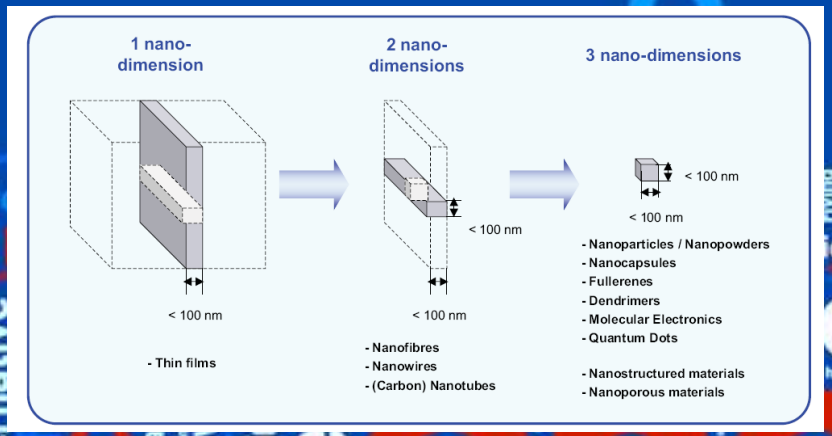
NanoTechnologies & NanoMaterials

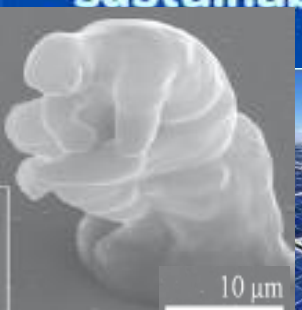
Nano - Solutions for Sustainable Development

E. Gaffet

NanoMaterials Research Group - UMR 5060 CNRS (Belfort – France)

President of Scientific Committee « NanoSciences & Nanotechnologies » / ANR (France)
Member High Council for Public Health (France) // Member SCENIHR –Nanodefinitions (Europe)
President of OECD / WPMN - Physico – Chemical NanoCharacterisation Community of Practice



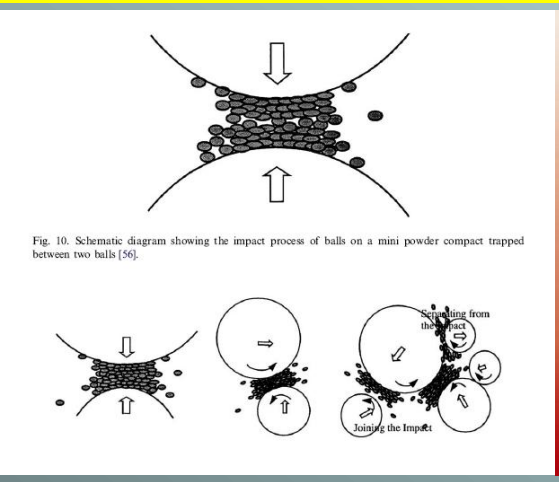


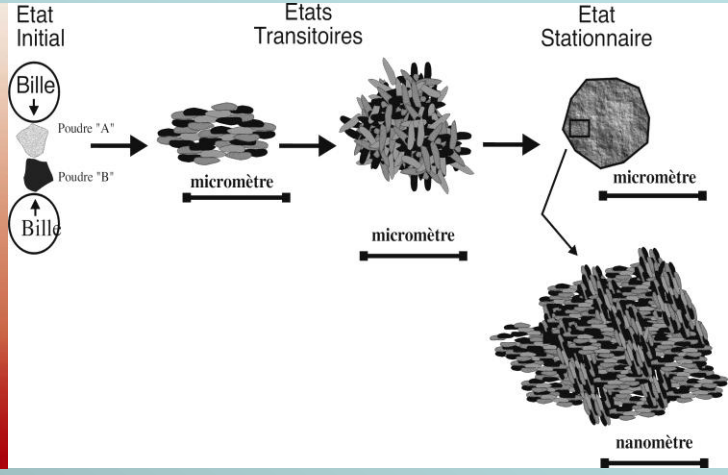
Eric.Gaffet@utbm.fr

International Environmental Symposium – Ljubljana - 20 May 2011

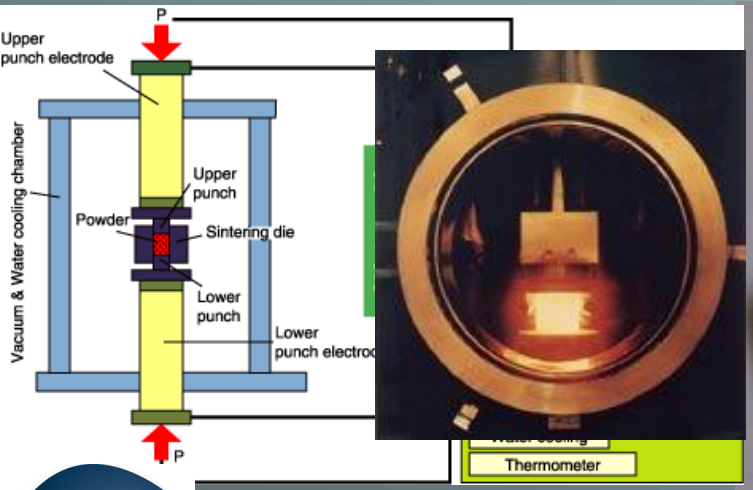
Research
(Far From Equilibrium Phase Transition)

Powder Metallury
i) Mecanosynthesis & Flash Sintering



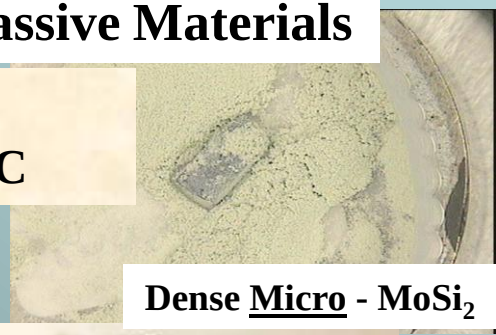


ii) Flash Sintering (SPS Consolidation) – From Powder to Massive Materials

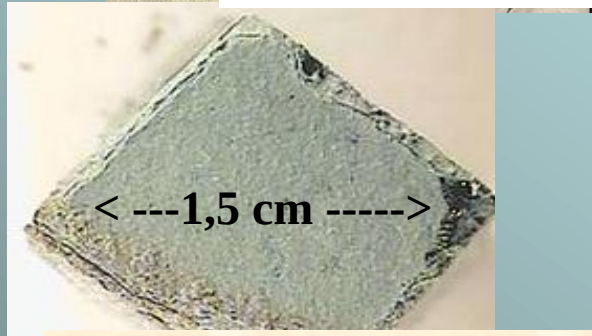


Corrosion
A week - 400°C

Full Pest Corrosion



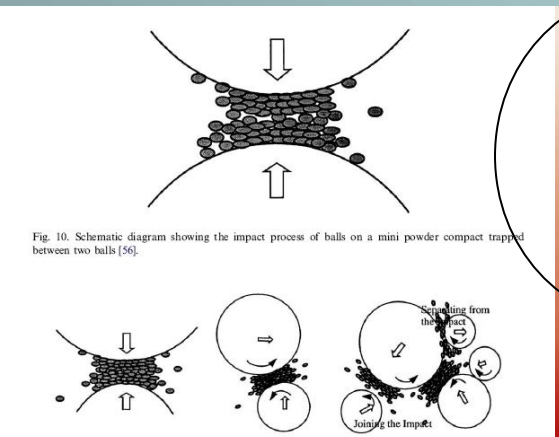
Dense <u>Micro</u> - $MoSi_2$



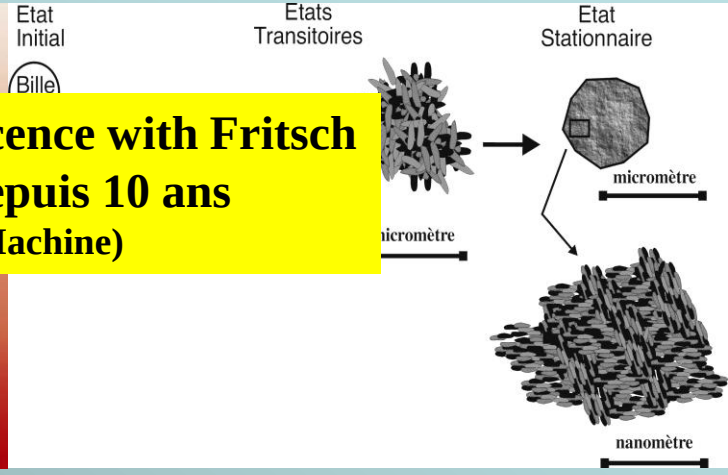
Dense <u>Nano</u> $MoSi_2$

Innovation
(Industrial Transfert)

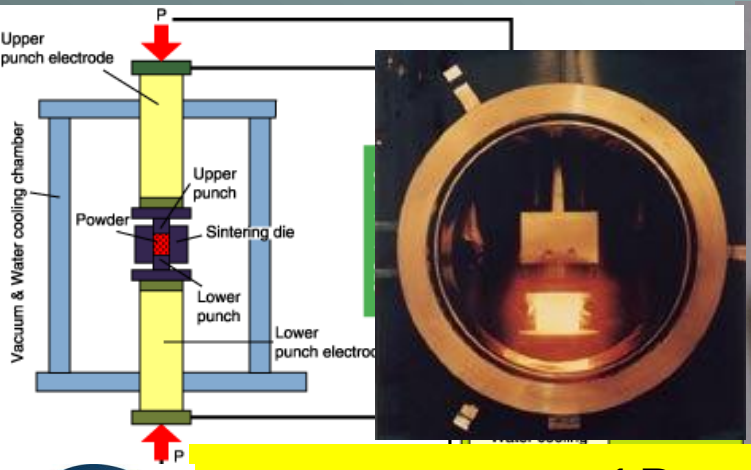
Powder Metallury
i) Mecanosynthesis & Flash Sintering

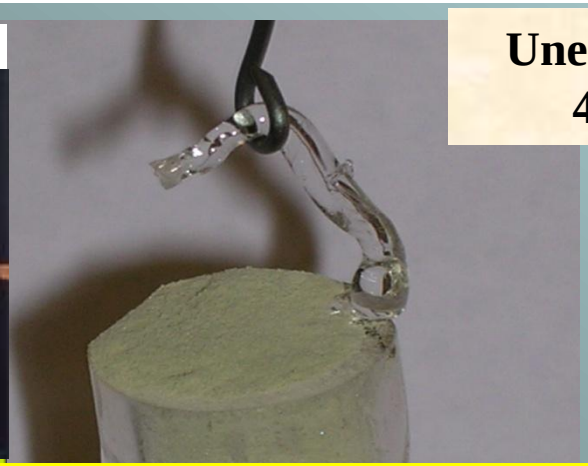


Know How Transfert Licence with Fritsch
15 machines /an depuis 10 ans
(15 kEuros par Machine)

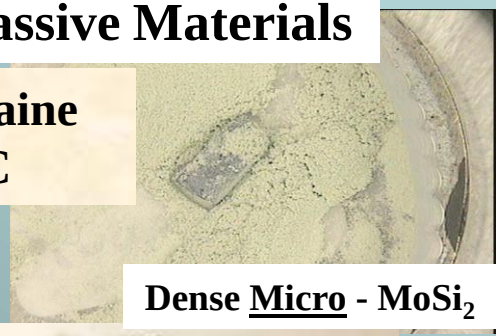


ii) Flash Sintering (SPS Consolidation) – From Powder to Massive Materials

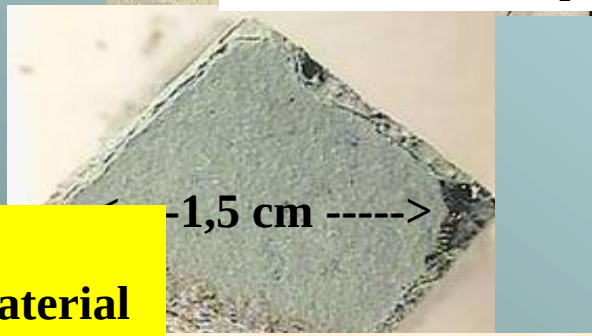




Une semaine
400°C



Dense <u>Micro</u> - $MoSi_2$



1 Patent France – USA
Mechanical Activated Flash Sintering – Dense Nanomaterial

Full Pest Corrosion

Outline

i) Définitions, Markets, Properties, Applications
Définitions, Prospectives, Propriétés, Applications

ii) Real Risks, Perceptual Risks, Regulations
Risques réels, perçus, réglementation

iii) NP Hazard (Eco/Toxicity)
Nanotoxicité

iv) Benefits / Risks analyses

THE ROAD TO THE NNI

1959

Richard Feynman, a famed US physicist at the California Institute of Technology, gives a speech envisioning the power of controlling things on a small scale.

1974

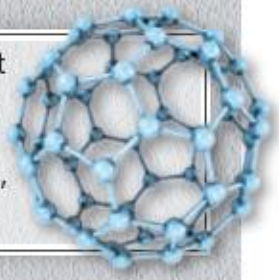
Norio Taniguchi at Tokyo Science University first coins the term 'nanotechnology'.

1981

Gerd Binnig and He… Research in Zurich, … scanning tunnelling … researchers to 'see' su… …t the atomic level.

1985

Richard Smalley and Robert Curl at Rice University in Texas and Harry Kroto at the University of Sussex, UK, discover buckminsterfullerene, popularly known as the buckyball.



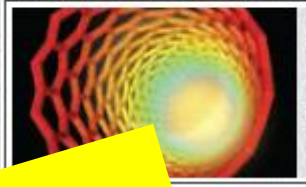
1986

Christoph Gerber at IBM in San Jose, California, and Calvin Quate and Binnig at Stanford University in California invent the atomic force microscope, which not only images surfaces at the atomic level, but can also manipulate individual atoms.

1990

Donald Eigler and Erhard Schweizer at IBM arrange individual xenon atoms to form the letters IBM.

1991



Sumio Iijima at NEC in Japan discovers carbon nanotubes.

…nal Science Foundation launches …st programme devoted to nanotechnology.

1998

A working group of science programme managers from eight US government funding agencies is formed to devise an agenda for nanoscience and technology research.

1999

Discussions of a US national initiative on nanotechnology heat up in the White House and Congress.

2000

The National Nanotechnology Initiative (NNI) is formed.

A yet long Story (starting in 1959 for modern age)

Nature Sept. 2010 – Small Wonders - http://www.nature.com/news/2010/100901/pdf/467018a.pdf

There came Dr. *Richard P. Feynman* *(Nobel laureate)*

1959

"There's Plenty of Room at the Bottom!"

Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?

… is possible in principle---in other words, … is possible according to the laws of physics.

- *Information storage at extreme small scale*
- *Better electron microscopes*
- *Marvelous biological system*
- *Problems of lubrication*
- *A hundred tiny hands*
- *Rearranging the atoms*
- *etc…*

Is widely considered to be the foreshadowing of nanotechnology.

The annual meeting of the American Physical Society, 9/29/1959, CalTech.

First "NanoTechnology"

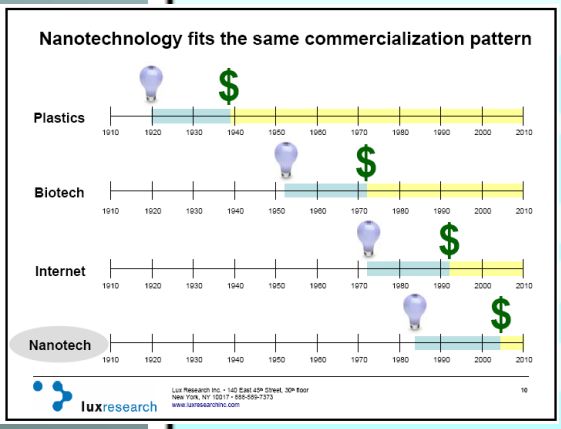
1974

The term 'nanotechnology' was coined in 1974 by Norio Taniguchi of the University of Tokyo. He used the word to refer to 'production technology to get the extra high accuracy and ultra fine dimensions, i.e. the preciseness and fineness on the order of 1 nanometer.

