Opportunities and Applications of Nanoparticles

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Nanoparticles

Good and bad

- New functionalities ie: luminescence, superparamagnetic free radical scavengers
- Building block for new materials
- Small size allows them to reach parts others cannot!

- Unknown effects on living cells
- Very bouyant in air
- More widely distributed than realised
- Difficult to keep in the nanoparticle form (agglomeration)

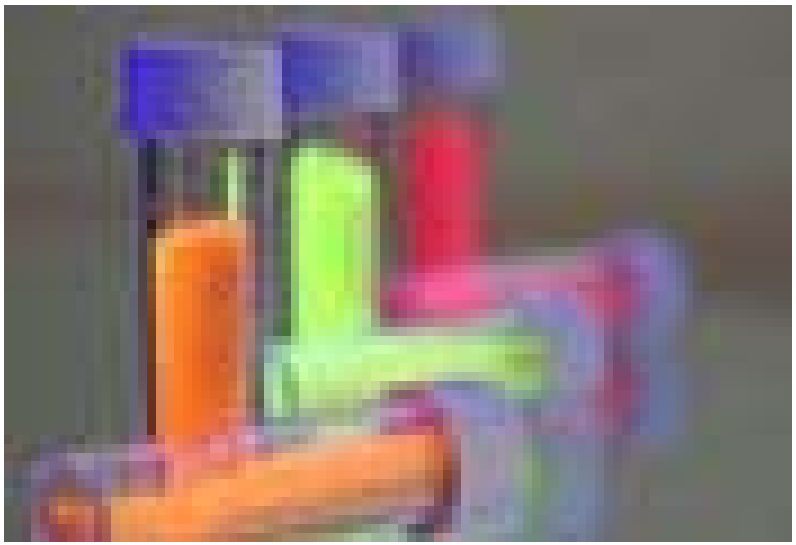
At what sizes do “size effects” matter?

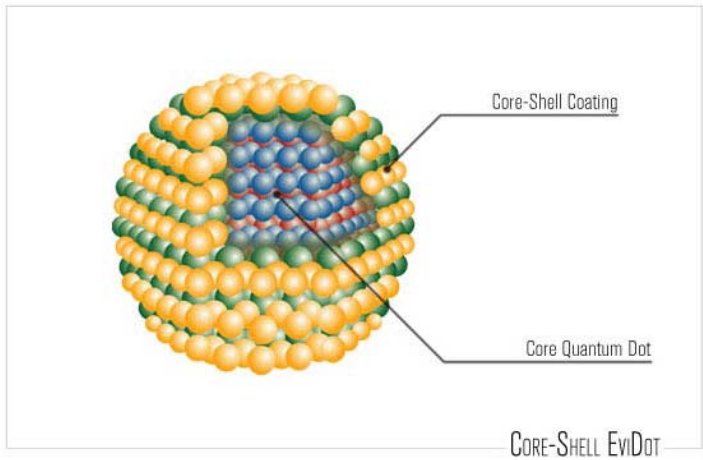
- Below 15 nm the electronic properties start to differ: new colours, luminescence etc…
- Below 5nm more than 30% of atoms are at the surface: new catalysts, very reactive.
- These two effects mean that the chemical behaviour differs: redox chemistry changed…
- Collective electron effects in small metal particles dominate optical properties <50nm: coloured glass, surface plasmons…
- Magnetic properties differ below 10-20 nm: superparamagnetic, implications for MRI….
- “Cluster Molecules” eg C60

Nanoparticle “Science”

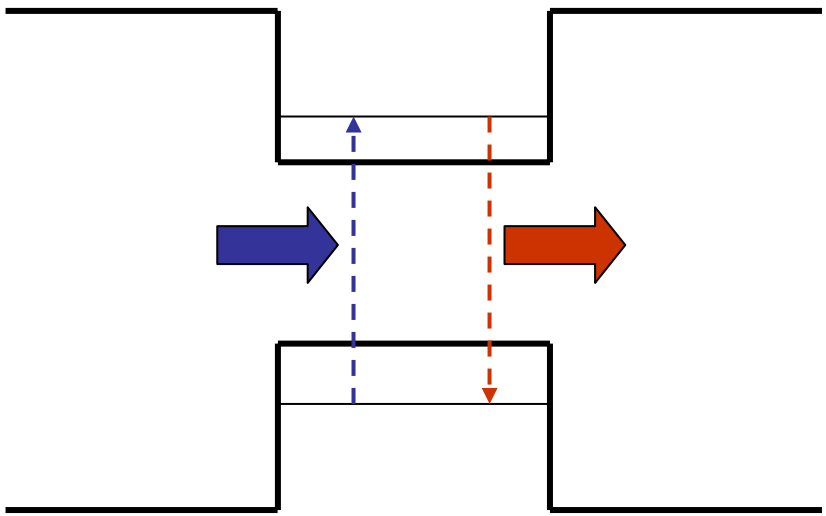
- Much is known about the changed properties of materials when in nanoparticle form
- New physical properties, different “colour” different electronic behaviour
- New chemical properties, large surface area per unit weight
- Catalytic behaviour enhanced

Quantum dots, small semiconductor particles < 10nm





These particles have an energy gap that is size dependent. The smaller ones emit light in the blue, larger ones in the red.

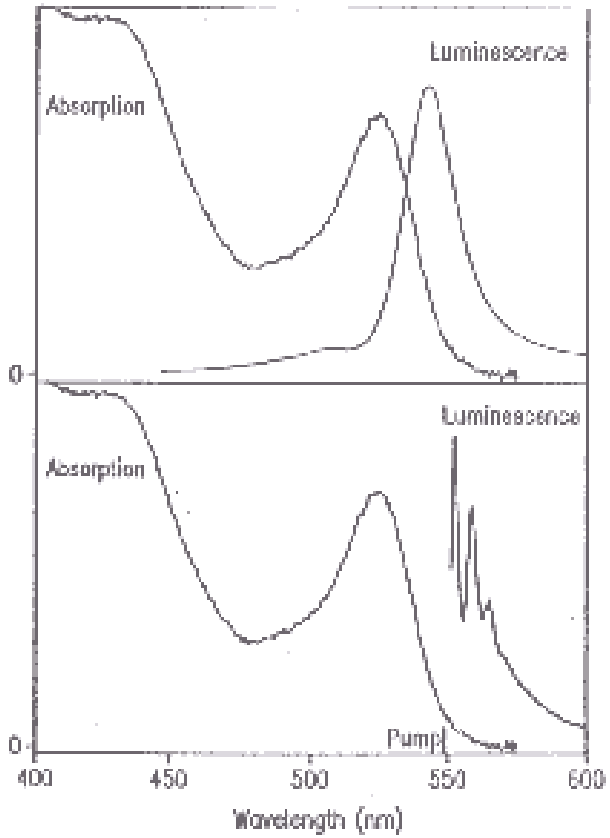


Optical absorption and emission spectra of CdSe quantum dots

Excitation of the luminescence at 440nm.

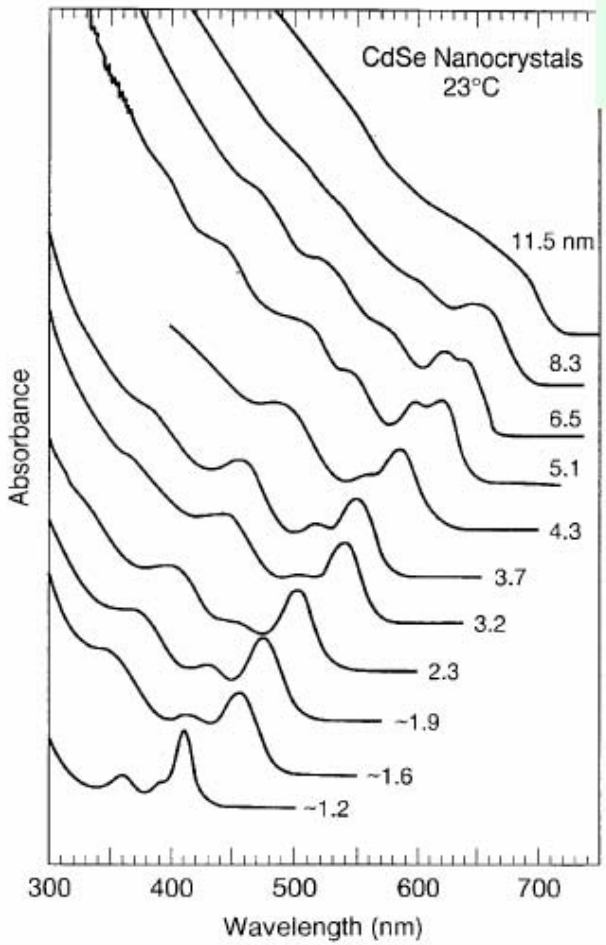
All sizes are excited

Excitation at 550nm for size selection, ie: only the larger particles are excited. Note the sharp lines and phonon features.



