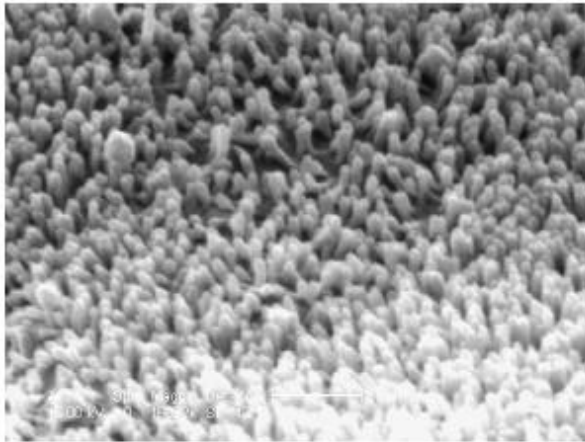


"If you increase the magnification another million times you can see the safety regulations."

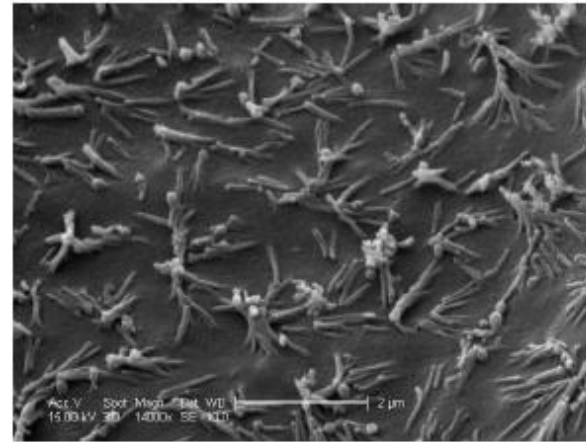
- Initially - Development driven by scientists excited about the new field of science → not user driven
- Relatively rapid (maybe too rapid) uptake by some industries (not the food industry though)
- Very little **communication** to the user:
  - Benefits not clearly addressed – Is this good for the user or good for the company (it should be both)
  - Risks not properly assessed
  - Boundaries between old and new blurred → when is it nano and when is it not

# This is what's scaring people..

## SEM Image of Microvilli After 24h Exposure



Control



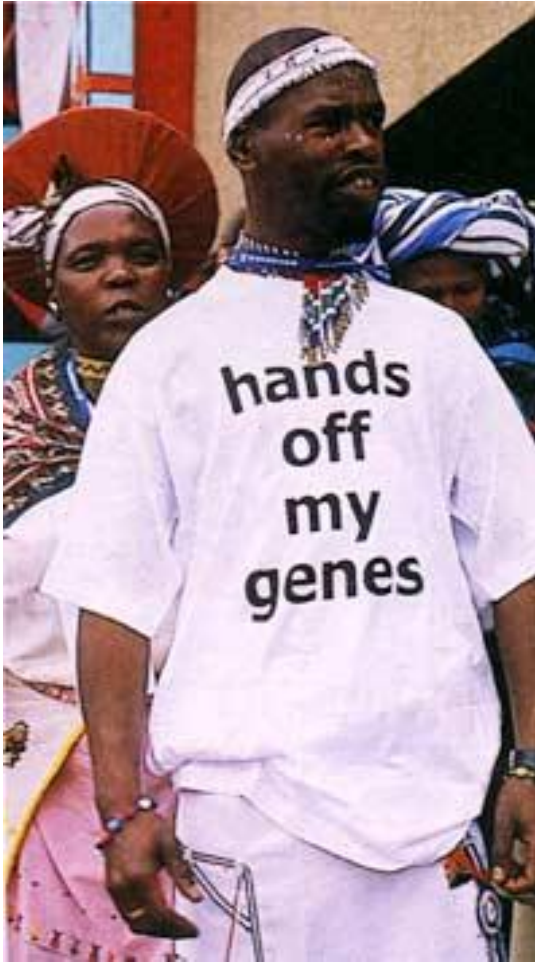
1000 ppm TiO<sub>2</sub>

TiO<sub>2</sub> flatten down the microvilli of cells

**Zhang *et al.*, 2007**

Changes in surface properties of CaCo2 cells after exposure to TiO<sub>2</sub> nanoparticles (40 nm)