('On the Basic Concept of "NanoTechnology"', Proceedings of the International Conference of Production Engineering, 1974)

≠ Technological Waves

1.000 - 3.000 Billions $



Microelectronics

Biotechnology

New Functional Materials

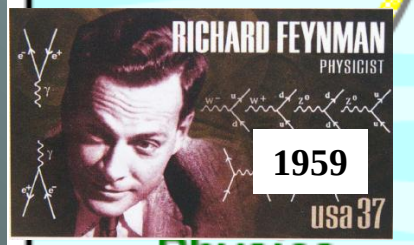
<-Phase Critique->

2008 - 170 Billions $

2007 - 150 Billions $

2006 - 50 Billions $

2004 - 13 Billions $



Physics

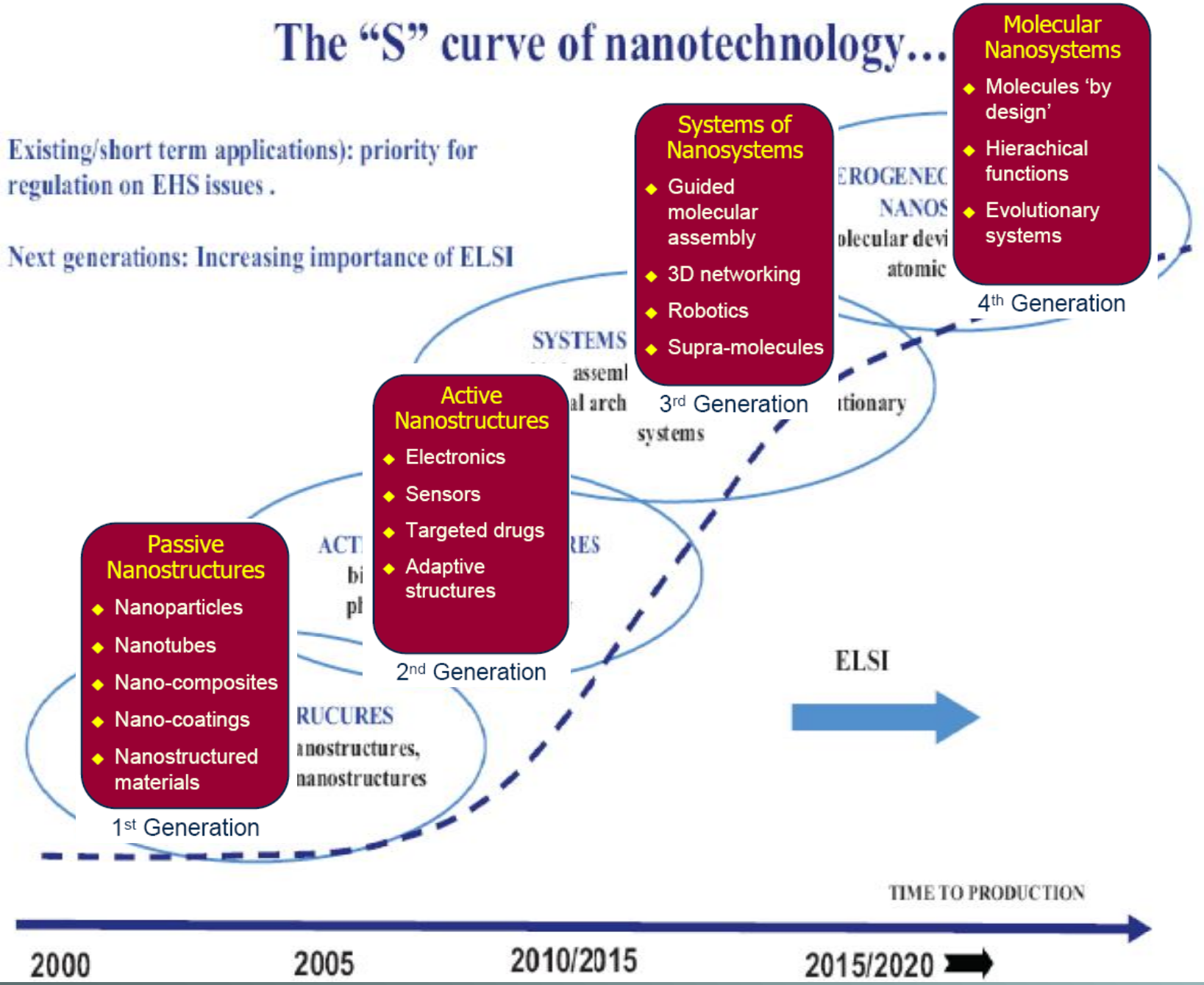
Biological Science

Nanoscience and Nanotechnology

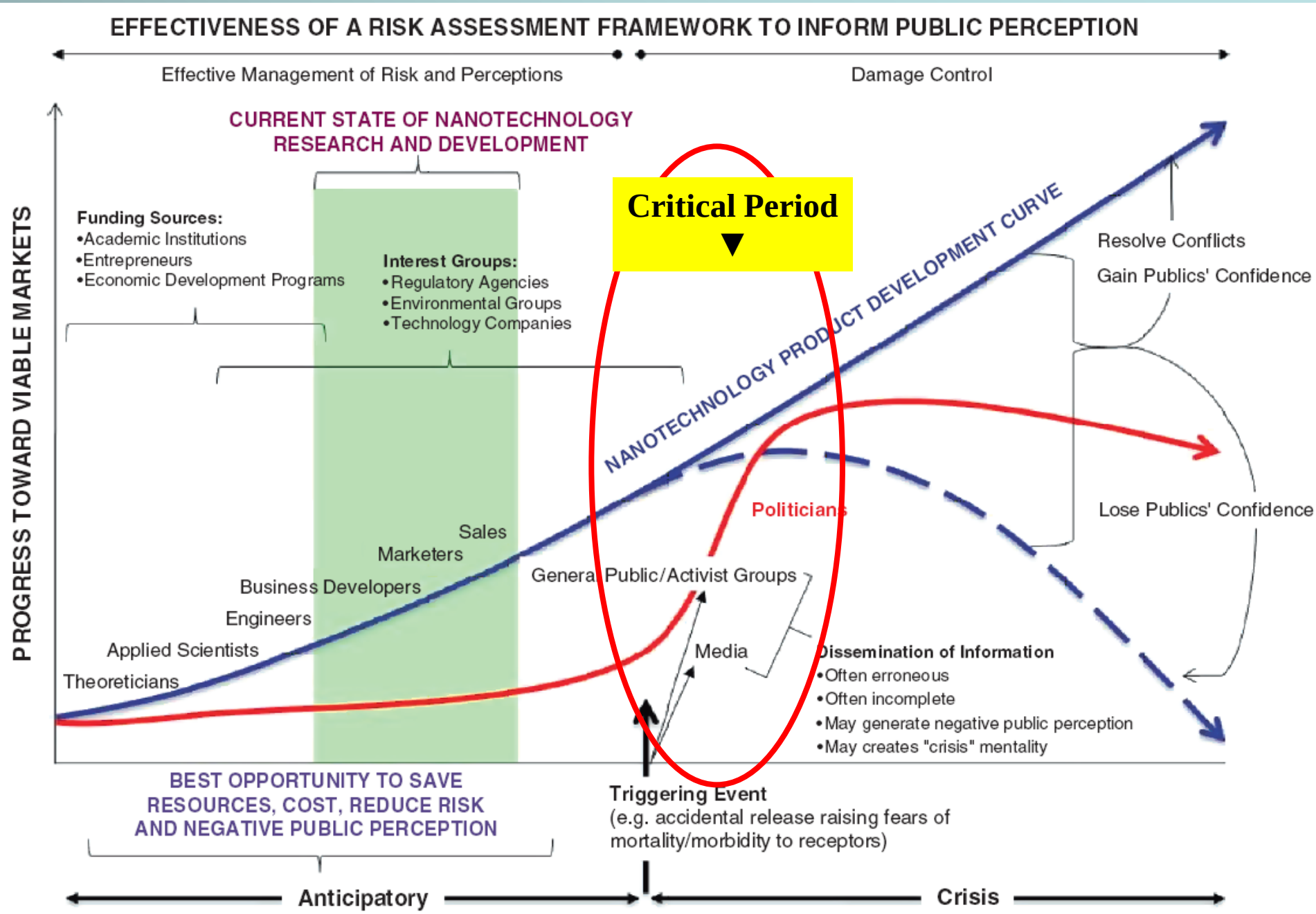
1950 1975 2000 2025

Source : Alan Smith – Association des Industries Nanotech – UK Nanoforum – Nov. 2007

The "S" curve of nanotechnology…



http://www.observatorynano.eu/project/filesystem/files/13%20AitkenObsnanoBERR%20v2.pdf



Lkapustka S. Chan-Remillard, S. Goudey, I. Linkov and J. Steevens (eds.), *Nanomaterials: Risks and Benefits, 149* Springer Science + Business Media B.V. 2009 (Proc. NATO Conf.)

HSE sectors	Economic categories according to ATECO with workers potentially exposed to nanoparticles	ATECO code	Employees
R&D in nanotechnologies			1337
University and research centers	University and research centers	–	1122
Companies	Companies	–	215
Existing ultrafine manufacturing processes			**9916**
Carbon black manufacturing		–	–
Precious metal blacks	Precious metal production	27.41	1613
Ultrafine TiO_2 manufacturing		–	–
Fumed silica		–	–
Fumed alumina		–	–
Carbon black manufacturing	Mining and agglomeration of hard coal	10.1	814
	Manufacture of man-made fibers	24.7	7489
Powder handling processes			**341,197**
Pigments and dyes	Manufacture of dyes and pigments	24.12	3006
Paint, etc.	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.3	20,875
Pharmaceutical products (including manufacturing)	Manufacture of pharmaceuticals, medicinal chemicals and botanical products	24.4	70,356
Cement	Manufacture of cement	26.51	9393
Ultrafine TiO_2	Manufacture of perfumes and toilet preparations	24.52	14,187
Carbon black	Manufacture of chemicals for office use and non-industrial consumption	24.66.5	835
	Manufacture of rubber products	25.1	48,334
	Manufacture of plastic products	25.2	169,965
	Manufacture of accumulators, primary cells and primary batteries	31.4	4022
	Manufacture of coke oven products	23.1	224
Total			**352,450**

The table concerns traditional industrial processes in which nanomaterials are intentionally produced or applied, together with nanotechnology R&D. The fourth column indicates the numbers of employees based on ISTAT data [18] corresponding to the ATECO category [17].

Italie

R&D in nanotechnologies
1.337

Existing ultrafine manufacturing processes
9.916

Powder handling processes
341.197

Total : 352.450

The table concerns traditional industrial processes in which nanomaterials are intentionally produced or applied, together with nanotechnology R&D. The fourth column indicates the numbers of employees based on ISTAT data [18] corresponding to the ATECO category [17].

F. Boccuni et al. / Journal of Cleaner Production 16 (2008) 949e956

- **i) Définitions, Markets, Properties, Applications**
  Définitions, Prospectives, Propriétés, Applications

ii) Real Risks, Perceptual Risks, Regulations
Risques réels, perçus, réglementation

iii) NP Hazard (Eco/Toxicity)
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Needs for standardization (June 2008)

1. **To support commercialisation and market development**
2. **To provide a basis for procurement through technical requirements, and quality and environmental management**
3. **To support voluntary governance structures and appropriate legislation and regulation**

Challenges: currently there are:

- ***No internationally agreed terminology/definitions for nanotechnology(ies).***
- ***No internationally agreed protocols for toxicity testing of nanoparticles.***
- ***No standardized protocols for evaluating environmental impact of nanoparticles.***
- ***Existing "methods of test" might not be suitable for nanoscale devices and nanoscale dimensions.***
- ***Measurement techniques and instruments need to be developed and/or standardized.***
- ***New calibration procedures and certified references materials are needed for validation of test instruments at the nanoscale.***
- ***Multifunction nanotechnology systems and devices will need new standards.***

Partial solutions

- ***Some existing standards are or might be applicable e.g. for chemical analysis and imaging (ISO TCs 201 and 202) and particle detection/sizing (ISO TC 24)***

TECHNICAL SPECIFICATION

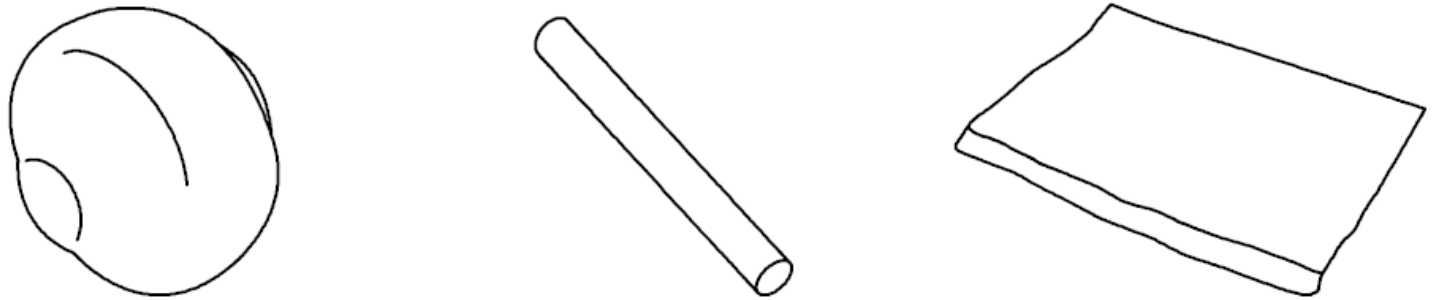
ISO/TS 27687

Nanotechnologies — Terminology and definitions for nanoparticles

Nanotechnologies — Terminologie et définitions relatives aux nanoparticules

26 Septembre 2008 !

This document is concerned with the definition of terminology and definitions for these small objects. These objects come in several different shapes as illustrated in Figure 1:



a) particle b) rod c) plate

Et !! Aggregates / Agglomerate !!!

Figure 1 — Schematic diagrams showing some shapes for nano sized objects

Commission Européenne : RECOMMENDATION on the definition of the term "nanomaterial“ (19 Octobre 2010)

Article 1

1. This Recommendation concerns the definition of the term "nanomaterial" used in Union policies and legislation applied within the European Union and the European Economic Area.

2. Member States, the Union agencies and Industry are invited to use the definition of the term "nanomaterial" when adopting and implementing legislation and programmes concerning products of nanotechnologies.

1. Nanomaterial: means a material that meets <u>at least one</u> of the following criteria:

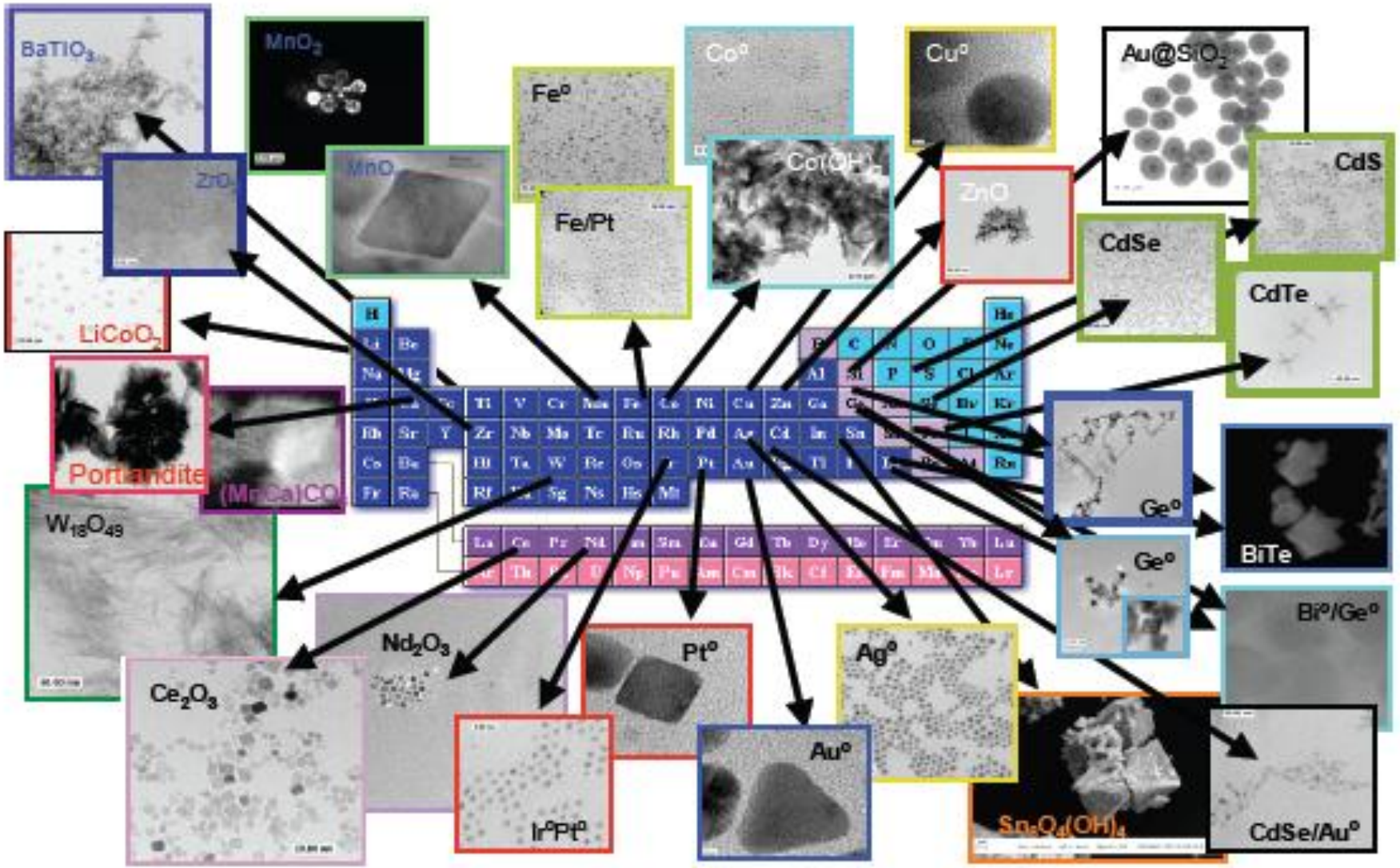
i) consists of particles, with one or more external dimensions in the size range 1 nm - 100 nm for more than 1 % of their number size distribution;

ii) has internal or surface structures in one or more dimensions in the size range 1 nm – 100 nm;

iii) has a specific surface area by volume greater than 60 m^2/cm^3, excluding materials consisting of particles with a size lower than 1 nm.