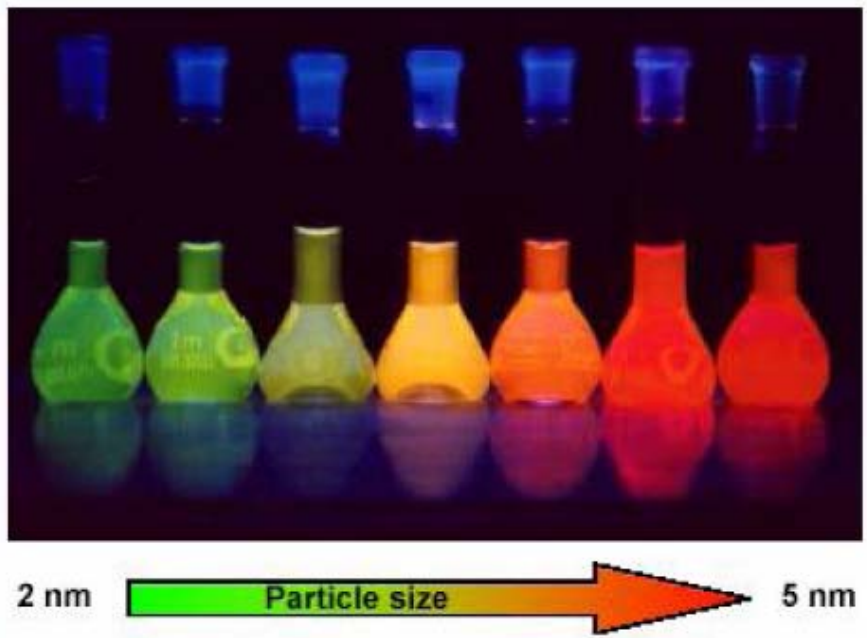
Bawendi et al J Chem Phys **96**, 946, (1992)

Optical properties of chemically prepared nanoparticles



absorption of CdSe-nanoparticles

emission of CdSe nanoparticles of different size



EviFluor Quantum Dot Conjugates

Quantum Dots Conjugated to Secondary Antibodies and Proteins

EviFluors are activated quantum dots coupled to proteins or secondary antibodies. EviFluors possess unique optical properties, enabling novel methods for life science researchers and developers to create new assays, diagnostic tools, products, or even enter new markets.

EviFluors are built upon **Evident's** wide range of prorietary molecular plated EviDot and EviTag technologies. EviFluors are antbodies conjugated to our PEG [Polyethylene glycol] lipid EviTags. Available EviFluors include Goat anti-Rabbit, Goat anti-Rat, Goat anti-Mouse, Streptavidin and Biotin.

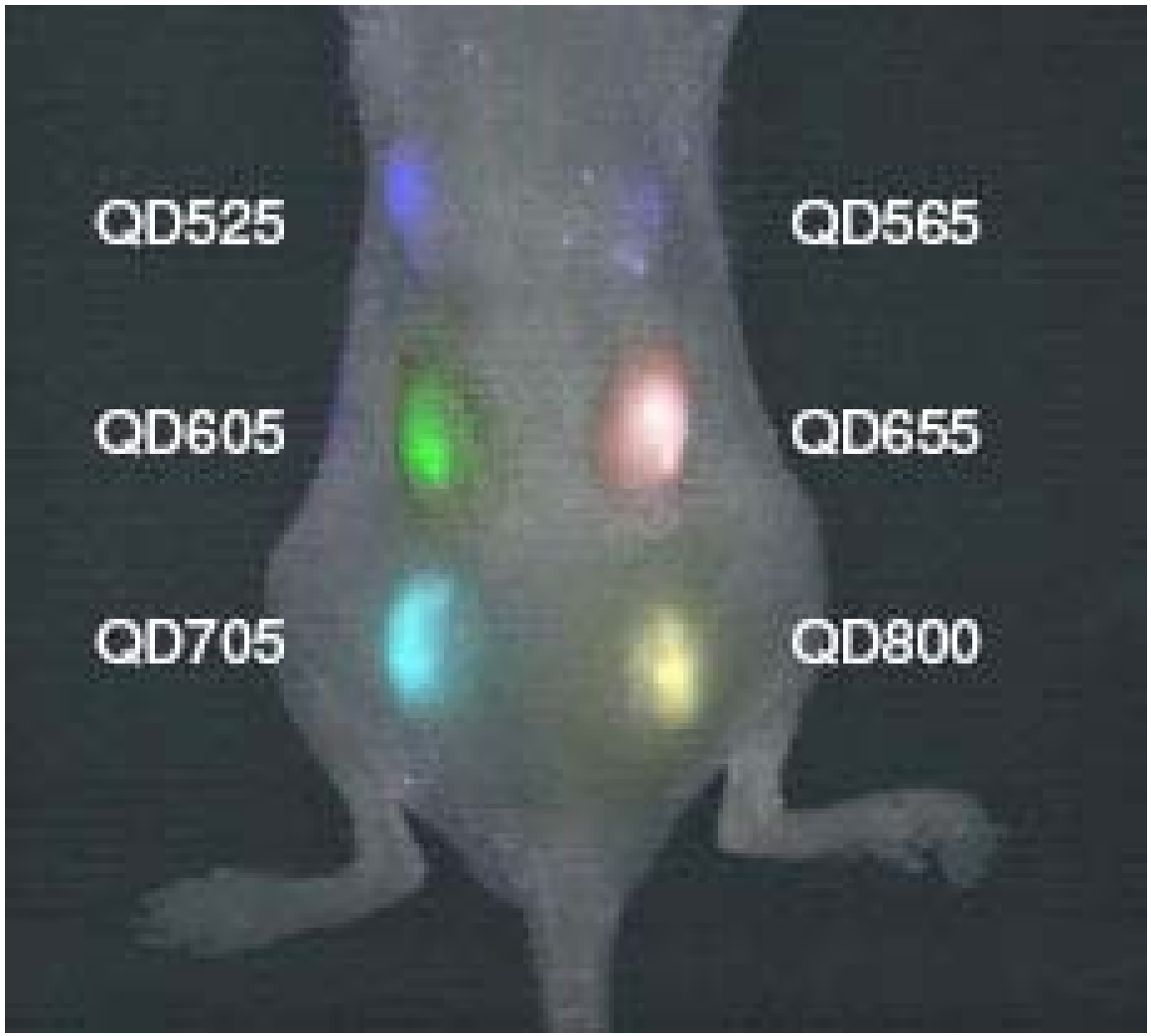
http://www.evidenttech.com/

Quantum dot bio-labelling

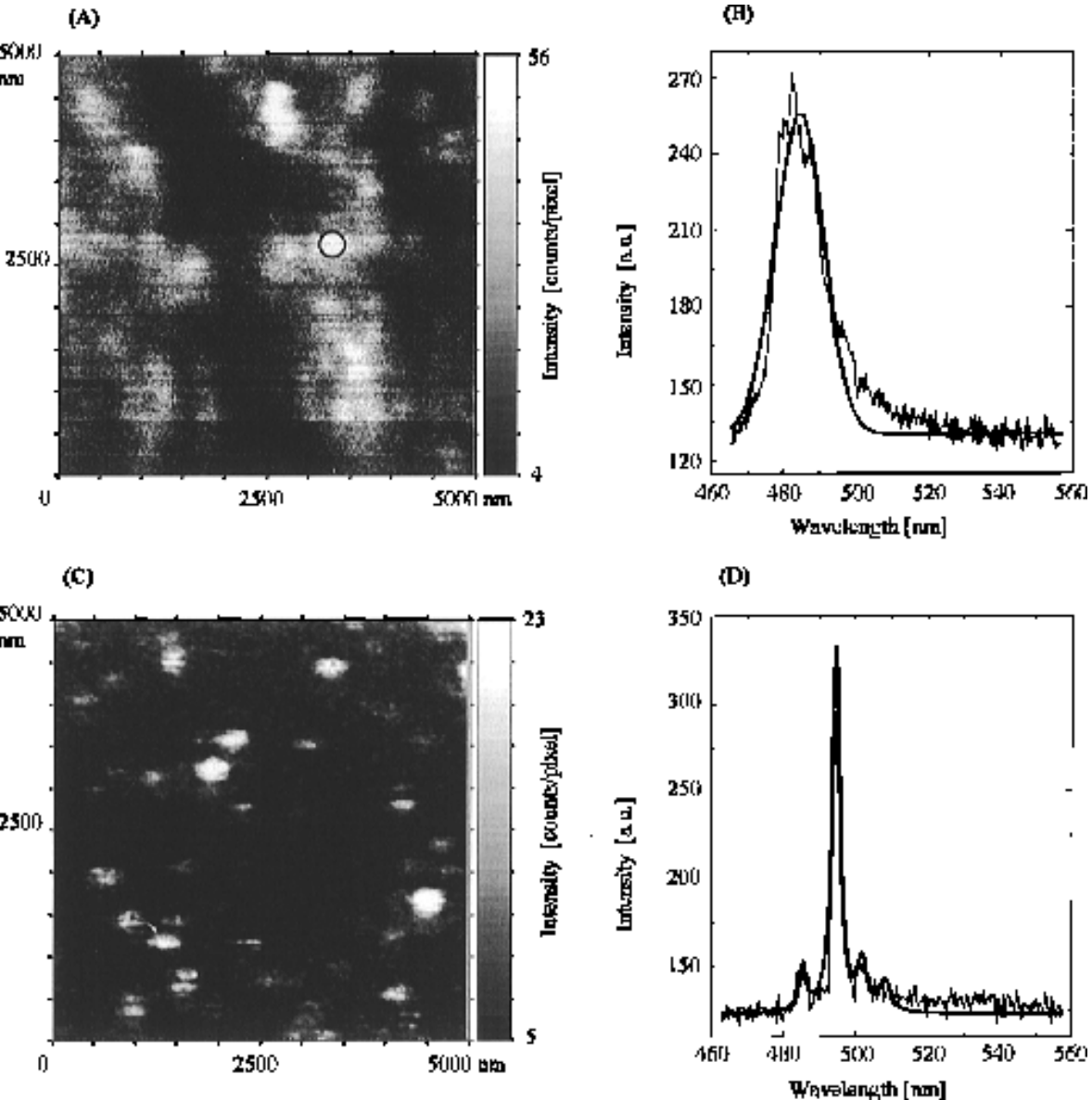
This example shows different stem cells labelled with different coloured quantum dots.