# Technology Backlash Looms Large

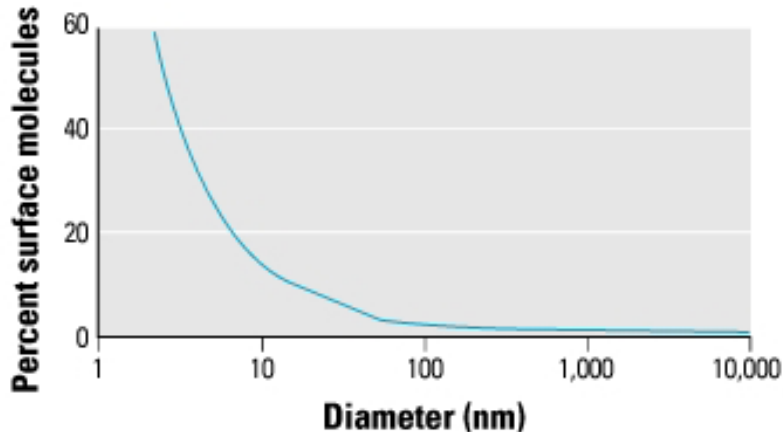


- Extremely high risk of repeating the mistakes of the biotech revolution
- New science was used to create new products without consumer input
- Pace was too rapid and not all stakeholders were at the same table
- **Risks and benefits** MUST be clearly communicated to the user
- Companies must weigh which of the exciting developments coming out of academia are acceptable and desirable to their customers (driver should not be cost cutting)

Need much more joint activities of all stakeholders, e.g. development based on clear consumer input → the science becomes part of the solution and not the problem



# The Issue of Risk ...



**Figure 2.** Surface molecules as a function of particle size. Surface molecules increase exponentially when particle size decreases < 100 nm, reflecting the importance of surface area for increased chemical and biologic activity of NSPs. The increased biologic activity can be positive and desirable (e.g., antioxidant activity, carrier capacity for therapeutics, penetration of cellular barriers), negative and undesirable (e.g., toxicity, induction of oxidative stress or of cellular dysfunction), or a mix of both. Figure courtesy of H. Fissan (personal communication).

**Are nanomaterials safe?  
How do we make applications of nanotechnology for foods safe?  
How do we test the safety of food applications of nanotechnology?**

*“It is a mistake for someone to say nanoparticles are safe, and it is a mistake to say nanoparticles are dangerous. They are probably going to be somewhere in the middle, and it will depend very much on the specifics.”*

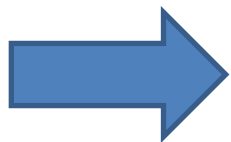
Vicki Colvin, Director of Center for Biological and Environmental Nanotechnology at Rice University (quoted in *Technology Review*, 2003)



# Need to Establish Clear Guidelines

- Open Questions:

- Size versus composition!!!
- Differences between inorganic and organic (edible) nanomaterials
- Differences between route: olfactory transport, dermal penetration → suitability of cell models??
- The issue of the food matrix...



This will be the focus of next years as users will demand answers to these questions!!

# Conclusions

- Rapid pace of developments in the food nanotechnology
- Transfer of nanoscience and technology to food and packaging systems led to emergence of food nanotechnology
- New science enables formulation of new food applications → significant increase in number of patents
- Driven by beneficial properties of products:
  - Improved safety/quality and health benefits (bioactives)
  - Reduced environmental impact (packaging)
  - Reduced cost and increased efficiency → has acceptance dangers
- Efforts broadening from basic research in academic institutions to applied research in companies
- BUT: much greater need to increase involvement of industry, governmental and consumer organizations → needs to happen immediately and will be the major focus of the next 10-15 years while new applications are being developed.