2. Particle: means a minute piece of matter with defined physical boundaries (ISO 146446:2007)

Extremely Broad Chemistries

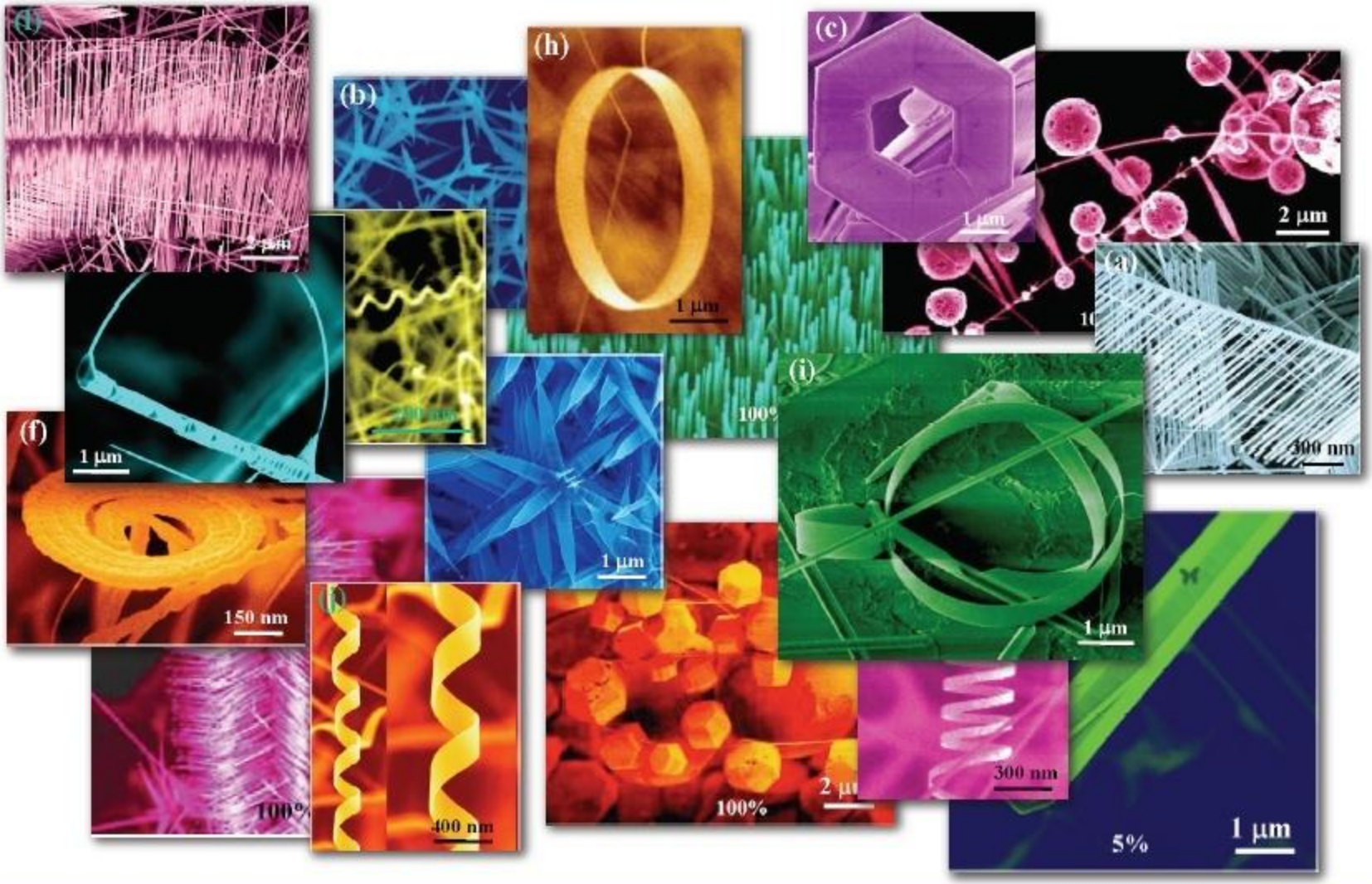


This from one set of labs at the University of New Mexico

http://www.lbl.gov/msd/msd_safety/assets/1.introduction_nanotoxicology.pdf

The Significance of Structure

ZnO: One chemistry, many shapes - Courtney of Prof. Z.L. Wang, Georgia Tech



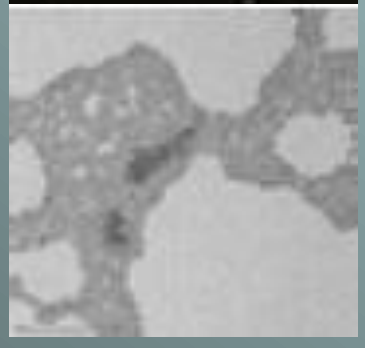
Particle Number = Fonction of the dimension

1gramme d'oxyde de Titane

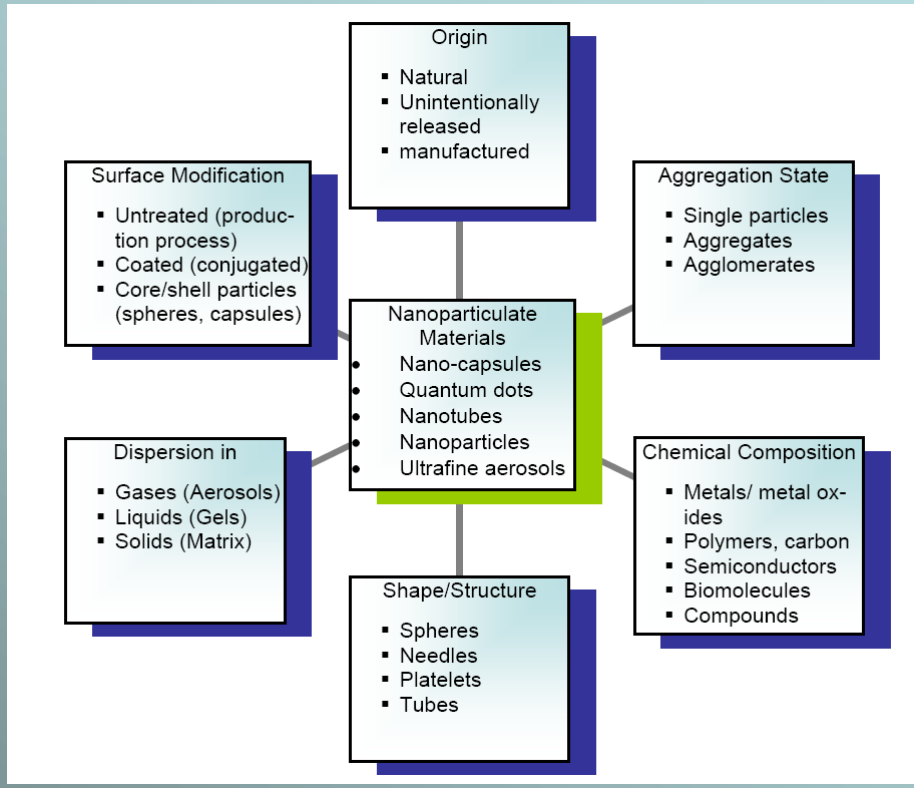
Bulk Scale
Dimension millimétrique
Ø = 1mm
54 particules

Micrometer Scale
Dimension micronique
Ø = 1 micromètre
10.000.000.000 particules
(10 milliards)

Nanometer Scale
Dimension nanométrique
Ø = 10 nanomètre
10^{16} particules
(10 Quadrillions ou
10 Millions de Milliards)



1 gramme de nanoparticules d'oxyde de Titane – 100 m^2



If only *2 grams of 100 nm diameter NPs were* to be evenly distributed there would be enough to provide every human worldwide with 300,000 particles each (Hardman 2006).

Source : K. Ausman Center for Biological and Environmental Nanotechnology

Surface (ϕ nm) = 10.000.000 x Surface (ϕ cm)

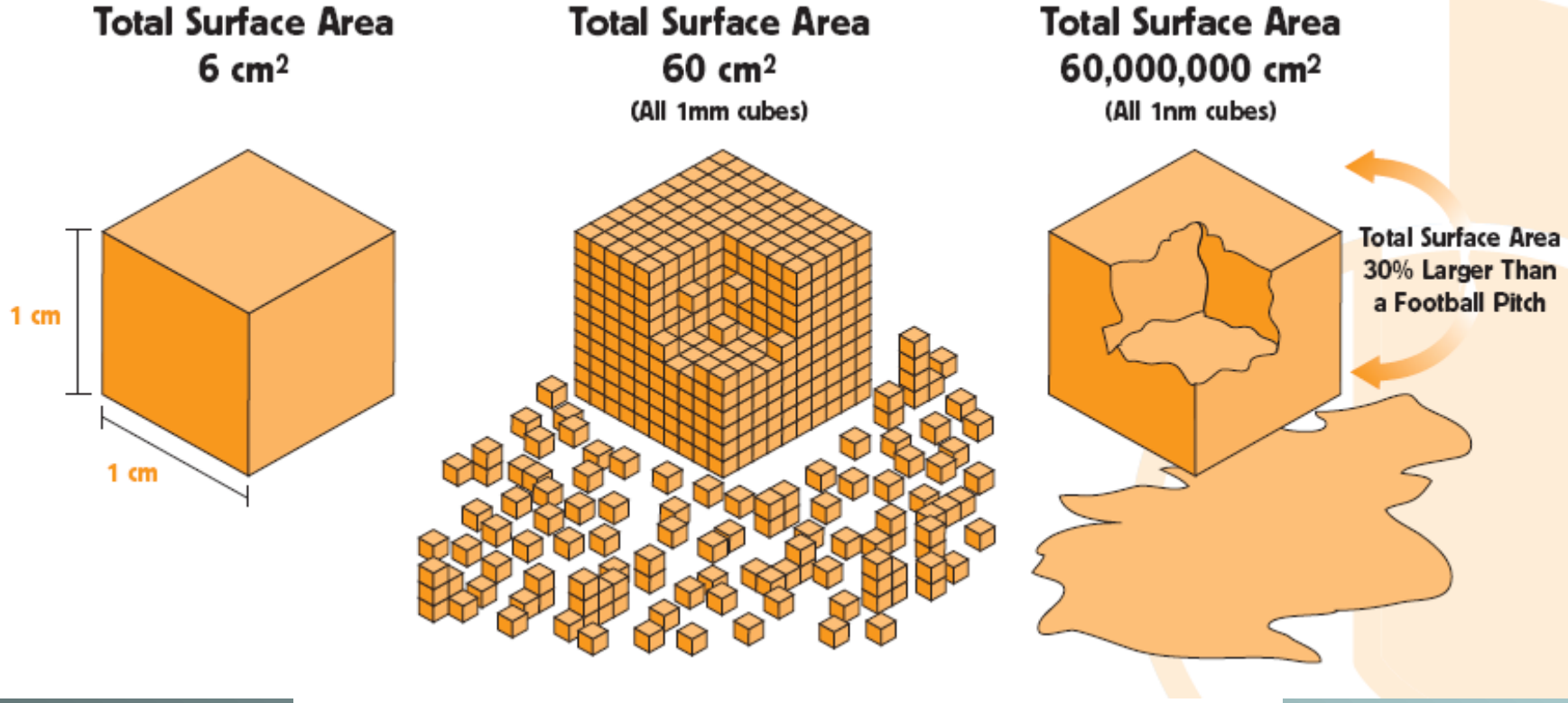
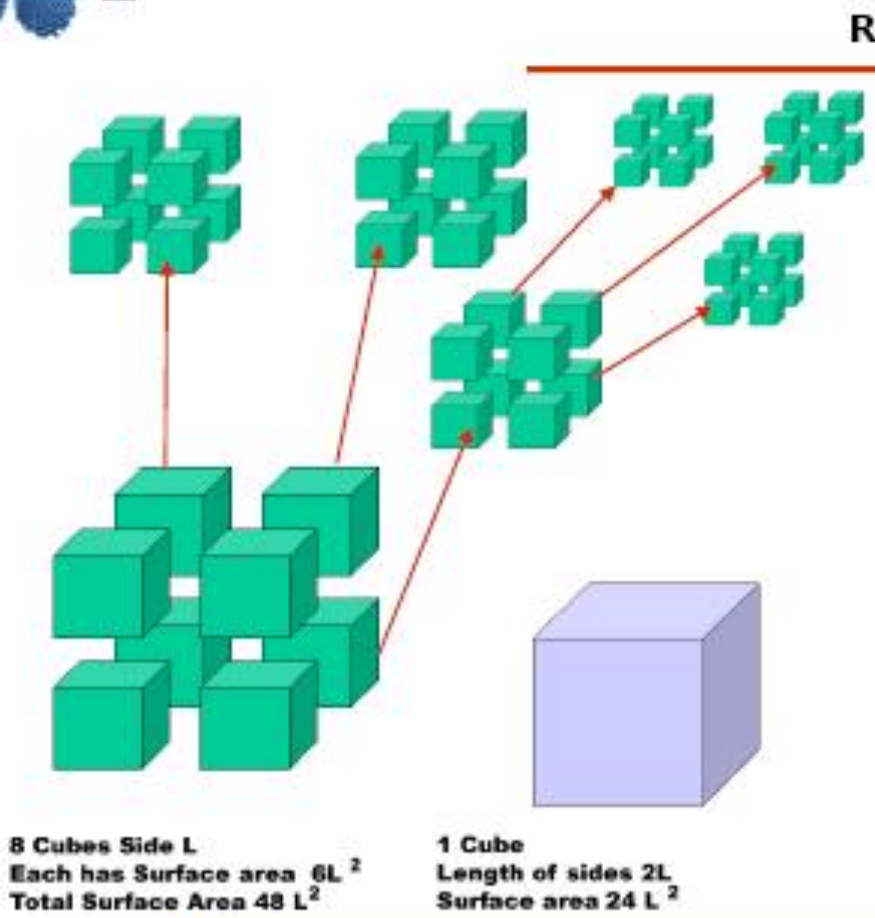


Illustration of the Small Mass: Large Surface Area Paradigm

NATIONAL NANOTECHNOLOGY INITIATIVE

Nanoscale = High Ratio of Surface Area to Vol.