Wu et al 2007

http://www.nanowerk.com/spotlight/spotid=2933.php



Luminescence from single quantum dots



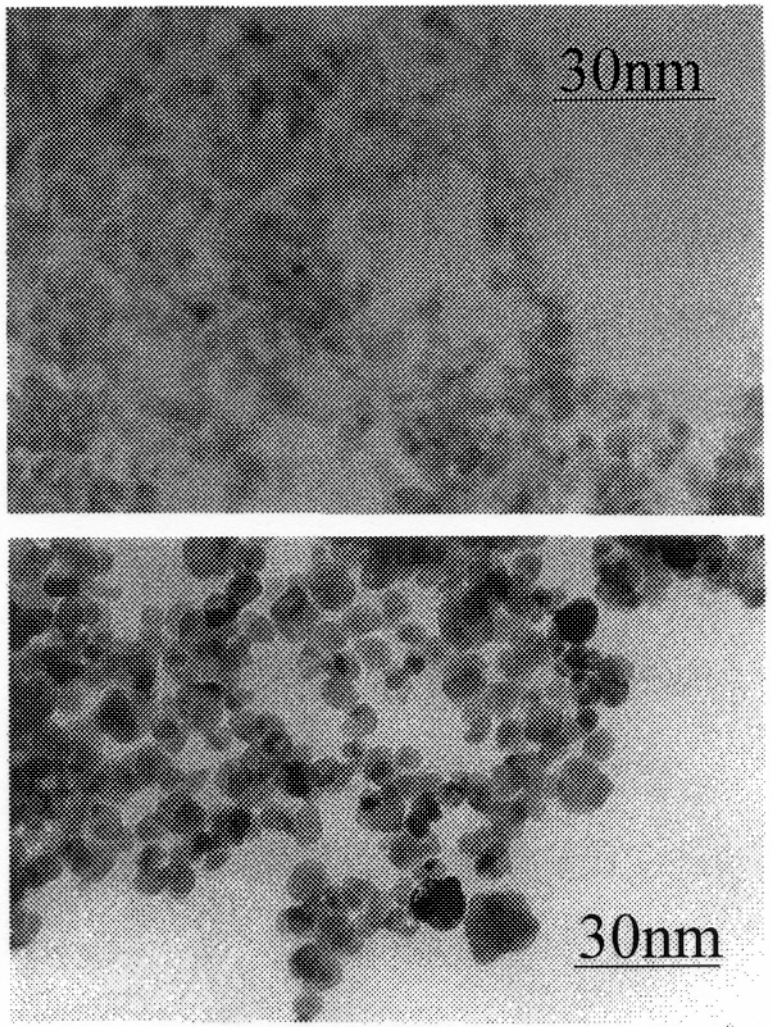
Tittel et al: J Phys Chem B **101** 3013 (1997)

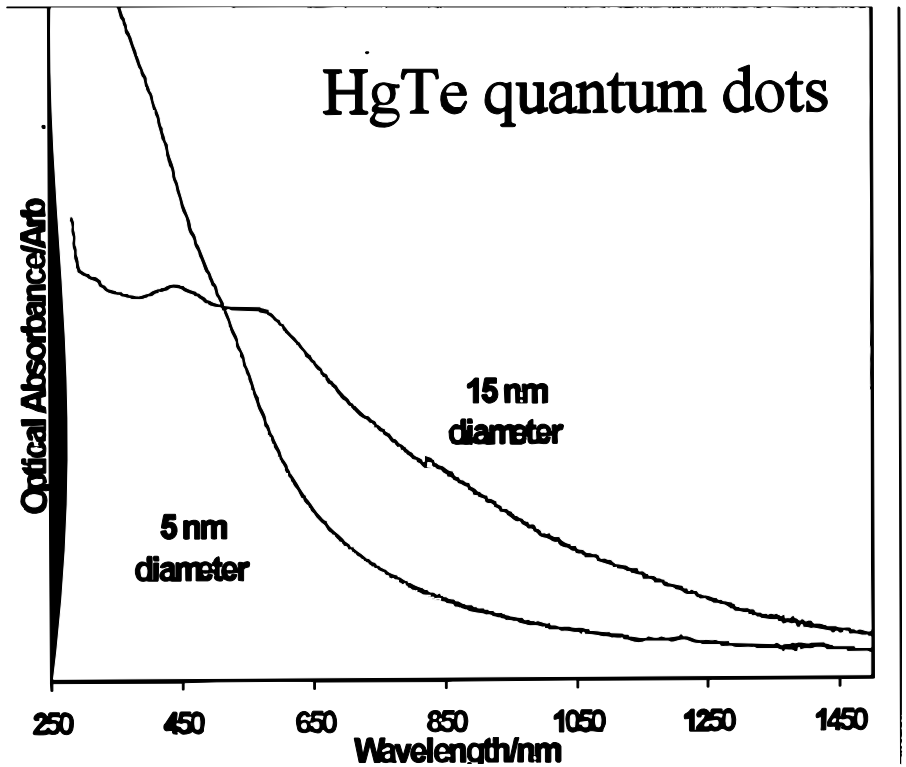
The lower picture shows some uniformly small CdS quantum dots with the fluorescence spectrum from one of them.

This spectrum shows sidebands due to energy loss/gain to phonons.

These have promise for the basis of lasers but…..

Early Oxonica products



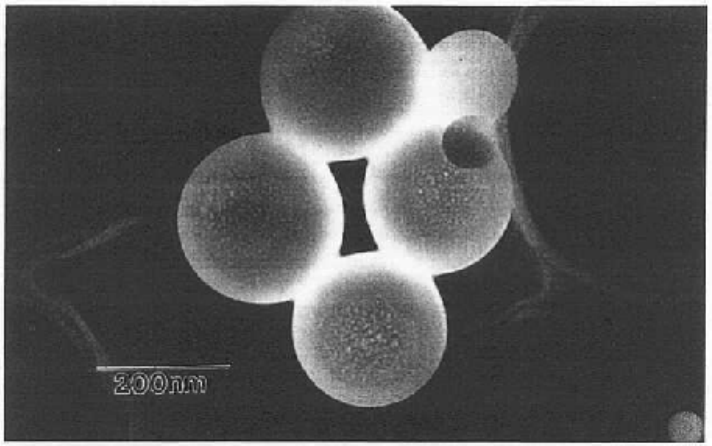


Grown by colloidal solution growth

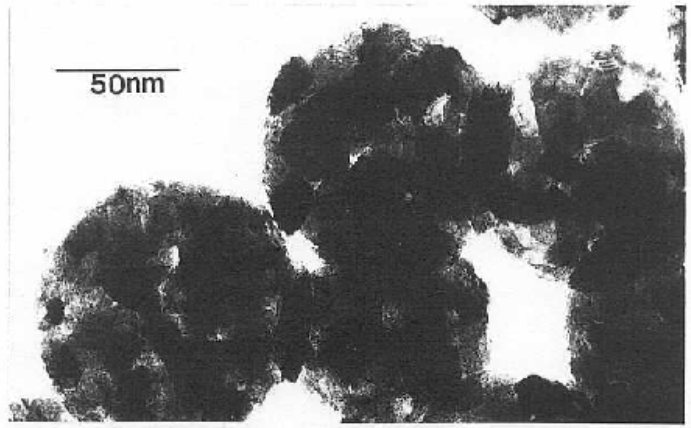
Size-tuning of optical properties

Quantum dots are still looking for a high value application!

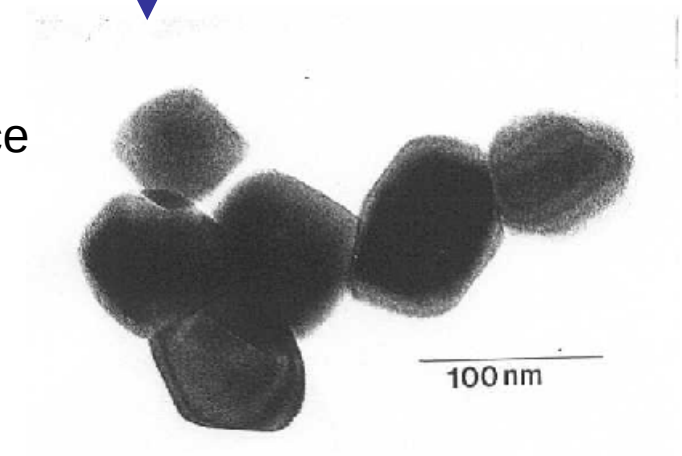
Nanophosphor particles Y_2O_3:Eu



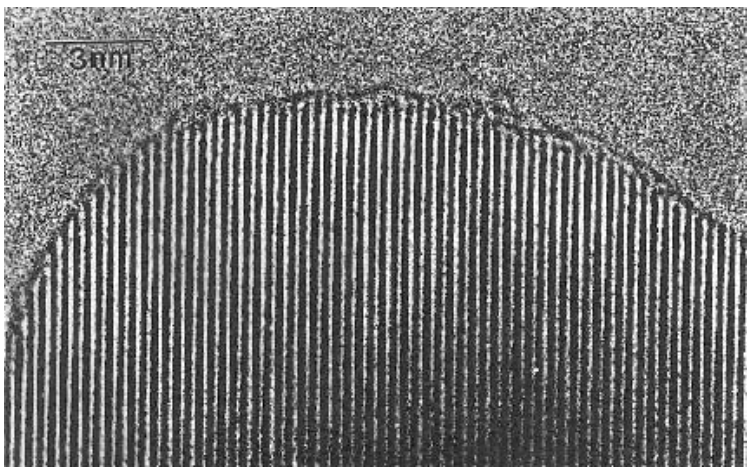
Mild anneal



High temperature heating



Detail of surface



Very promising for low voltage bright phosphors

The early lessons

- Discard the idea of pushing clever nanotechnology
- Try to provide a complete solution to a market need
- Quantum dots were “fashionable” but where is the market? (this is true today!)