1 g de nanoparticules de 10 nm
10 Millions de Milliards

For example, 5 cubic centimeters - about 1.7 cm per side - of material divided 24 times will produce 1 nanometer cubes and spread in a single layer could cover a football field

Source: Clayton Teague, NNI

http://dspace.unimap.edu.my/dspace/bitstream/123456789/7952/1/An%20Introduction%20And%20Overview.pdf

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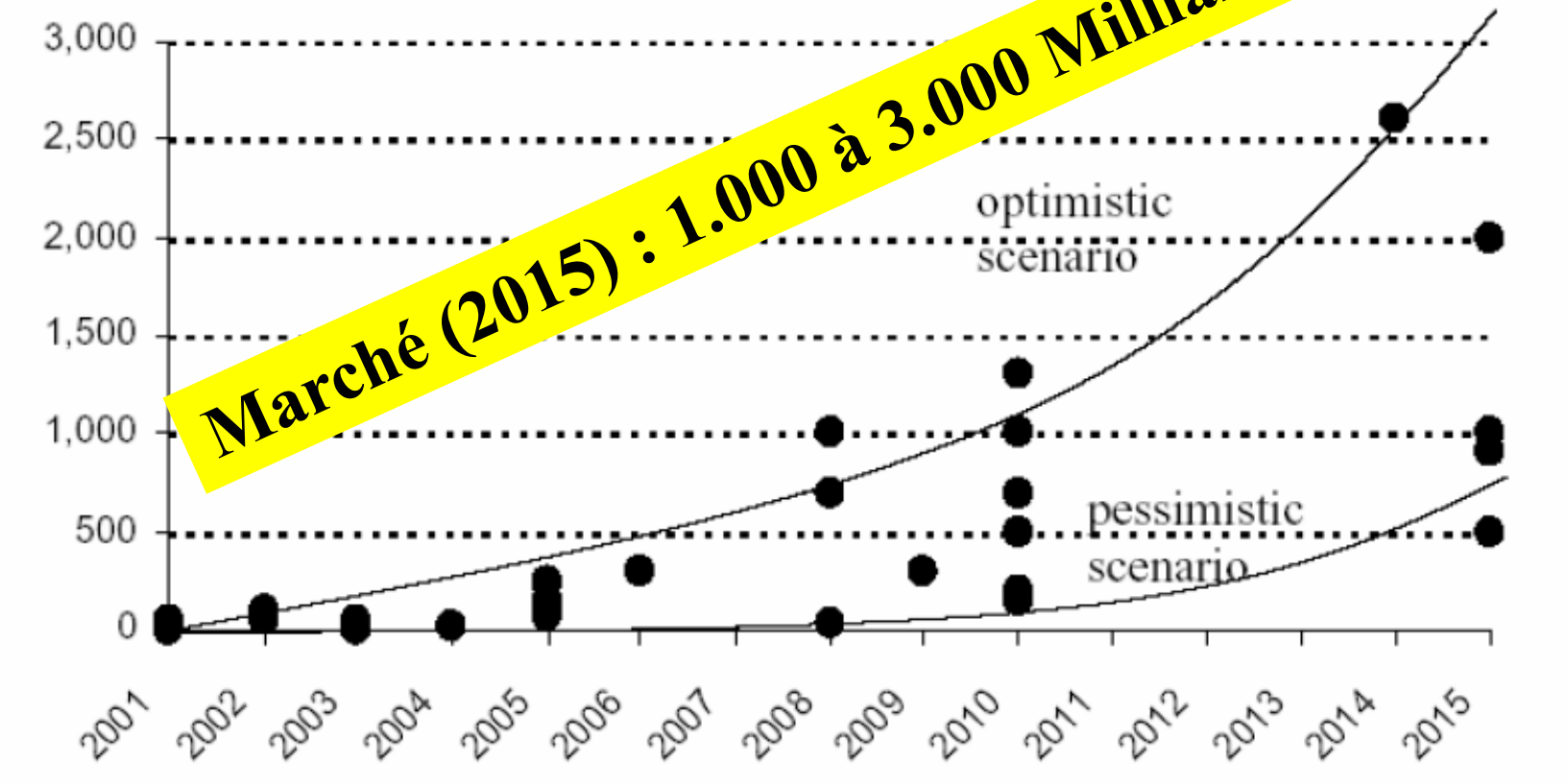
Nanotoxicité

iv) Benefits / Risks analyses

Why Nano?

Significant Growth

Marché (2015) : 1.000 à 3.000 Milliards $



Compiled by Hullman (2006), based on data from German Government, Evolution Capital, NSF, Sal. Oppenheim, DG Bank, DTI, US Nanobusiness Alliance, Cientifica, In Realis, Mitsubishi Research Institute, Deutsche Bank, Nomura Research Institute, BCC, GEMZ corp., Helmut Kaiser Consultancy, and Lux Research

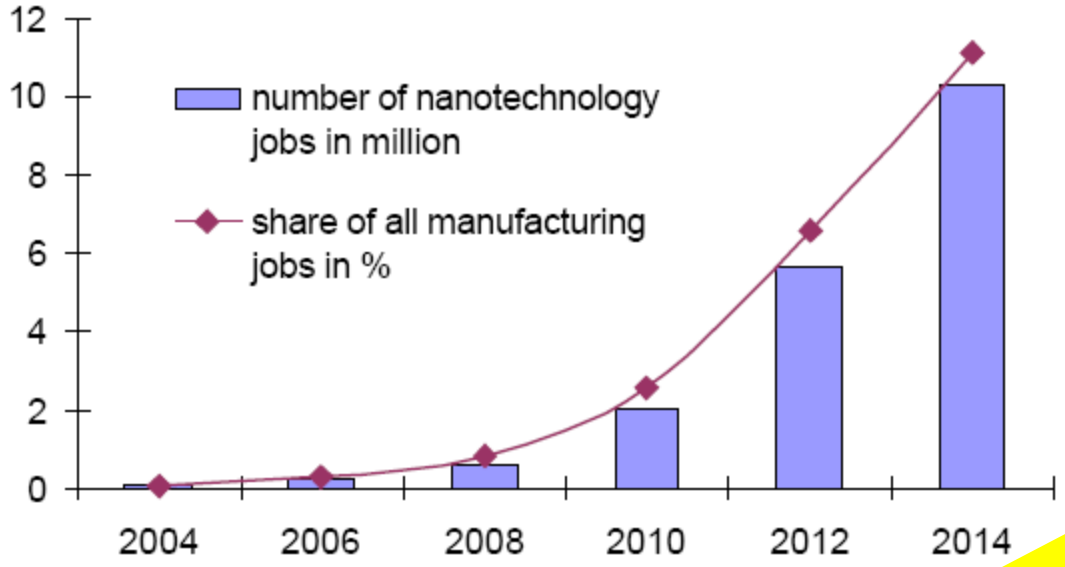
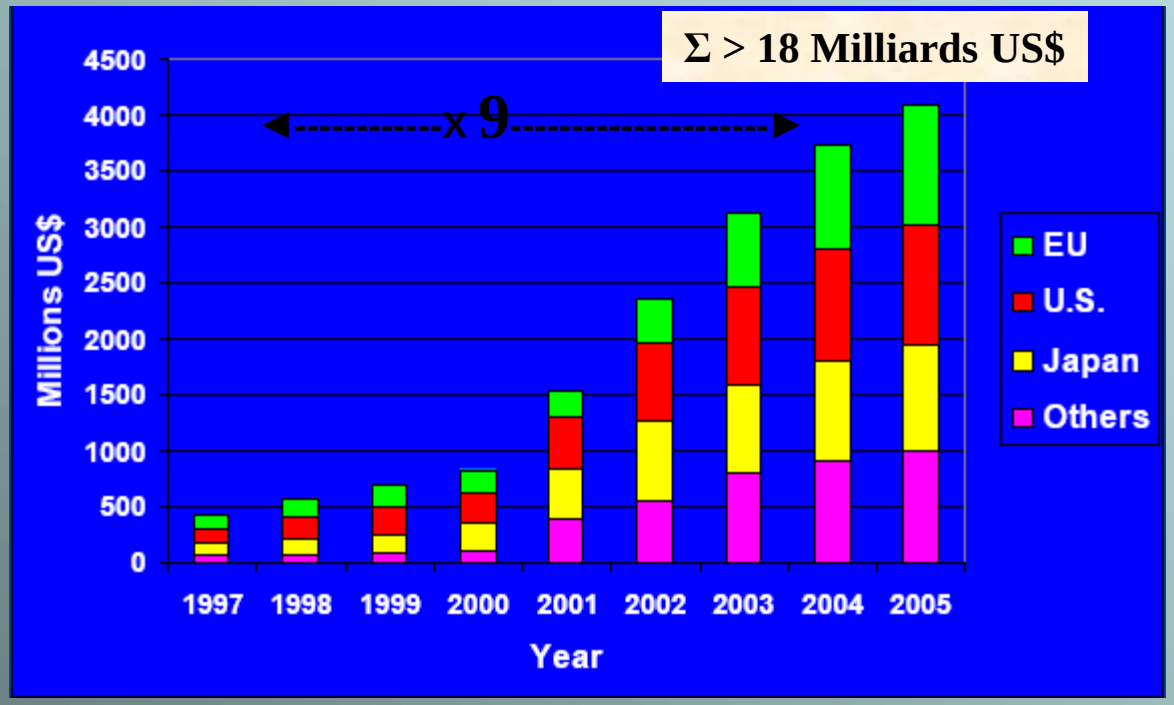


Figure 9: Number of nanotechnology jobs in million and the share … nology jobs of all manufacturing jobs in percent. Source: Lux Research

Many of these jobs will be created in SMEs, but not e… in the past few years, many already well established companies expanded th… logy portfolio to nanotechnology in order to maintain their competitiveness… ains why companies were identified as being nanotech oriented that someti… xisted 100 years ago or even longer. Typical examples are big compani… ical and pharmaceutical industry, optics and electronics (Bayer, BASF …, Agfa-Gevaert, General Electrics, Philips, all created before 1900), thoug… blished companies form a minority in the list of all existing nanotech companies.

2015 : > 10 % Main d' œuvre Secteurs Industriels

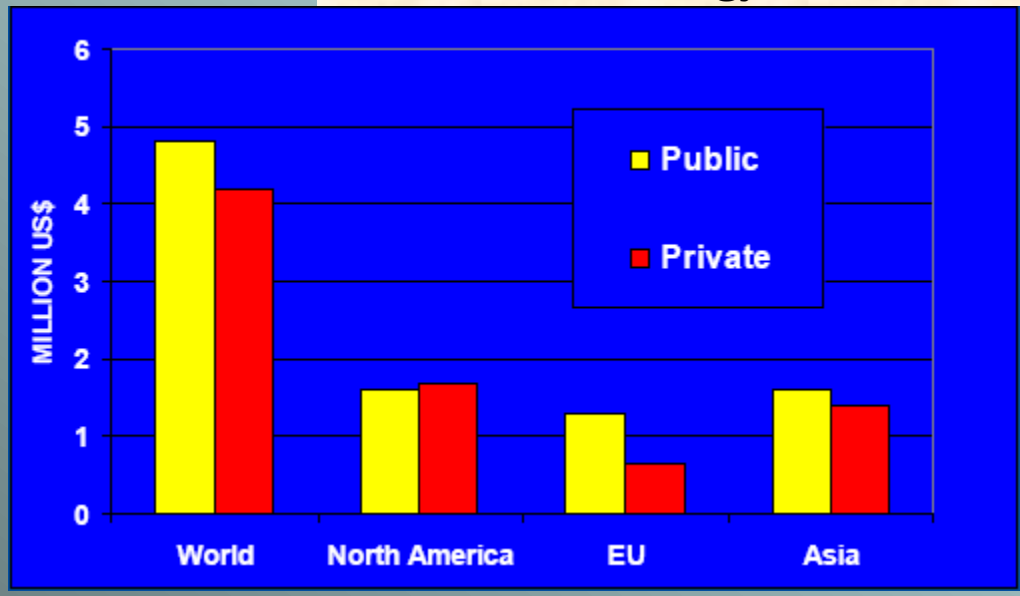
The economic development of nanotechnology-- Angela Hullmann–EC/DG Research 28 Nov. 2006



◄ Estimate of Public Funding for R&D in Nanoscience and Nanotechnology Worldwide (1997 – 2005 / US$ million)

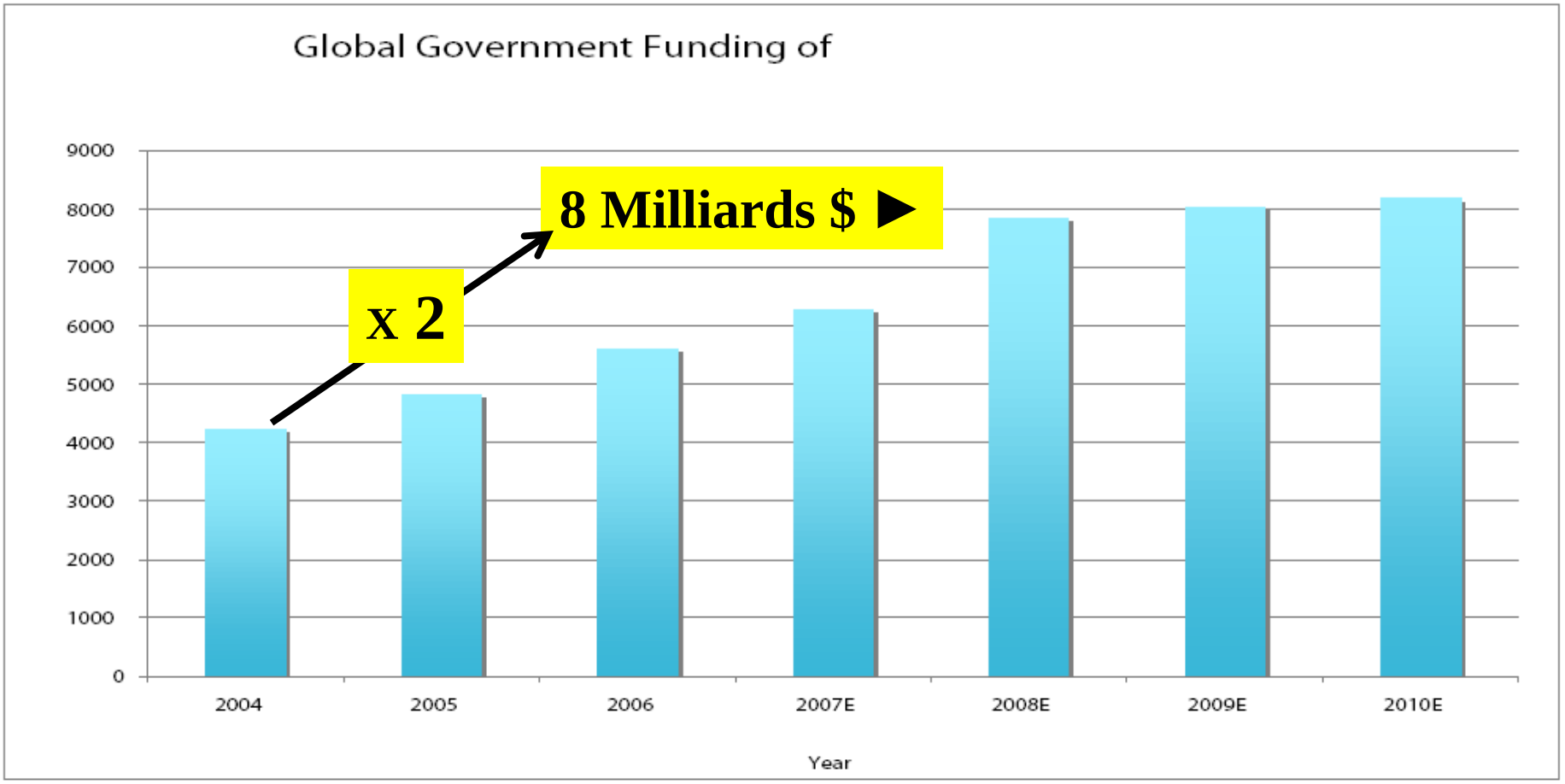
Others include: Australia, China, Eastern Europe, FSU, South Korea, Singapore, Taiwan and other countries with nanotechnology R&D.