Nanoparticles and safety aspects

- Nanoparticles can be adsorbed in the lungs and the skin
- More work is needed to establish how this happens and what the consequences are
- This is being addressed by EU FP6 NANOSAFE2 (Oxford University and Oxonica are in this project)
- Two examples will be now given that have resulted from our concern for human safety
  - Nanoparticle catalysts to eliminate carbonaceous nanoparticles in exhaust
  - Nanoparticle sunscreens to give improved UV protection

Penetration issues

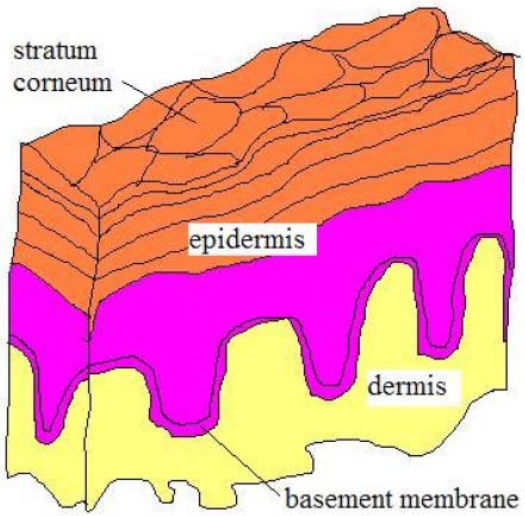


Figure 1
schematic representation of human skin; Stratum corneum is the top of the five layers making epidermis, it is composed of keratinised dead cells glued by lipids. It is shed off and replaced every two weeks. Depending on the part of the body its thickness varies from 0.05 mm to 1.5 mm.

Very little evidence for skin penetration so far

Other parts of respiratory system may be more effective

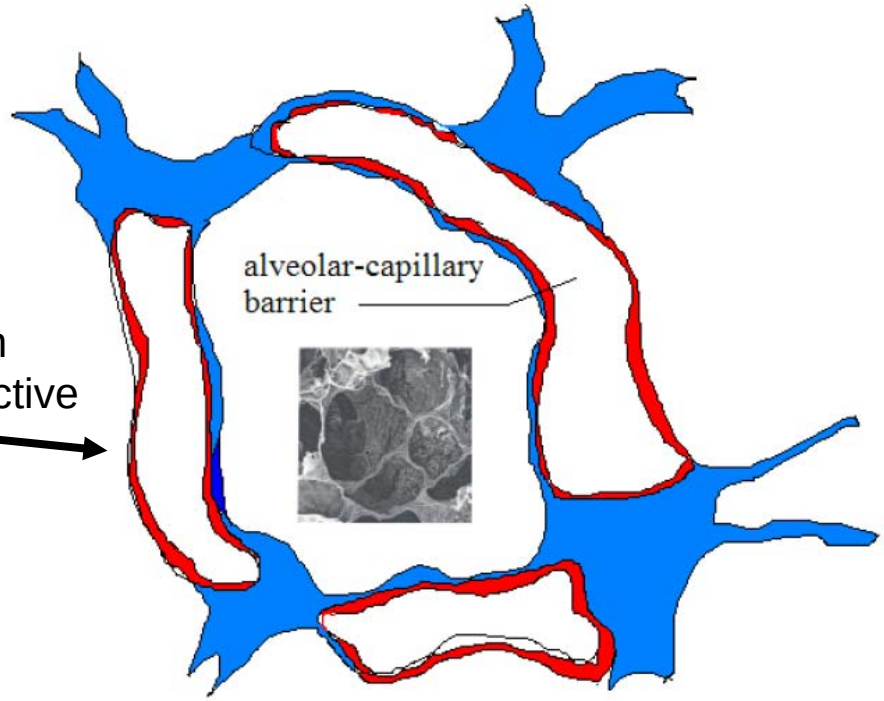


Figure 2
Cross-section of alveoli; Schematic cross-section of alveoli showing a very thin (500 nm) separation between blood and air. An SEM image of the alveoli is shown in the inset.

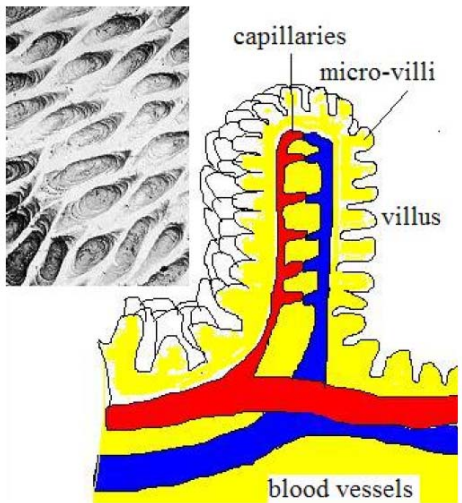


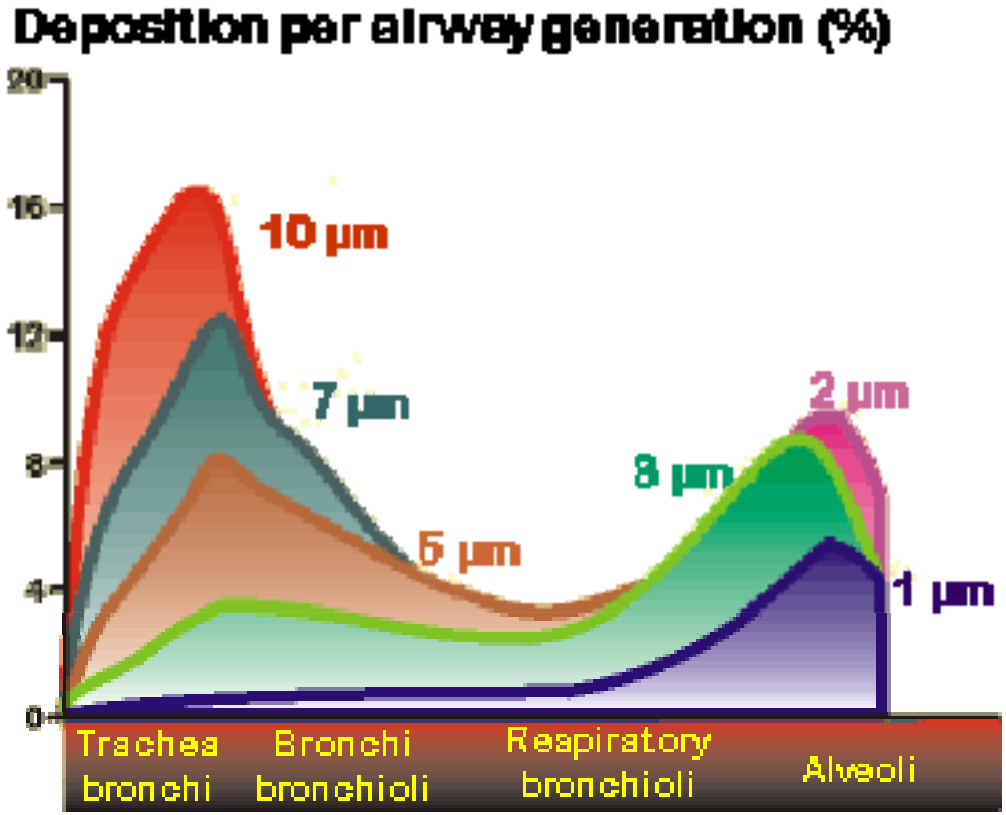
Figure 3
Villi in small intestine; A surface structure of villi covered with micro-villi is dramatically multiplies the area of gastero-intestine tract to 200 m^2. Inset shows an SEM image of villi.

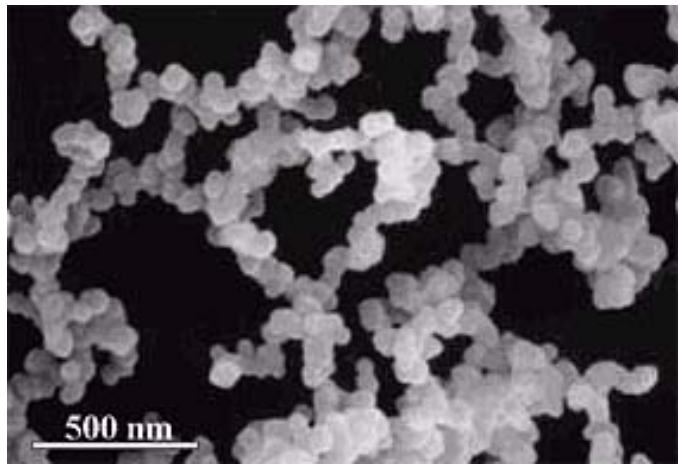
Three critical situations in the body for nanoparticle interaction

Hoet et al: J Nanobiotechnology **2**:12 doi 10.1186/1477-3155-2-12

http://www.jnanobiotechnology.com/content/2/1/12

Particle deposition in the airways



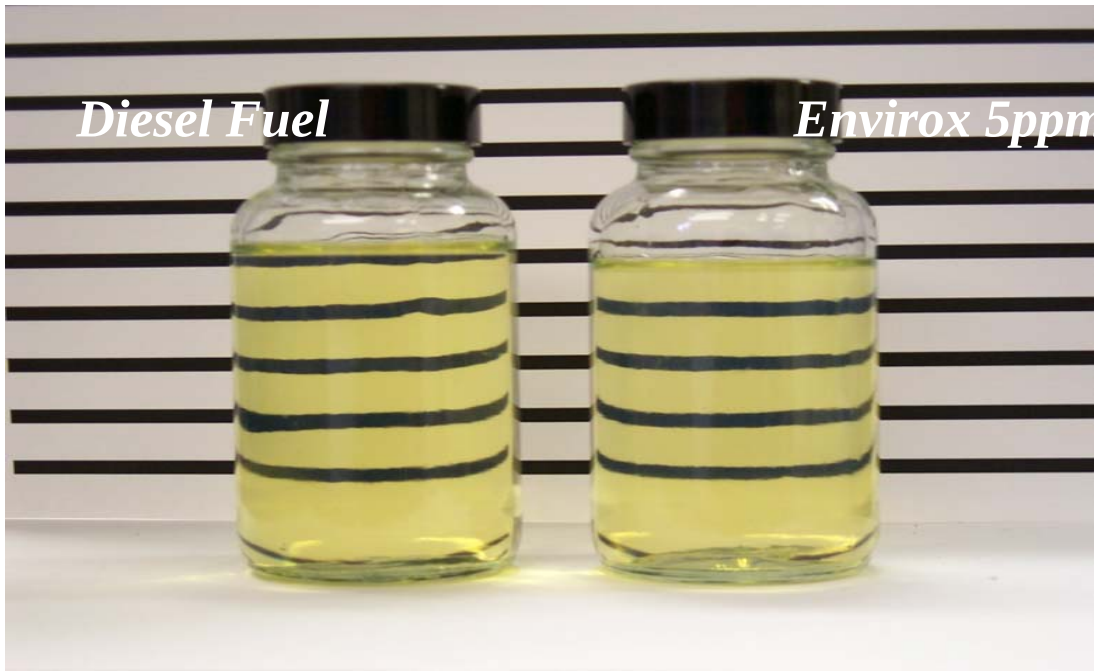


Example of some carbonaceous nanoparticles from a diesel engine

This can be harmful but it points a way to deliver drugs
We will first examine how to reduce diesel particulates.

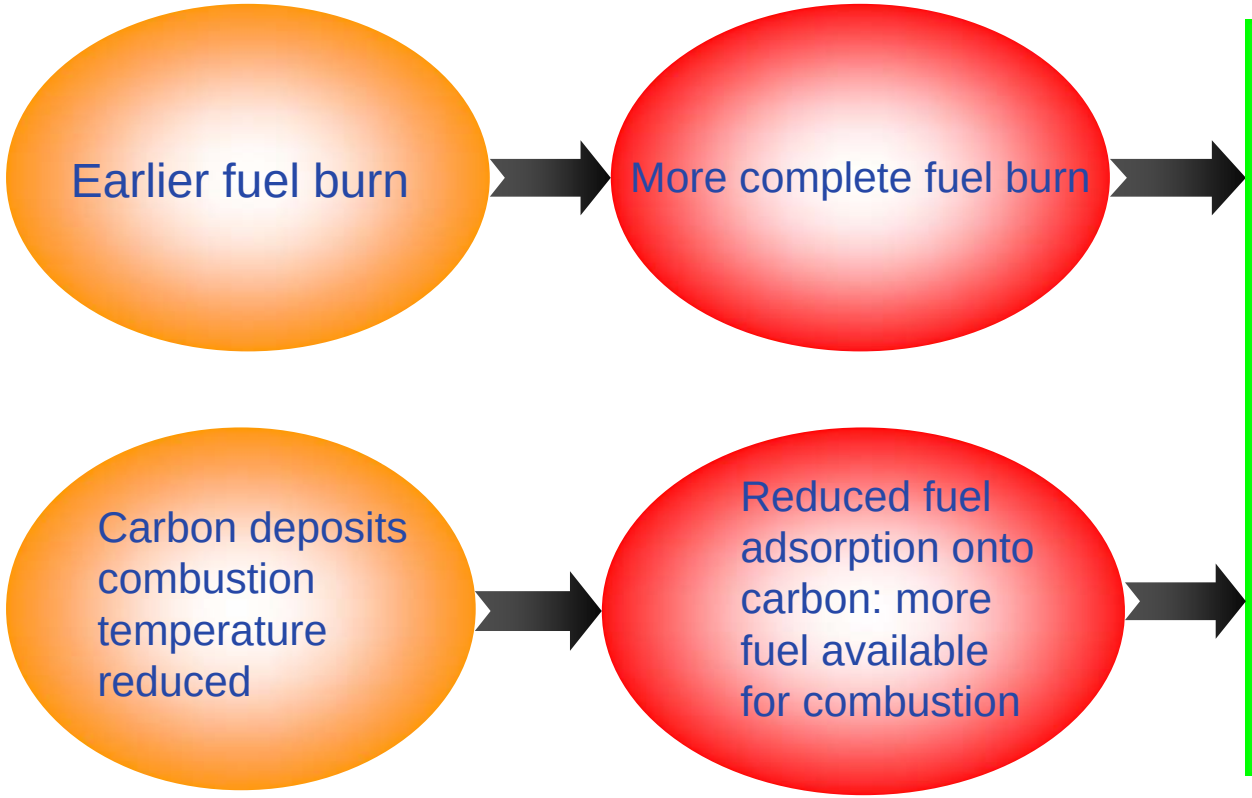
Envirox™: Technology reduces diesel particulates- “particles to eliminate particles”

- **Based on a Cerium Oxide dispersed in hydrocarbon solvent**
  - Fuel-borne additive
- **Nanoscale particle size**
  - Extremely high catalyst surface area
- **Direct addition to diesel fuel:**
  - Fuel-borne catalysis
- **Approx. 5ppm Cerium Oxide**
  - Low application rate – only 1 litre of Envirox to 4000 litres of fuel
  - No engine modifications required



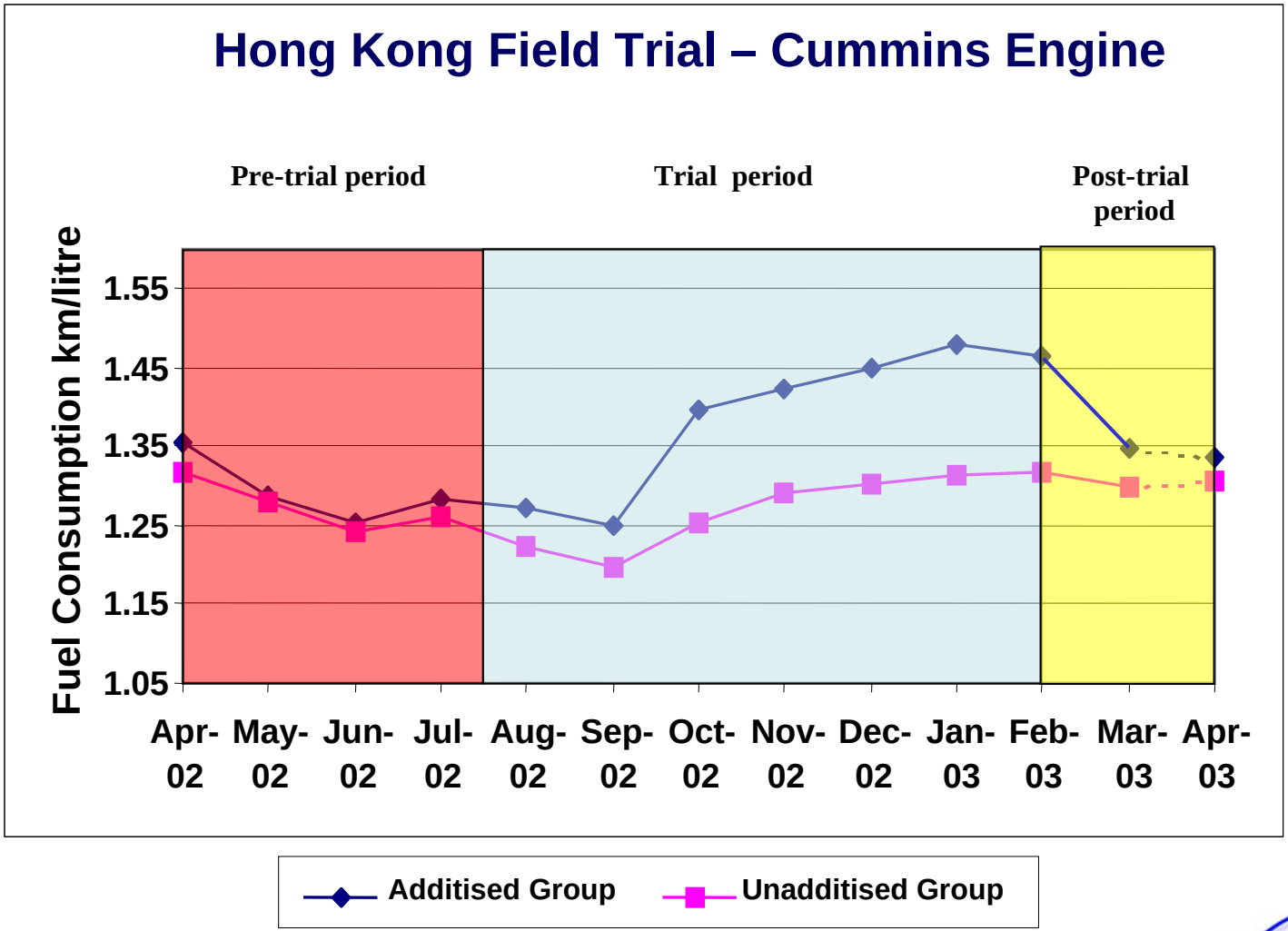
Diesel fuel with Envirox 5ppm 10nm particles added. Key point is that fuel must be stable and remain haze free.