Private and Public Private & Public Expenditures Expenditures in 2004 ► *Source*: Lux Research & NSF (public includes national, regional and state funding)



By the end of 2005 governments had sunk eighteen billion dollars (US$18 billion) of taxpayers money into nanotechnology R&D. With an additional six billion dollars (US$6 billion) forecast for 2006, nanotechnologies will then have received the same level of funding in absolute dollar terms as the entire Apollo program

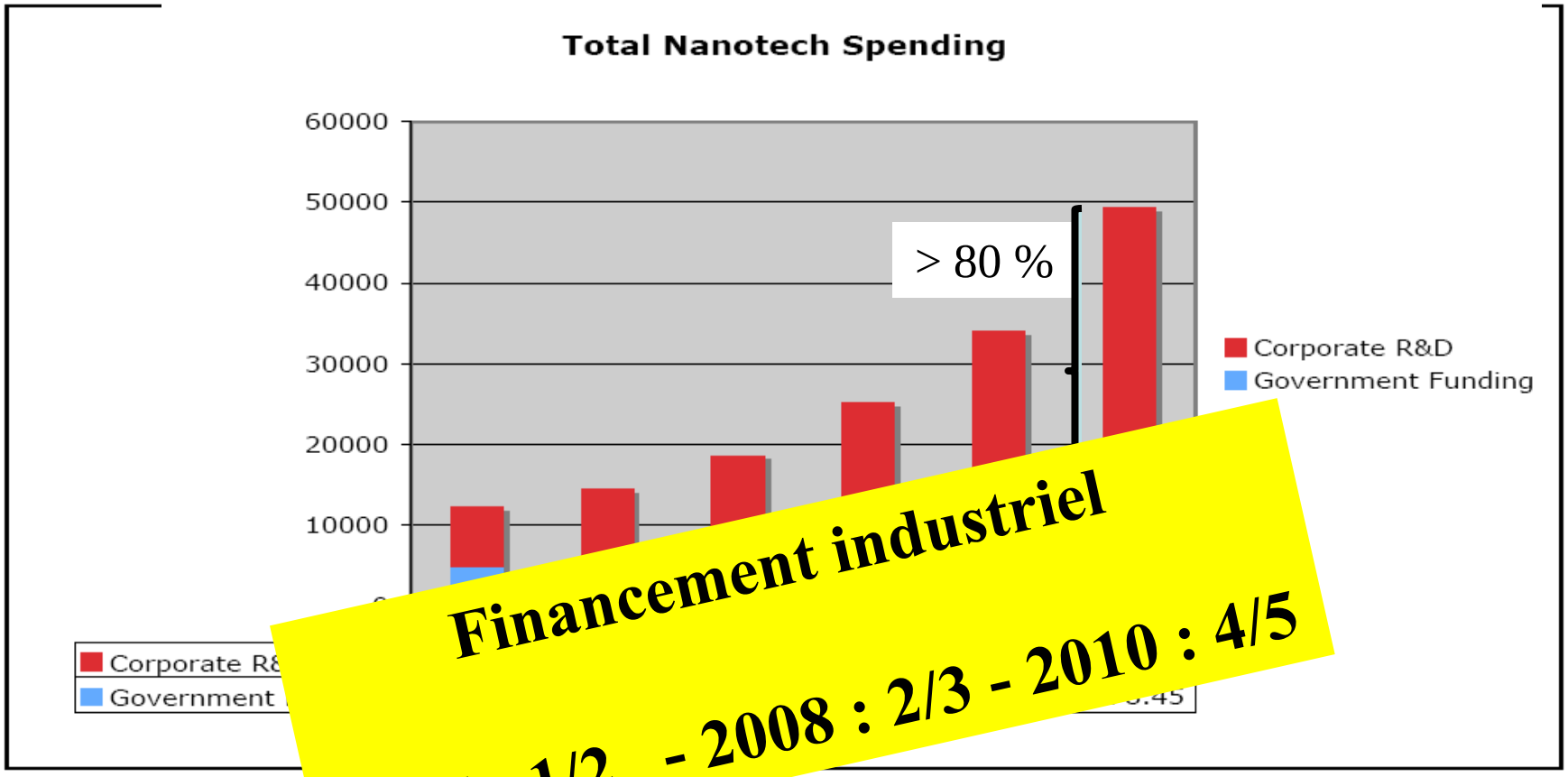
NANOTECHNOLOGY GLOBAL FUNDING (Cientifica – June 2008)



Nanotechnology has attracted more public funding than any single area of technology. On a global basis, governments will spend nearly $8 billion in 2008 on nanotechnology research, with each year seeing a fresh effort by Europe, the US and Japan to outbid the others.

Juin 2008
http://www.cientifica.eu/images/Whitepapers/nor-sample.pdf

NANOTECHNOLOGY GLOBAL FUNDING (Cientifica – June 2008)



Since the last NOR, [illegible]unding has changed dramatically toward corporations taking on a much larger share [illegible] funding of nanotech research. In 2003, we announced that Corporate R&D funding was near the same levels of government funding. By 2005 the ratio had permanently changed and corporations were taking on the lion's share and the difference is only increasing. By our estimates in 2010 of the nearly US$50 billion that will be spent globally on nanotech research and development corporations will be spending over 83% of that amount.

Juin 2008
http://www.cientifica.eu/images/Whitepapers/nor-sample.pdf

Government Investment in Nanotechnology 2009[36]

	% of total	% of total adjusted for PPP*
EU (27 members + FP7)	27%	27%
Russia	23%	25%
U.S.A	19%	16%
Japan	12%	9%
China	10%	18%
Korea	4%	
Taiwan	1%	
India	(<1%)	
Rest of world	4%	

** Purchasing Power Parity*

(Cientifica's 2009 white paper on global funding o… not see the global recession having an imp… ment funding. Cientifica sees the slowd… …from basic research to application-f…

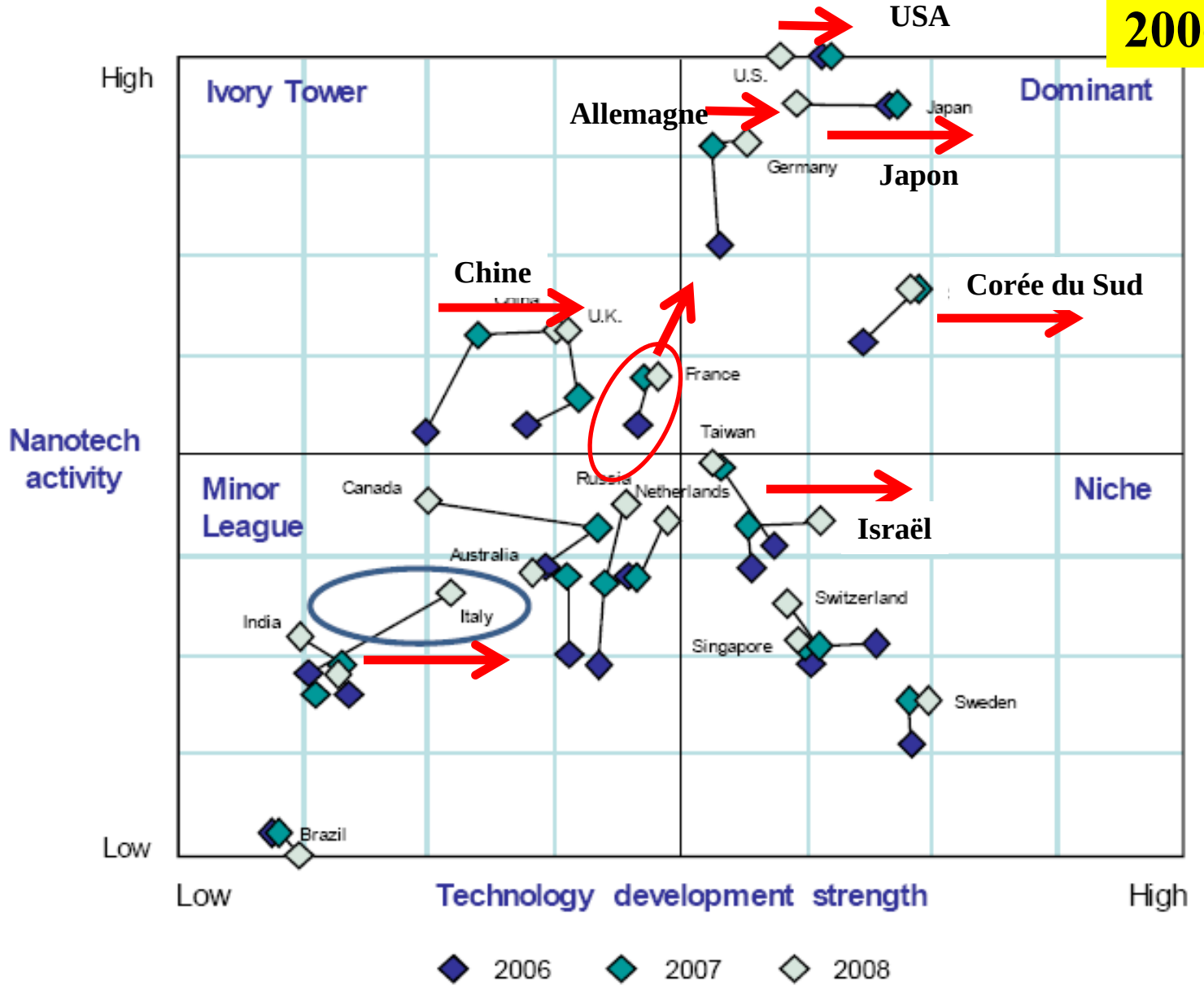
Strong worldwide Competition

Strong Competition

While the U.S., the EU and Japan are still out in front in terms of expertise, infrastructure, and capacity, market analyst firm Cientifica reports that the share of the top three in R&D was just 58% of global R&D spending by governments by 2009, compared with 85% in 2004.

http://www.etcgroup.org/upload/publication/pdf_file/nano_big4web.pdf

2006 → 2008


USA
High
Ivory Tower
Dominant
U.S.
Allemagne
Japan
Germany
Japon
Chine
U.K.
Corée du Sud
France
Taiwan
Nanotech activity
Minor League
Canada
Russia
Netherlands
Niche
Israël
Australia
Switzerland
India
Italy
Singapore
Sweden
Brazil
Low
Low
Technology development strength
High
2006
2007
2008

Projection 2012

► Initiative Nano Innov
Mai 2009 (70 Millions Euros)
► Nano 2012
(2,3 Billions d'Euros R&D)

- **i) Définitions, Markets, Properties, Applications**
  Définitions, Prospectives, Propriétés, Applications

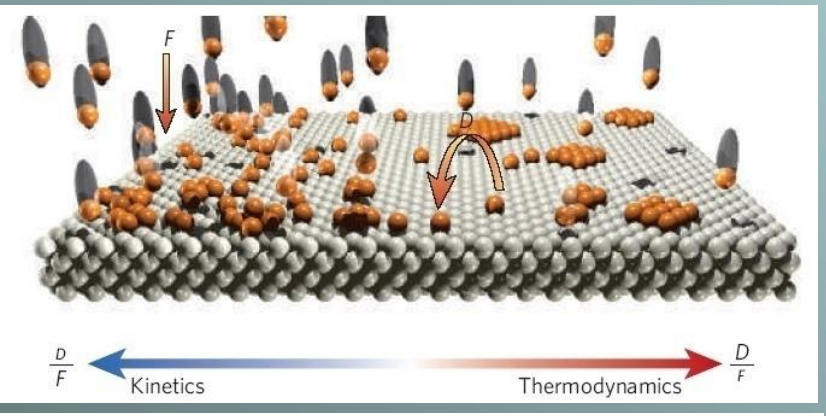
ii) Real Risks, Perceptual Risks, Regulations
Risques réels, perçus, réglementation

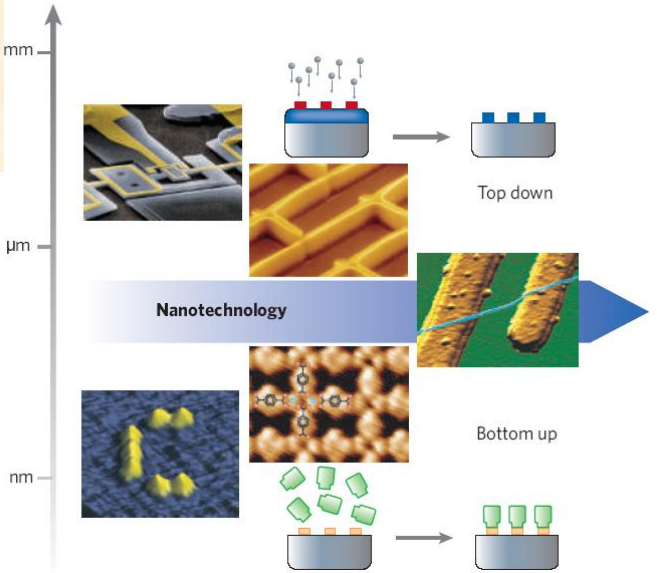
iii) NP Hazard (Eco/Toxicity)
Nanotoxicité

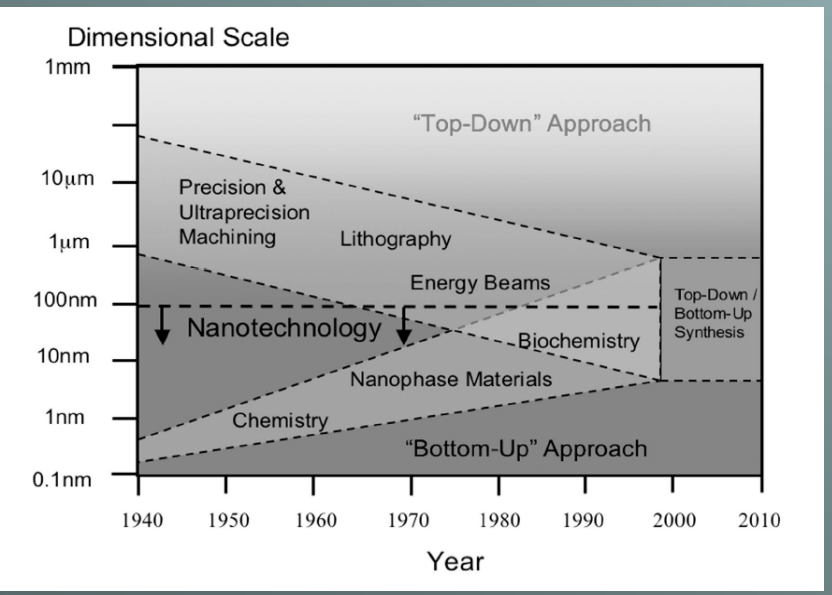
iv) Benefits / Risks analyses

NanoParticules Manufacturées
Manufactured NanoMaterials

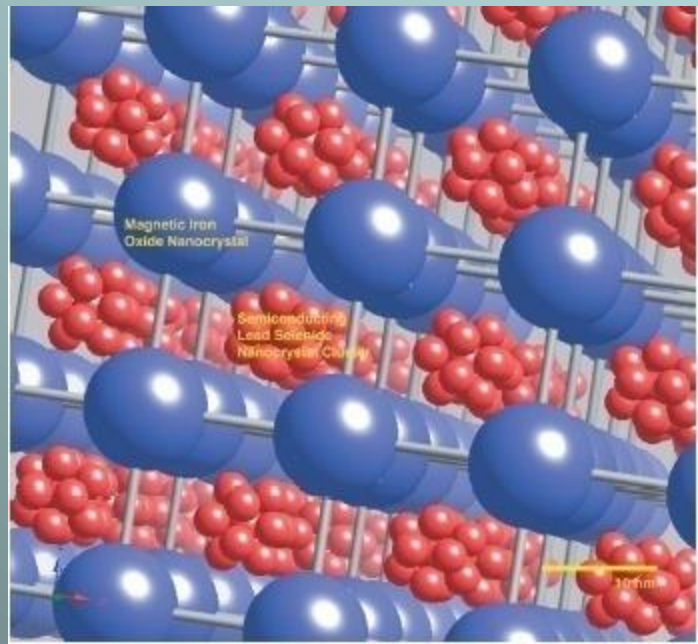
2 Méthodes : Descendante / Ascendante
2 Main Approaches : Top Down / Bottom Up