Envirox™: The Process



OXONICA

Envirox™: Fuel Economy Performance



Envirox™: Emissions Reduction

- Tests carried out at a range of independent laboratories

  Immediate reduction of up to 14% in particle and hydrocarbon emissions – may further improve over
  time

- No increase in ultra fine particles emitted

- Potential to enhance Diesel Particulate Filters performance – lower emissions and reduced regeneration temperature

OXONICA

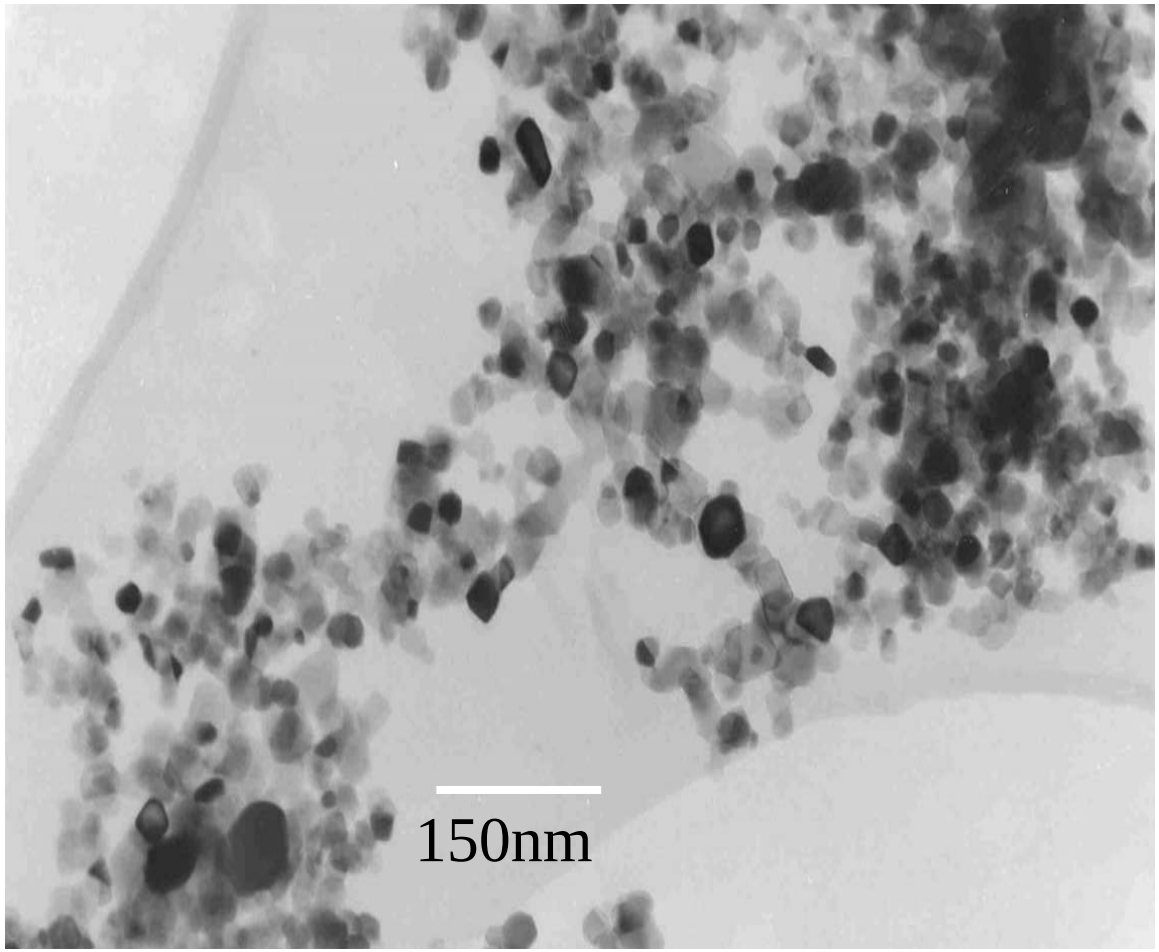
More scope for combustion improvement?

- Biodiesel can be treated
- Extension to two-strokes?
- Gasoline engine?
- Gas turbine improvement?
- Heavy Oil combustion

Nanoparticle combustion catalysts will improve air quality and reduce carbon dioxide emissions

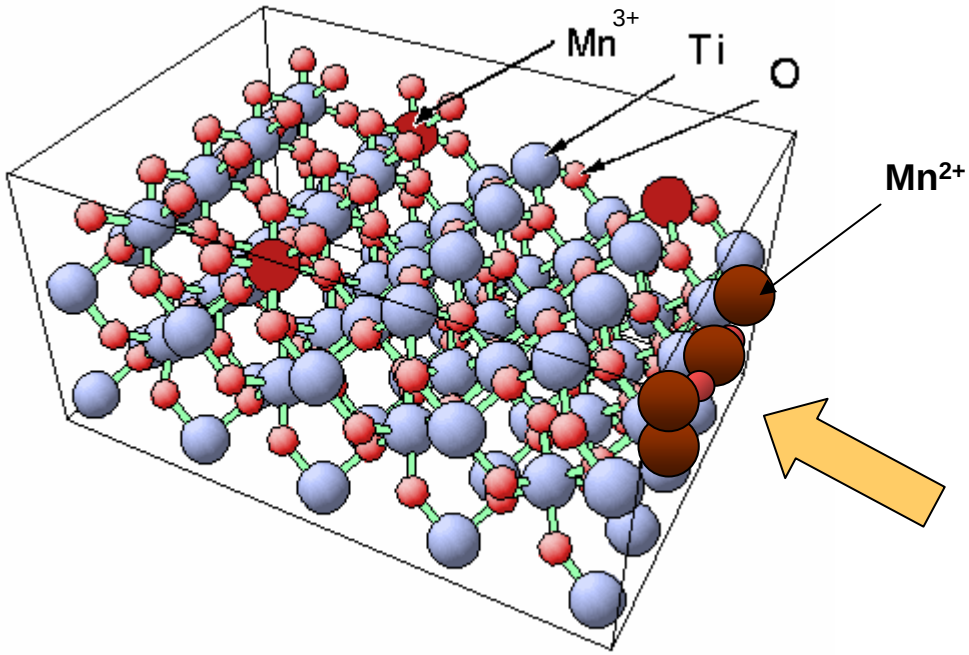
Optisol TM

- Nanoparticles of titania are used so that they appear transparent to visible light on the skin, but block UV
- The titania is doped in a special way so that it does not behave as a photocatalyst (that would cause skin damage)
- The new titania particles prevent the formation of “free radicals” and hence the formulation lasts much longer in sunlight and protects the skin.



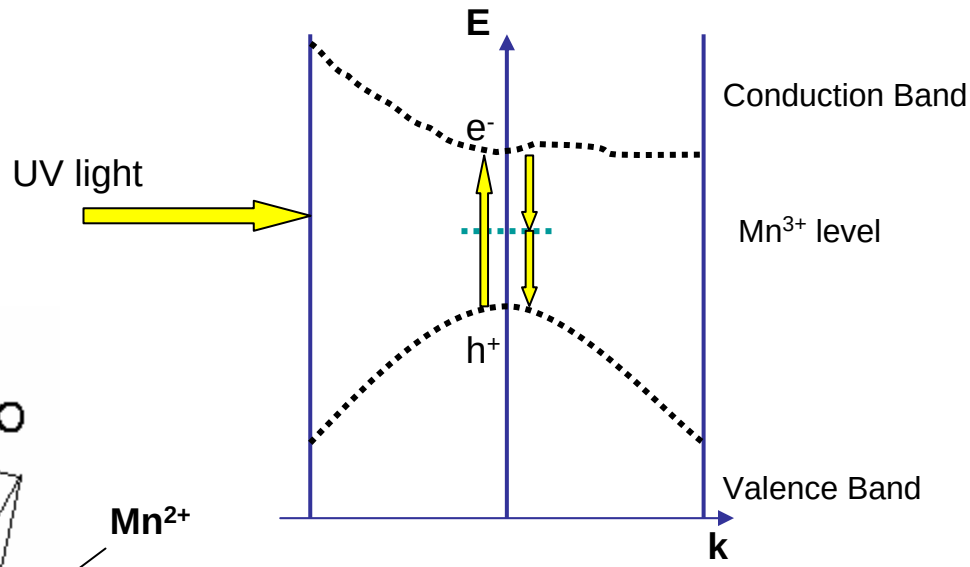
TEM of titania sunscreen particles.

Optisol TM : Mode of action



Rutile P4$_2$/mnm Titanium Oxide lattice

Schematic band structure



Surface Mn^{2+} free radical scavenging

$$Mn^{2+} \Leftrightarrow Mn^{3+} + e^-$$

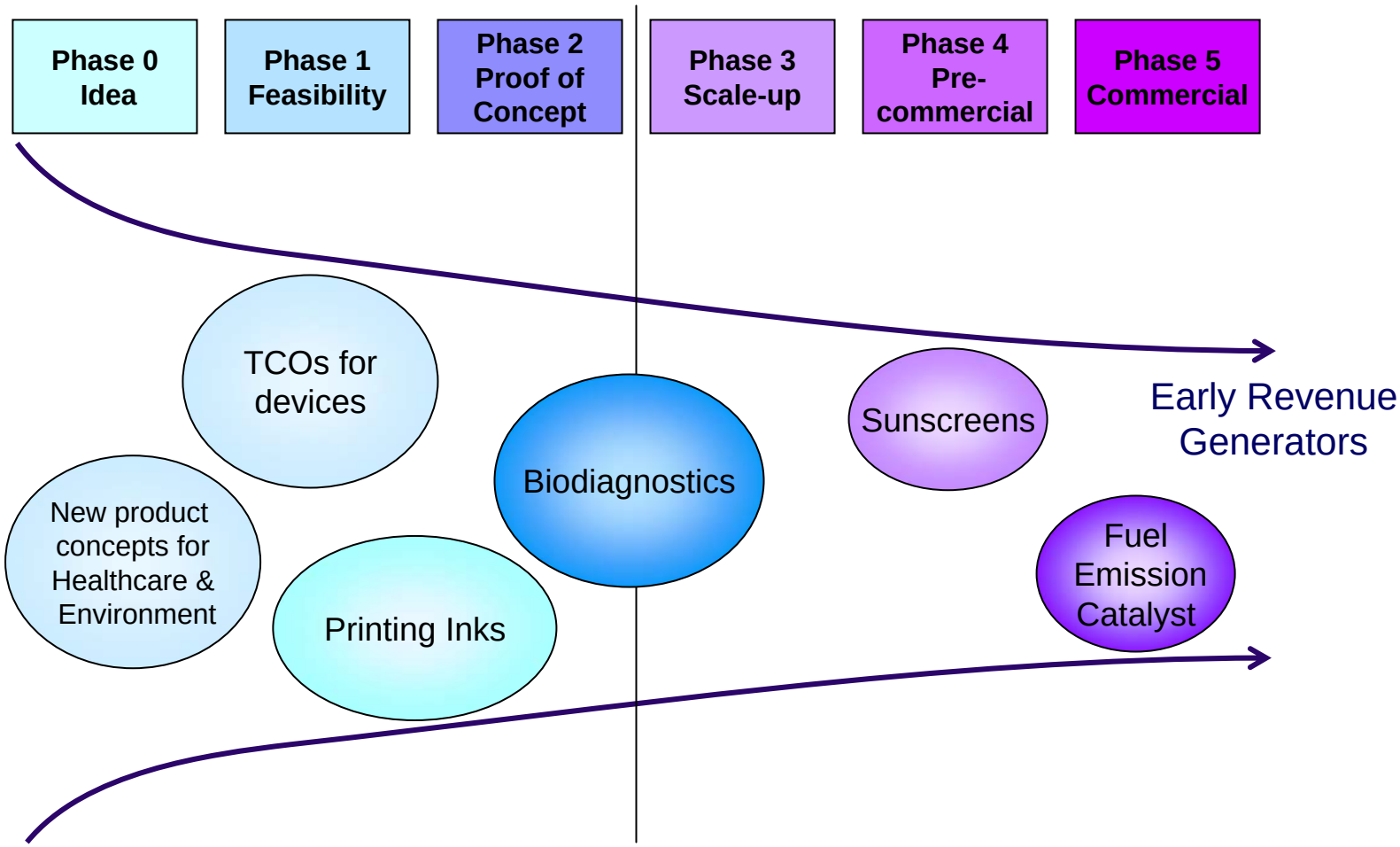
$$Mn^{2+} + OH^{\bullet} \Rightarrow Mn^{3+} + OH^-$$

$$Mn^{3+} + {}^{\bullet}O_2 \Rightarrow Mn^{2+} + O_2$$

New doped titania products

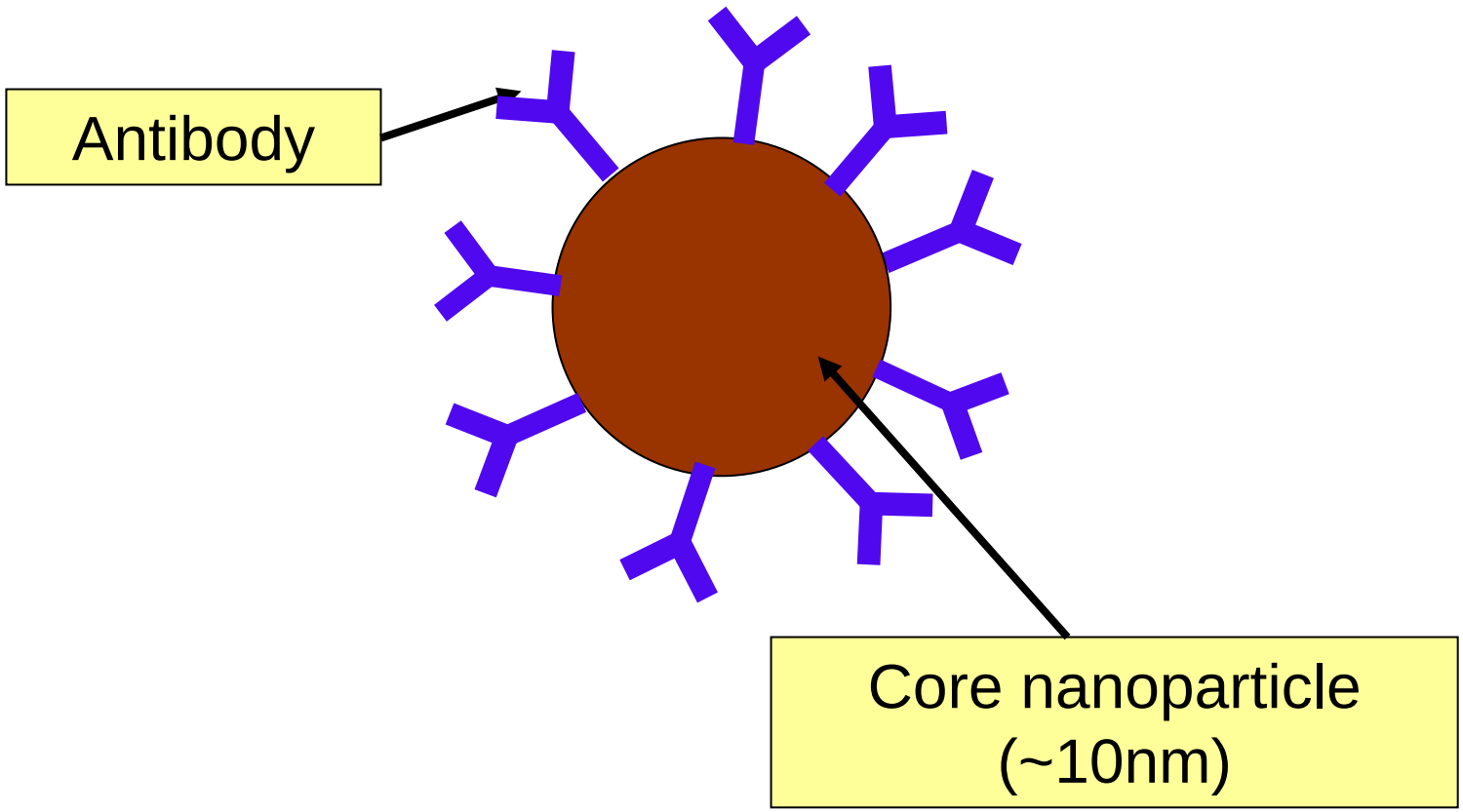
- Enhanced performance for many other cosmetic foundation formulations
- Possible use as a uv protective agent in coatings and polymers: “Solacor”®
- Basis for solar cells (Graetzel-type)
- Self-cleaning and super-hydrophilic layers (when highly n-type)
- UV enhanced water cleaning.

Oxonica product pipeline



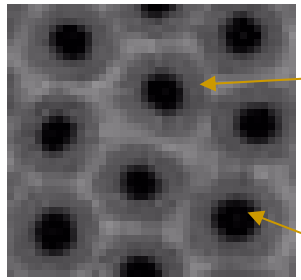
Nano-Bio Applications of Nanoparticles

- They can be functionalized to attach to almost anything
- Core particle can be magnetic, metallic/plasmonic semiconducting/luminescent or hollow to contain drug

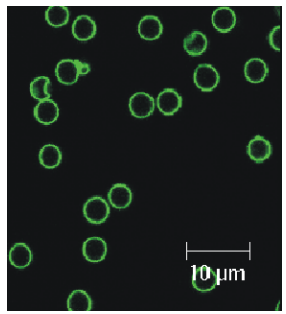


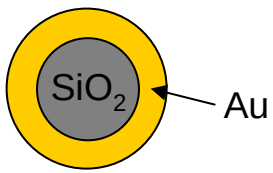
Core-Shell Nanostructures: new design paradigms

- Provide multifunctionality



- Enable templating





- Exploit collective effects of electrons that give colour

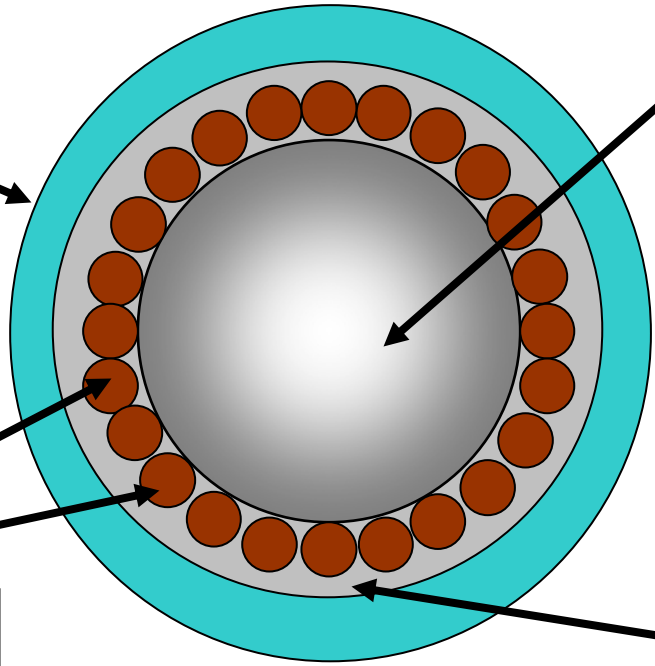
Design for biosensing and other duties

Functional material

Protein, dye, metal etc.