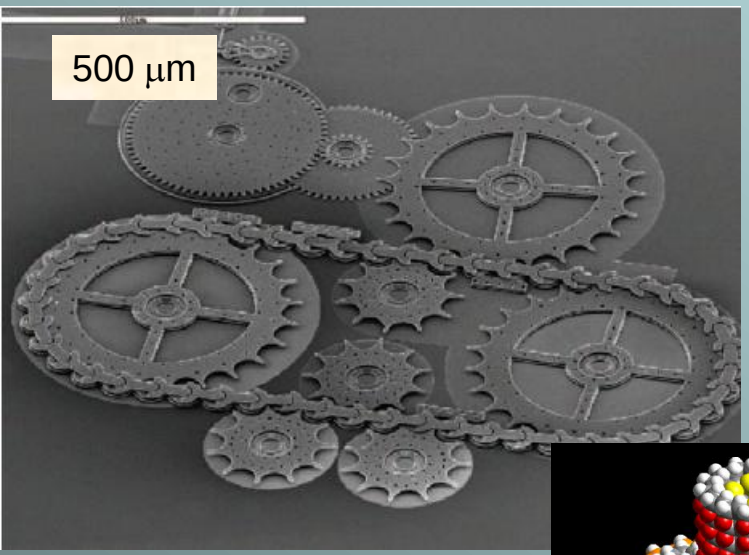


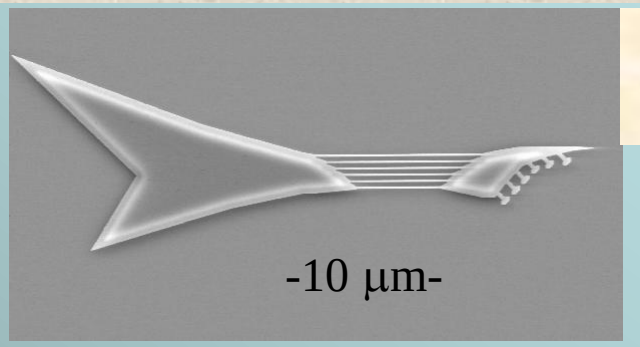


Métasynthèse

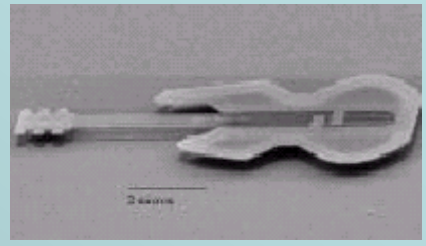


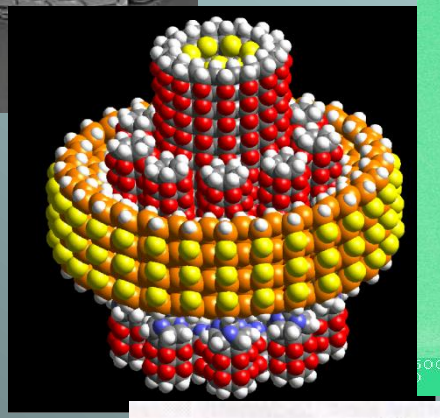
NanoDevices - NanoMachines

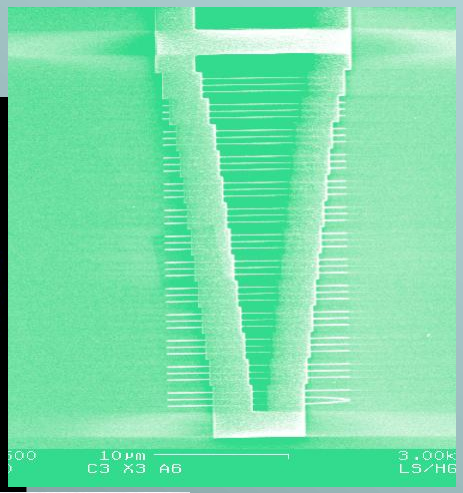


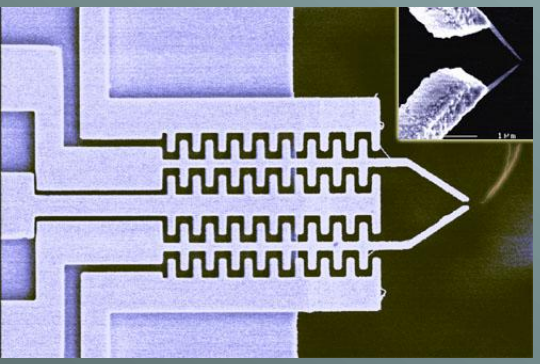


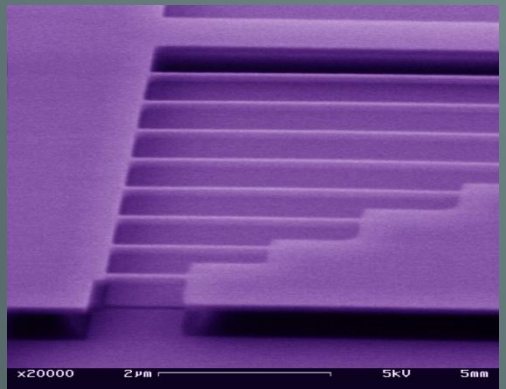
8 octaves / LASER
> seuil audition humaine

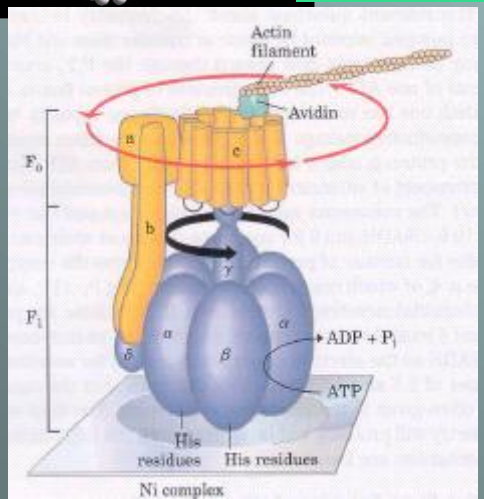


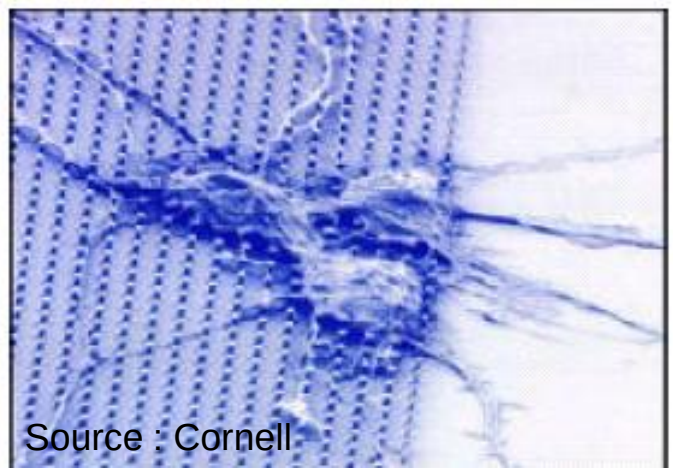




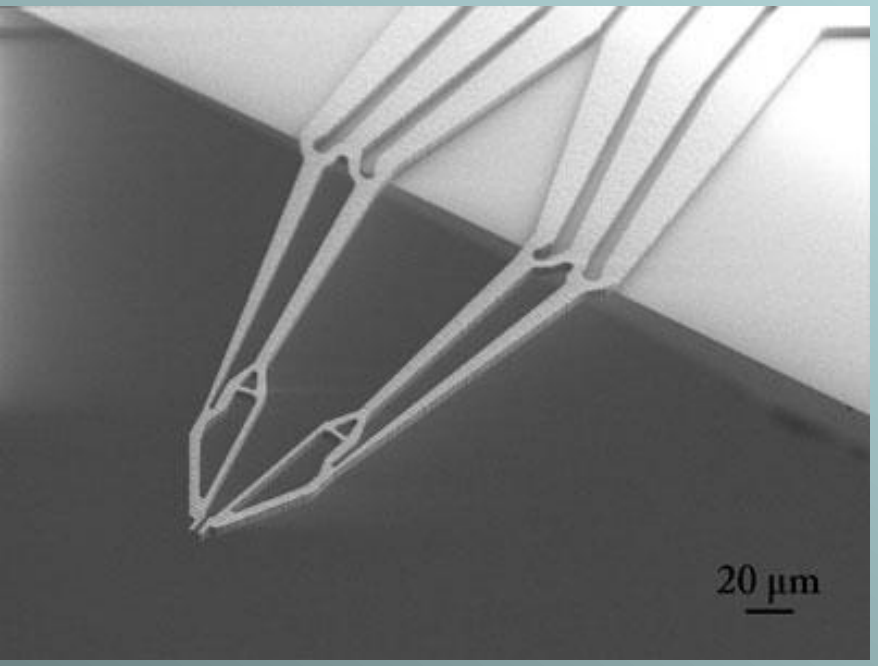


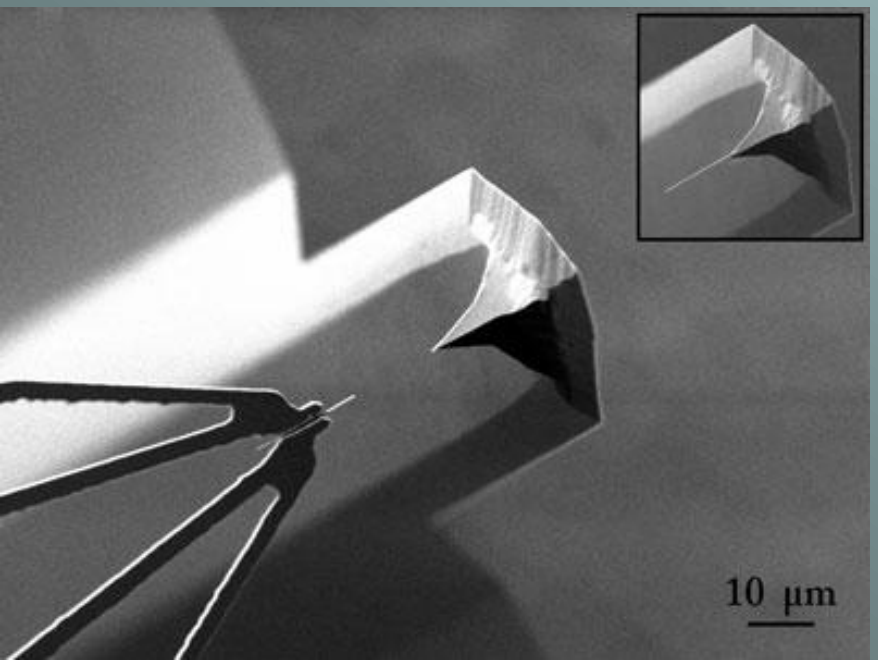




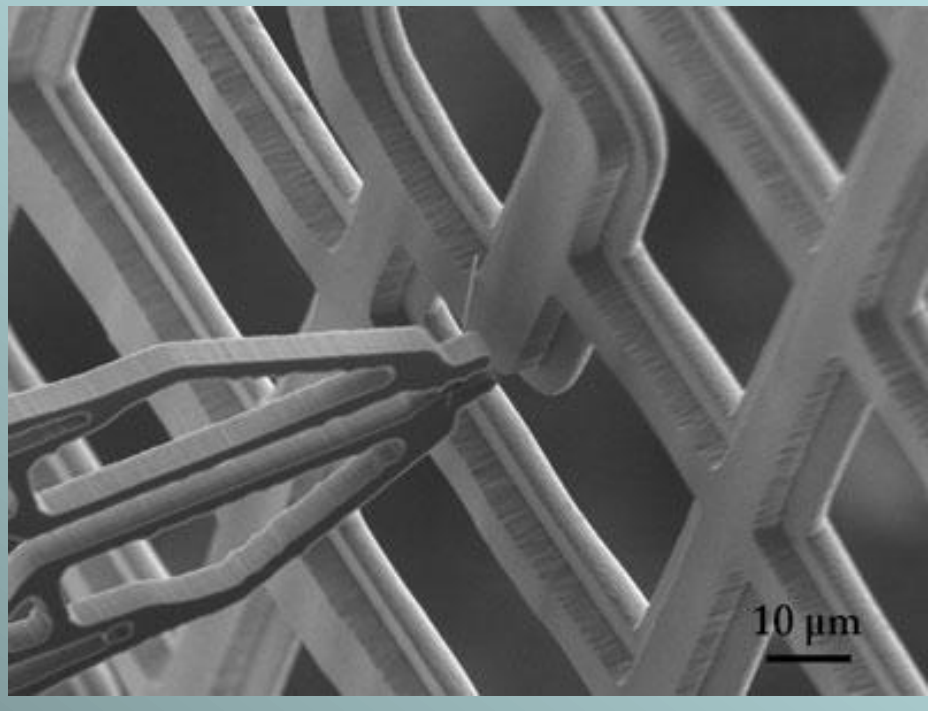


NanoHand





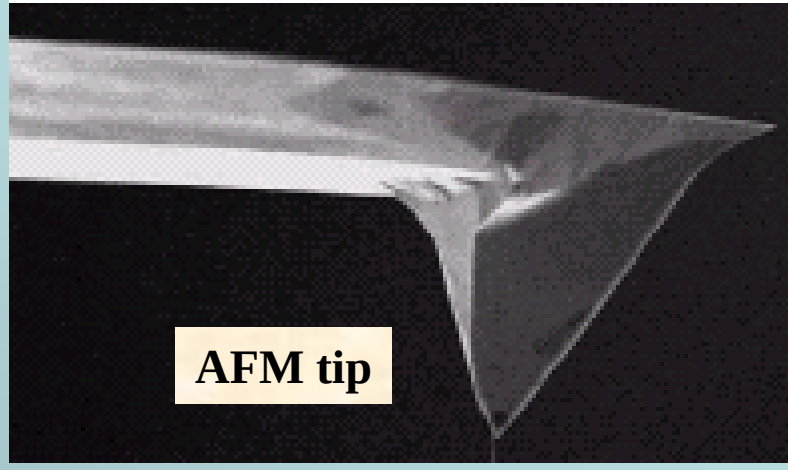
These 'nanogrippers' are not quite down to the level of atomic precision yet, but they're getting a lot closer.



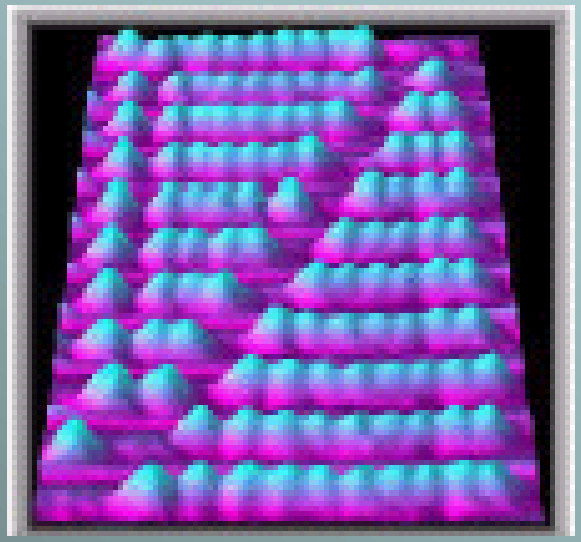
http://crnano.typepad.com/crnblog/atom.xml **(Nov 2008)**

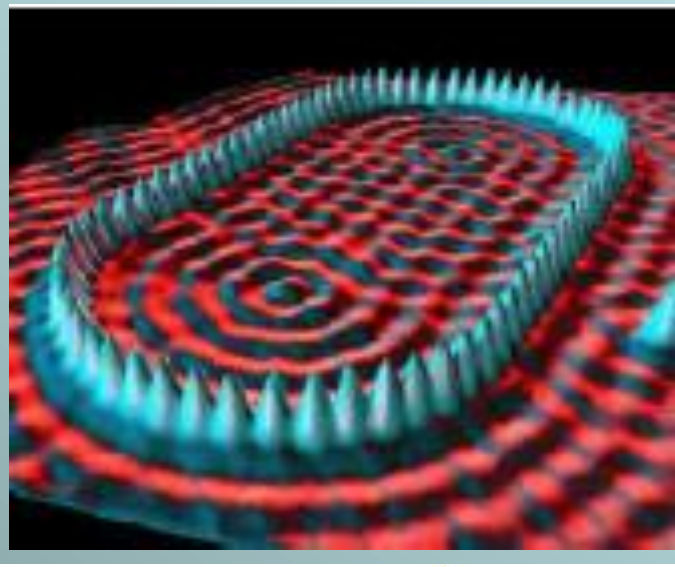
Reproducible assembly of CNT-enhanced AFM super-tips using topology-optimized microgrippers. (Image: Özlem Sardan, DTU)

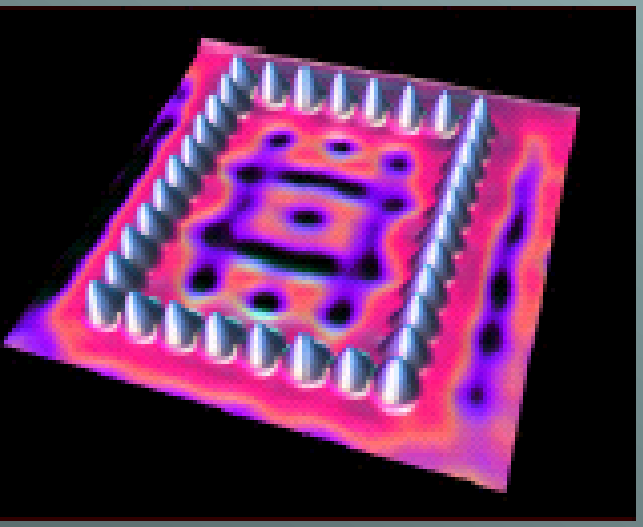
http://www.nanowerk.com/spotlight/spotid=8390.php

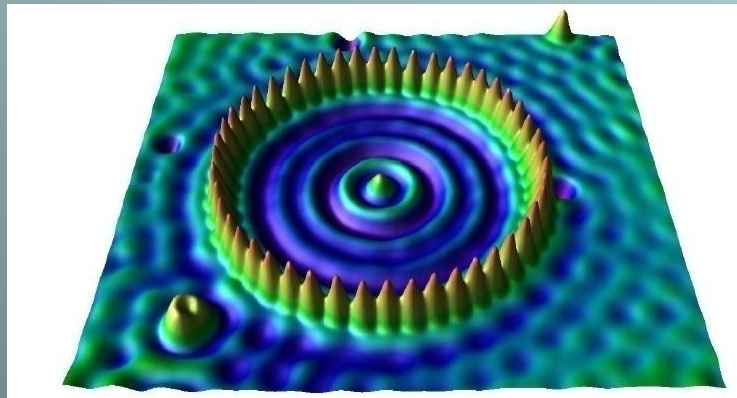


IBM logo spelled out with 35 atoms of xenon (1989)









STM of a square Fe atom corral on a Cu substrate. (Eigler & al. http://www.almaden.ibm.com/vis/stm/corral.html

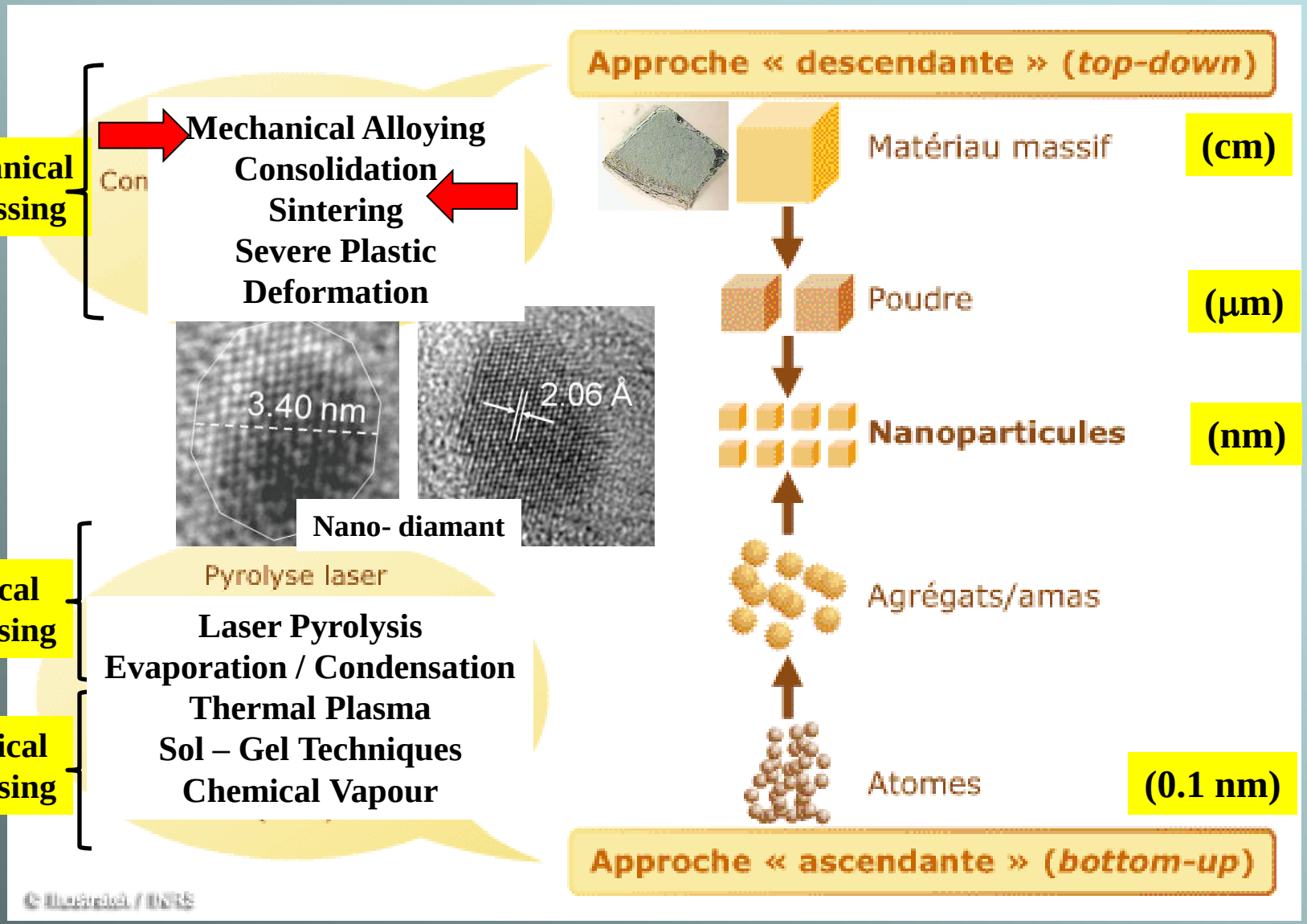
Grey Goo – Gelée Grise (E. Drexler – Engine of Creation 1986)
Assembleurs Moléculaires

Manipulation d'atomes individuels :
10^{-14} g de matière par an,
0.1 mg depuis la création de l'univers
A la conquête du NanoMonde – D. Luzeaux, T. Puig
Editions du Félin - 2007

Individual Atoms Handling

Monde vivant :
Taux d'erreur séquences de protéines : 1 pour mille
Suffisant pour la synthèse organique
Mais 6 à 9 ordres de grandeurs supérieurs pour des composants numériques
(dans une logique binaire !!)
A la conquête du NanoMonde – D. Luzeaux, T. Puig – Editions du Félin - 2007

Why the future doesn't need us – Bill Joy
4 Avril 2000 repris dans Nanoethics : The Ethical and Social Implications of Nanotechnology
Ed. John Wiley & Sons, Inc. – 2007
Genetics – Nanotechnology – Robotics
Self Replication : Even Peptides do it
A 32 amino – acid peptide can autocatalyze its own synthesis…
Stuart Kauffman, Nature (1996)



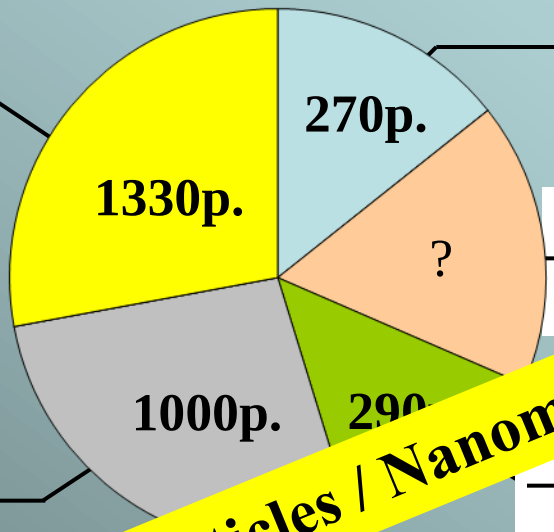
http://www.inrs.fr/inrs-pub/inrs01.nsf/IntranetObject-accesParReference/Dossier%20Nano/$File/Visu.html#ancreGeneralites

France

Nanomatériaux: Industries et Laboratoires en France

Rapport « Nanomatériaux et sécurité au travail » Afsset - 2008

afsset
agence française de sécurité sanitaire de l'environnement et du travail



Silice
(485.000 t)
2 Millions* Tonnes

Terres rares et Argiles
(faible quantités) (380p.)

Alumine
(469.000 t)

Dioxyde de titane
(250.000 t)
2 Millions* Tonnes

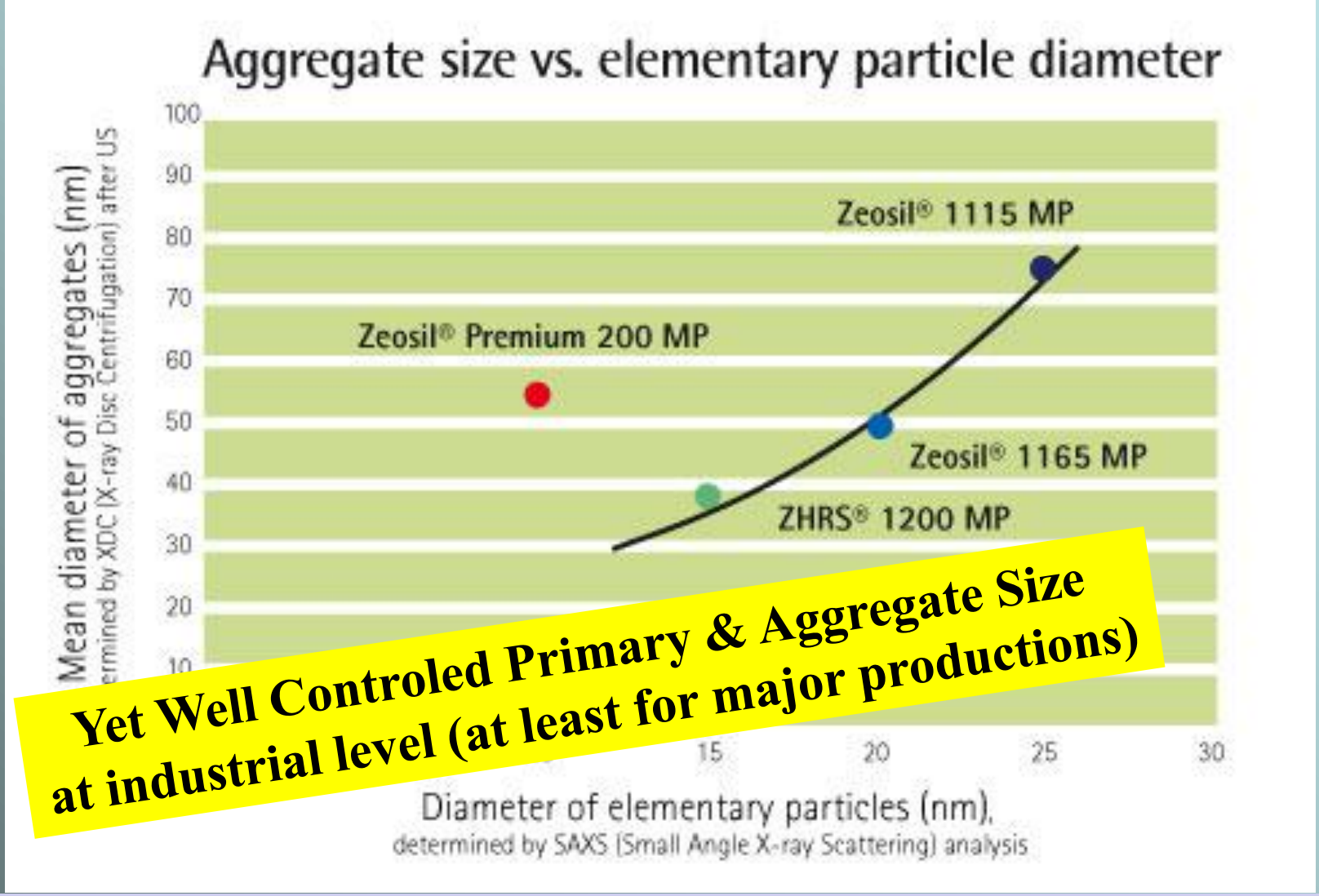
Carbonate de calcium
(300.000 t)

Carbone
(240.000 t)
10 Millions* Tonnes

Yet Mass Productions of Nanoparticles / Nanomaterials

- **Estimation du personnel de production potentiellement exposé dans les entreprises: 3.300**
- **Estimation du personnel potentiellement exposé dans les laboratoires: 7.000**

*** Worlwide Production**



Yet Well Controled Primary & Aggregate Size at industrial level (at least for major productions)

Cutting edge silica technology with unique performance

Zeosil® Premium is the first generation of high surface silicas which combines easy dispersibility, excellent reinforcement and low hysteretic properties.

Zeosil® Premium offers unique performance, resulting from a new compromise between silica aggregate and elementary particle size (Specific Surface Area).

http://www.rhodia-silicas.com/markets/zeosil.htm

- **i) Définitions, Markets, Properties, Applications**
  Définitions, Prospectives, Propriétés, Applications

ii) Real Risks, Perceptual Risks, Regulations
Risques réels, perçus, réglementation

iii) NP Hazard (Eco/Toxicity)
Nanotoxicité

iv) Benefits / Risks analyses

NanoMaterials « Historics »

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 in glass

Silver in glass

25 nm Sphere

100 nm Sphere

100 nanometers = 0.0001 millimeter

200 nm

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:

50 nm Sphere

40 nm Sphere

100 nm Sphere

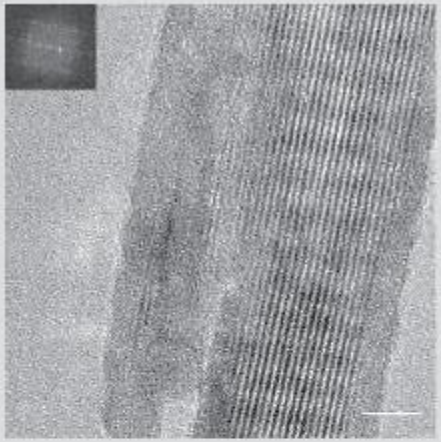
100 nm Prism

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

*Approximate

Source : D.H. Marcero
AF&PA Committee week
May 2006

Carbon nanotubes in an ancient Damascus sabre



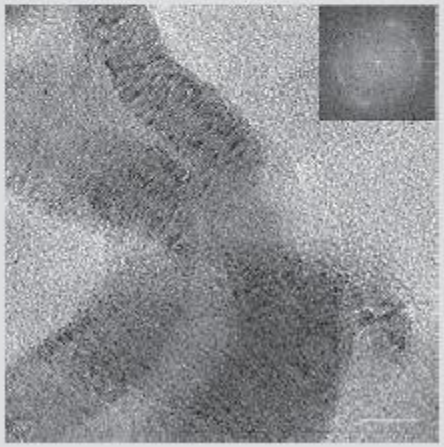


Figure 1 | High-resolution transmission electron microscopy images of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid. **a**, **b**, Multiwalled tubes with the characteristic layer distance $d \approx 0.34$ nm (ref. 12), as indicated by the Fourier transforms (see insets). Scale bars: 5 nm (**a**) and 10 nm (**b**). In **b**, the tubes are bent like a rope. **c**, Remnants of cementite nanowires encapsulated by carbon nanotubes, which prevent the wires from dissolving in acid. Scale bar, 5 nm. The fringe spacing of the wire is 0.635 nm, taken from the Fourier transform (inset), and is attributed to the (010) lattice planes of cementite.

By empirically optimizing their blade-treatment procedure, craftsmen ended up making nanotubes more than 400 years ago.

M. Reibold, P. Paufler, A. A. Levin, W. Kochmann, N. Pätzke, D. C. Meyer
NATURE-Vol 444-16 November 2006

"Nano before Nano was cool!"

Particle size between 4 and 20 millimicron

- Manufacturer of a Variety of High Surface Area Materials:
  - Silica, alumina, titania, zircon
    ceria, and "hydrophobic"
    grades
  - Used in rh
    reinf
- Th
  Chemistry
  Oxford English
  ary for "Nano" is 1947
  after commercialization of AEROSIL®

nano – Silice

Depuis Avril 1949 par Degussa (Evonik en 2008)

"Farbe & Lacke" April 1949

American Chemistry Council

Silver Nanotechnology Working Group (SNWG)

The SNWG provided the SAP meeting with a detailed historical and technical analysis that demonstrated that these materials have a long established commercial history as engineered particles of nanoscale size.[1] Despite changes in terminology, the underlying material being described is in fact the same that has been used for decades. i.e. nanoscale silver.