Dielectric core

Silica



Superparamagnetic particles

Iron Oxide

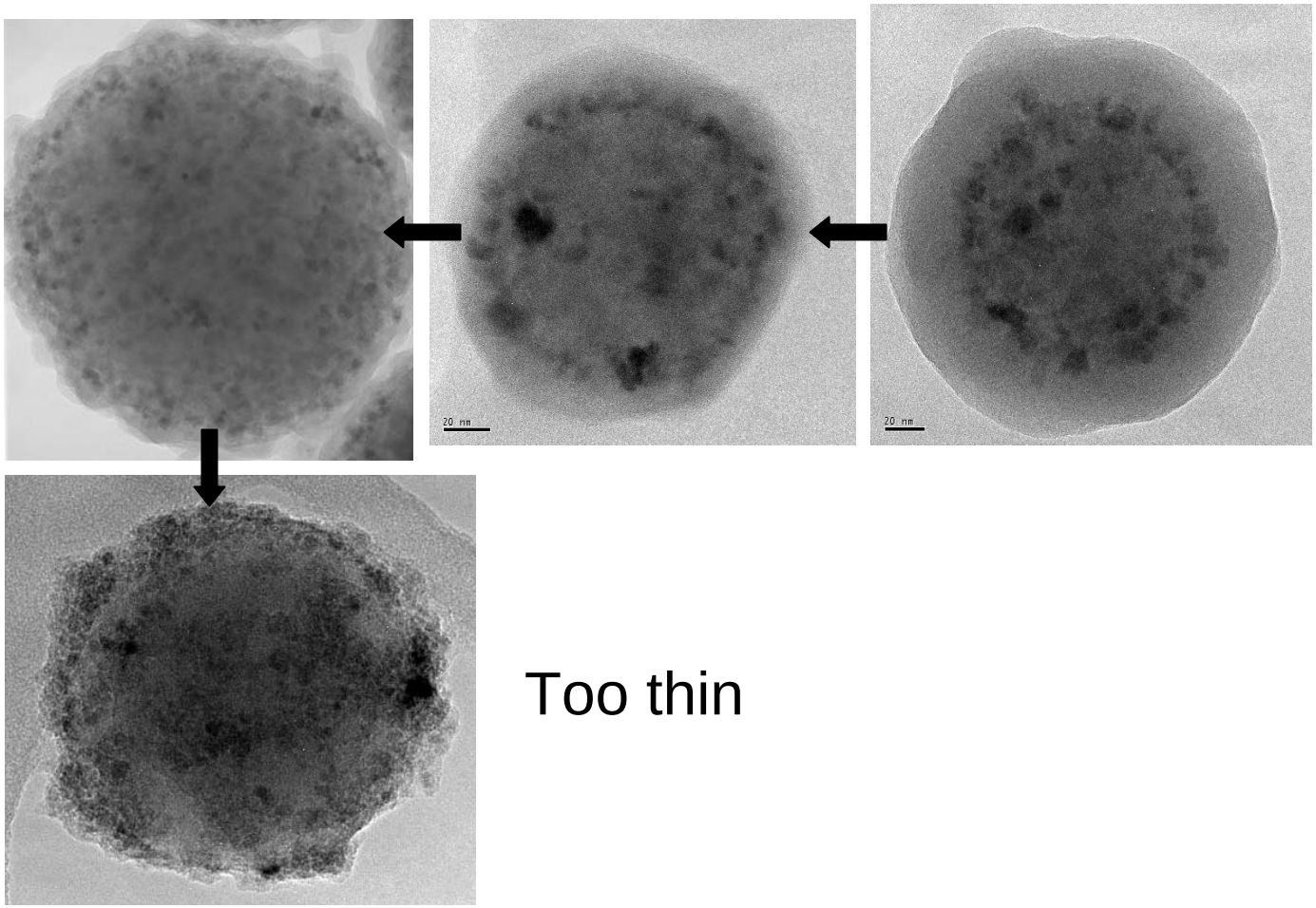
Dielectric Shell

Silica

Robin Taylor and Peter Dobson, (2002)

Sol-gel coating process requires some trial and error to find the optimum thickness!

Too thick



Too thin

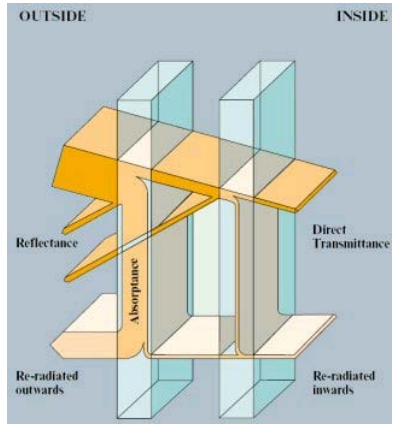
Recent work has shown that it is possible to add several shells in a controlled way

Nanoparticles are going to add value

- New nanocomposite materials for improved windows, solar cells
- New methods of medical diagnosis
- New methods of drug delivery
- Form the basis for regenerative medicine
- Environmental sensors (water and air)
- Assist with environmental clean-up
- Possibly lead to new quantum computing

NanoCoat for large area energy efficient substrates

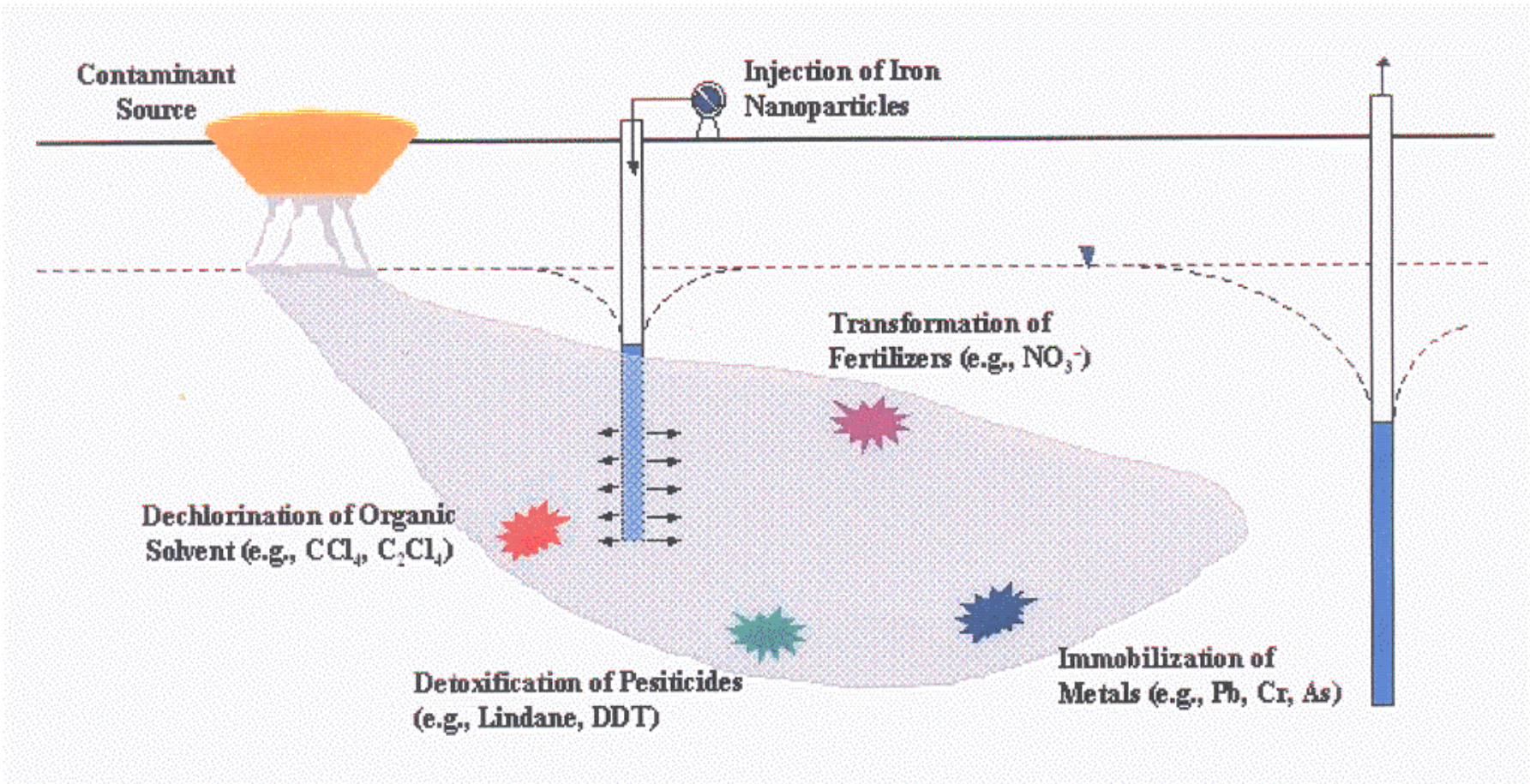
- **Energy saving in production and use**



- **Composite materials**
  - Nanoparticles incorporated into dielectric matrix (controllable properties for enhanced functionalities – conductivity, catalysis)
- **Design of optical properties with plasmons**
  - Coloration of glass
  - Control transmission and reflection in the infrared
- **Tuning plasmon resonance frequency with matrix of different refractive index**

Spray deposition of gold nanoparticles incorporated into TiO_2 matrix before (left) and after (right) annealing at 400 °C

Nanoparticle groundwater clean-up



Iron nanoparticles can destroy chlorinated hydrocarbons.

Zhang W-X. J Nanoparticle Res. **5**, 323 (2003)

The lessons

- Remember that a solution driven approach in a market-led situation is more likely to succeed
- Do nanoparticles add to value?
- Do not be seduced by technology
- Allow for the scale-up and reproducibility issues
- Remember the safety aspects

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