A careful examination of the EPA public registration database for silver over a period of 6 decades reveals:

- **The very first registered silver product was a colloidal nanosilver algaecide product that has been safely used by millions of consumers for over 50 years (registered since 1954).**

- **Every EPA silver registration between 1970 and 1990 was either a colloidal nanosilver or nanosilver-composite product.**

- **The very first NON-nanosilver product registered by EPA was not registered until 1994.**

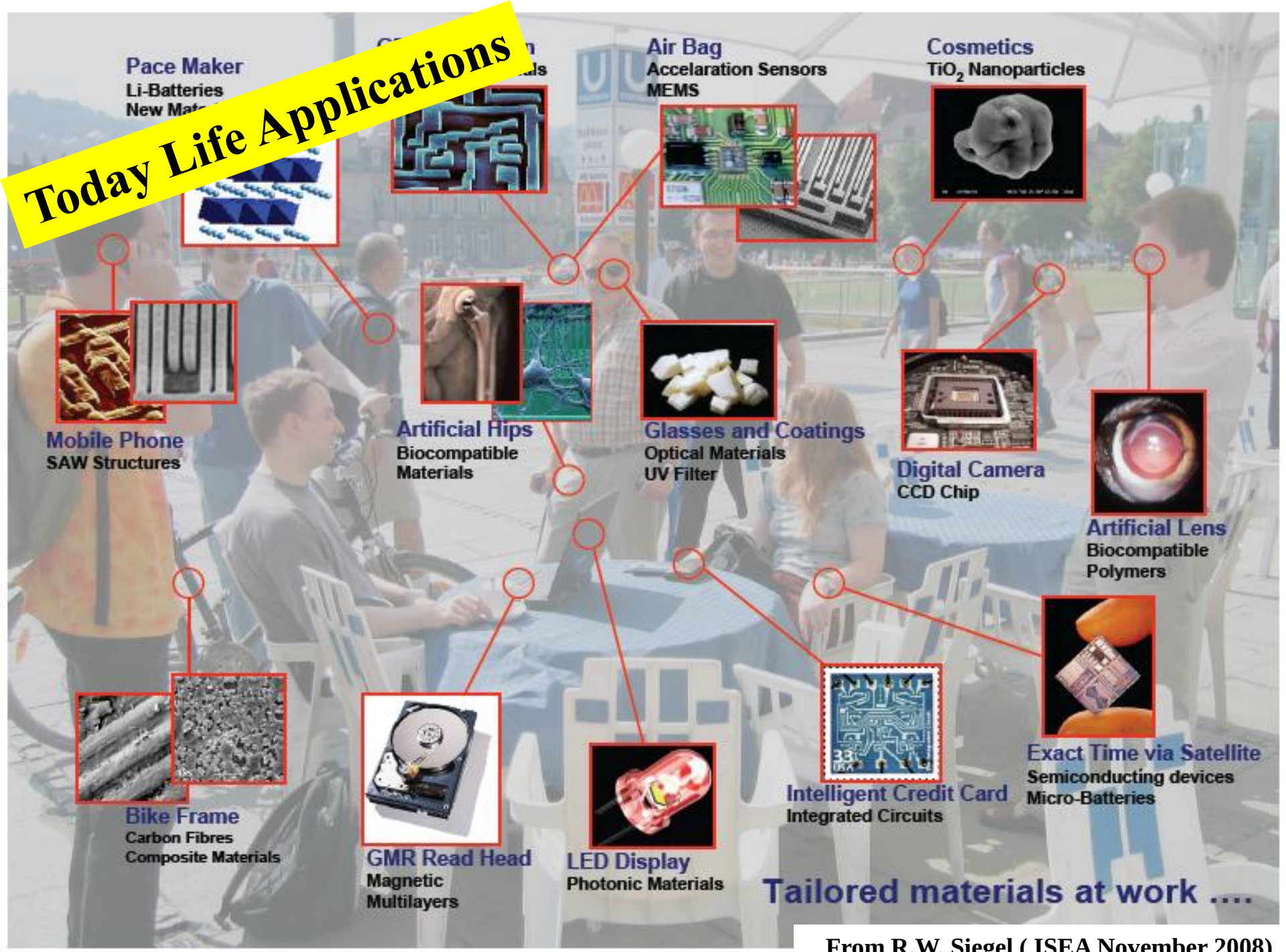
- **An overall analysis reveals that today over 50% of all EPA registered silver products are in fact based on nanoscale silver.**

http://www.silverinstitute.org/images/stories/silver/PDF/snwgpr09.pdf

Today Life Applications

From R.W. Siegel (ISEA November 2008)

Today Life Applications



From R.W. Siegel (ISEA November 2008)

AEROSIL et Sipernat pour l'industrie alimentaire

Sipernat® : silices et silicates synthétiques <u>précipitées</u>, amorphes
AEROSIL® : silices synthétiques <u>pyrogénées</u>, amorphes
(Degussa /Evonik)

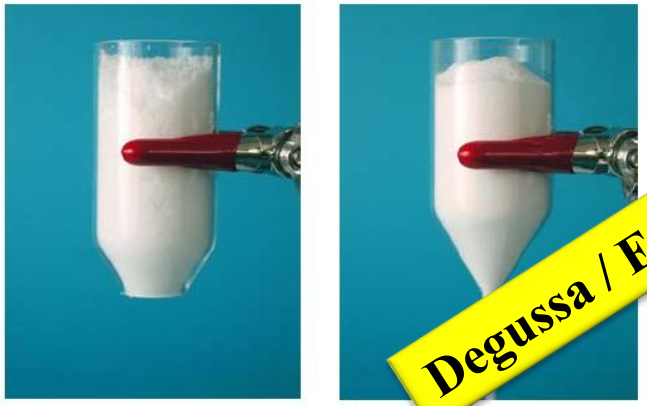


Figure 3: Sel marin avant et après addition de silice.

- Cacao en poudre
- Caséinates
- Hydrolysats de protéines végétales
- Lacto-sérum
- Mélanges pour salaisons
- Paprika en poudre
- Piment en poudre
- Potages en poudre
- Poudre d'ail
- Poudre d'oignon
- Poudres de fruits
- Poudre de tomate
- Poudre pour boisson instantanée
- Sucre en poudre

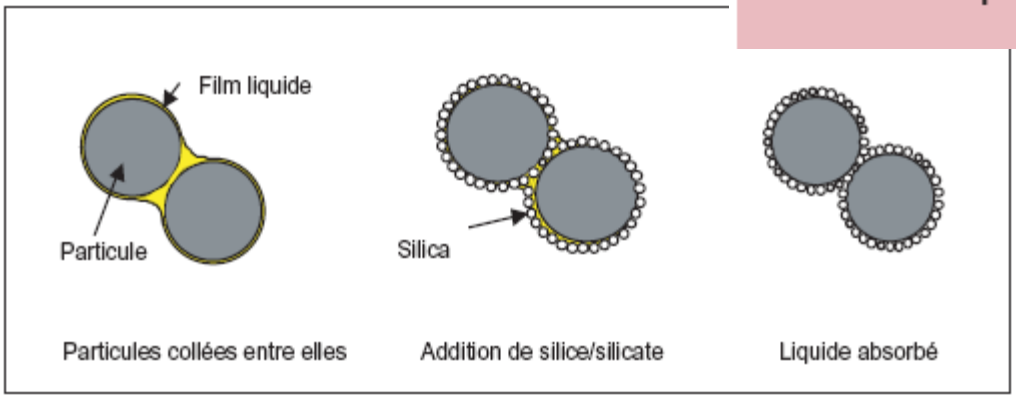


Figure 1 : Action des silica comme agent d'écoulement des poudres

Quantification of total silica and nanosilica in food products

Code	Product description	total silicon in mg/g	total silica* in mg/g	nanosilica in mg/g (50-200nm)	percentage silica in nano-form
F1	Mix for lasagne sauce	2.5	5.4	0.3	5 %
F2	Instant noodles	-	-	<0.1	-
F3	Minced meat seasoning mix	1.2	2.6	0.2	7 %
F4	Pancake mix	1.3	2.8	<0.1	<4 %
F5	Instant asparagus soup	0.3	0.6	0.2	33 %
F6	Spicy pepper rub	0.5	1.1	<0.1	<12 %
F7	Sweets sticky rub	2.8	6.0	0.4	7 %
F8	Steak house rub	2.0	4.3	0.2	4 %
F9	Roasted vegetable rub	2.3	4.9	0.6	12 %
F10	Sea food rub	2.2	4.7	0.5	11 %
F11	Burrito seasoning mix	3.3	7.1	0.3	5 %
F12	Coffee creamer (brand a)	2.4	5.1	1.0	19 %

* Total silica (SiO_2, molecular weight 60 g/mol) was calculated from the total silicon content (Si, molecular weight: 28 g/mol) by multiplying with 60/28.

rivm

S. Dekkers et al. – Nanotoxicology (2010)

Food Packaging

http://www.co-nanomet.eu/content/co-nanomet/ENF09%20Workshop/Johnstone%20Presentation.pdf

Augmentation de la durée de conservation

Diminution des pertes & Importations d'origine lointaine, hors saison

Strawberries in a conventional food container (upper row) and nano-silver container (lower row). (Test series and pictures: The Innovation Society Ltd.)

http://www.nanowerk.com/news/newsid=9292.php

Nano (?) Particle Film Technology → Edible Packaging

Peaches, plums, apples, cherries, apricots, pears and nectarines usually need at least two sprays of Surround after the flower petals fall off the tree and two weeks later. These timely sprays will keep worms and/or larvae such as plum curculio, oriental fruit moths, and codling moths from your fruit. Surround protects with a cover of clay that prevents insects from laying eggs on your fruit. This spray is a … celebration for gardeners who wish to grow organically delicious … in the Roseacious family. It works on Japanese Beetles, …

It's actually edible! OMRI listed … Review Institute (OMRI) is a … input products are … Listed or … und… Agen… Surro… dry b… group … **… parsley and spinach) in Canada.**

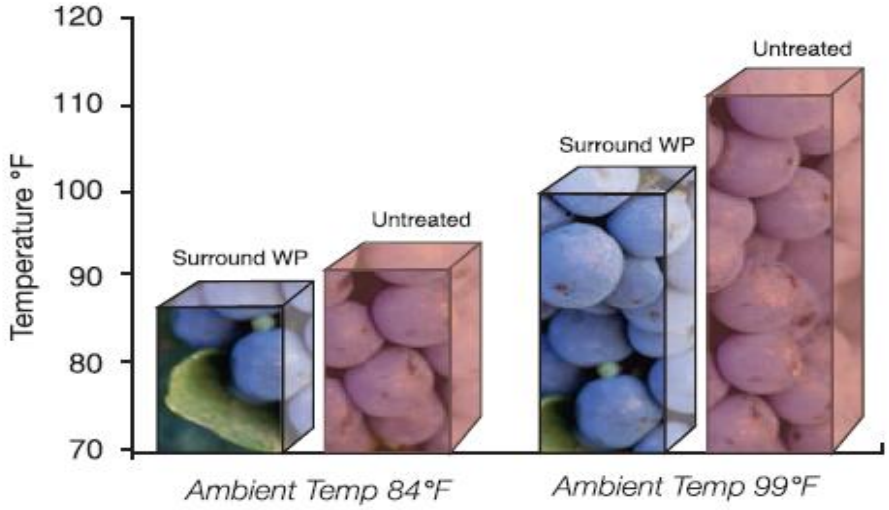
Surround ® WP Organic Spray (// Laponite)
Suppression Pesticides / Insecticides « Chimiques »
Augmentation Rendement (20%)
Suppression des multi – emballages (réduction des déchets)

http://www.eat-it.com/plants.php?func=view&id=261

http://attra.ncat.org/attra-pub/PDF/kaolin-clay-grapes.pdf

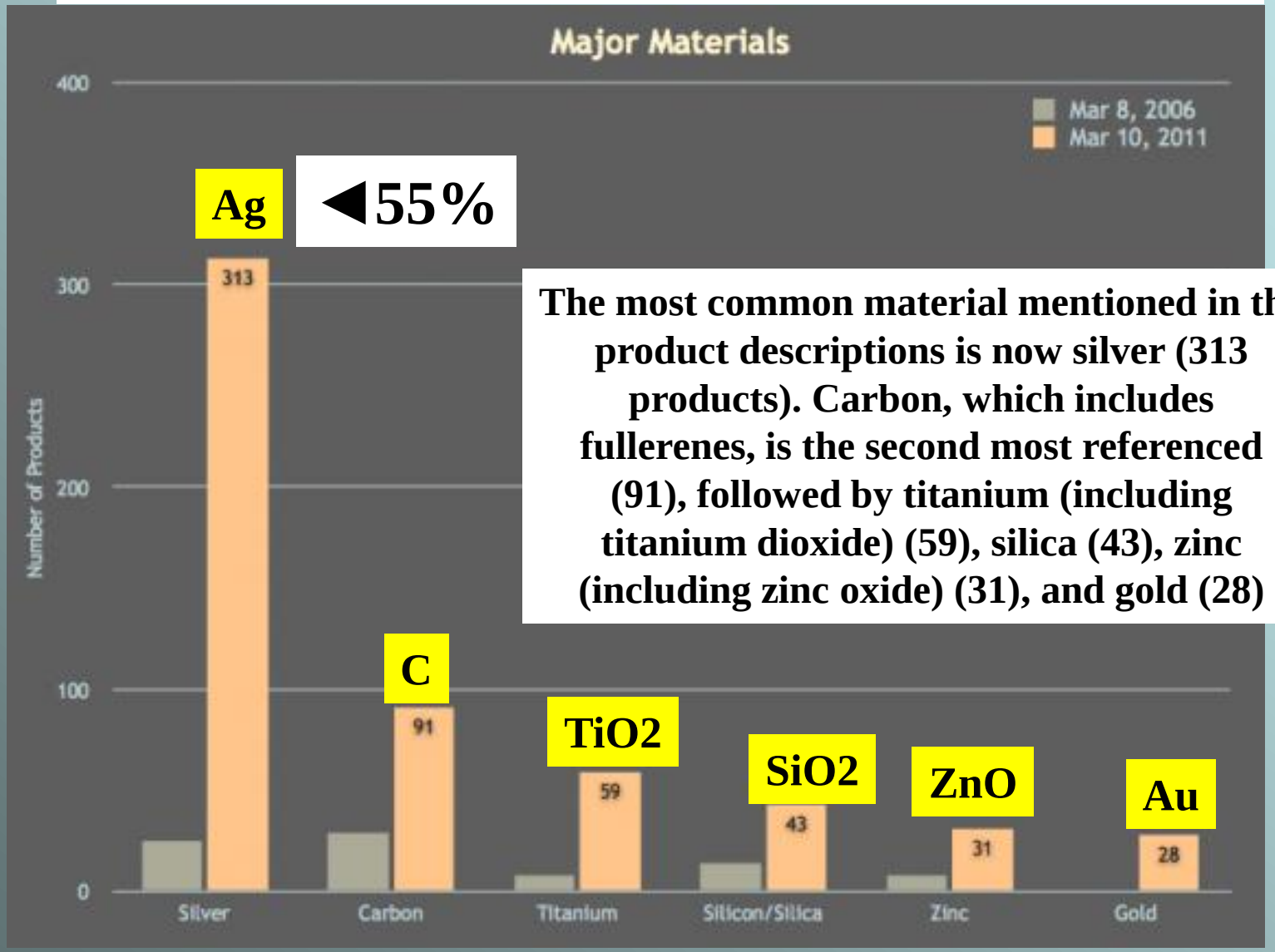
http://www.orfeteknik.com.tr/MyNewDir2/pdf/US.grape.brochure.pdf

The … ect of Surround® on Grape Leaf Temperature




Yet on the Market
➢1.317 NanoProduits (Woodrow Wilson Institute – updated in March 2011)
➢9,509 products (Cosmetic (Environmental Working Group – 2006)
➢526 Produits Nano- Argent (http://www.ec21.com/ec-market/nano_silver.html)
➢ 2.200 NanoParticules (w3.nanowerk.com)
➢150 Milliards $ en 2007 (Emballages alimentaires 4 Milliards $ en 2008)
TiO2
ZnO
TiO2
nClay
TiO2
Clay
Ag
nC
nClay
Franz Ziener Jacket
TiO2
TiO2
nTC
Ag
nTC

Numbers of products associated with specific materials



The most common material mentioned in the product descriptions is now silver (313 products). Carbon, which includes fullerenes, is the second most referenced (91), followed by titanium (including titanium dioxide) (59), silica (43), zinc (including zinc oxide) (31), and gold (28)

10 March 2011
http://www.nanotechproject.org/inventories/consumer/analysis_draft/

Europe / Octobre 2010 - ANEC – BEUC Inventory

Categories	Number of products investigated	Percentage
APPLIANCES	27	5,68
AUTOMOTIVE	72	15,16
CROSS CUTTING	66	13,89
ELECTRONIC & COMPUTERS	6	
FOOD & DRINK	27	
PRODUCTS FOR CHILDREN		
HEALTH & FITNESS		41,89
HOME & GARDEN		12,63
TOTAL	475	

NGO's Inventory - ONLY !!
(No State Agency Inventory)

Categories/Sub categories	Number of products investigated	Percentage
APPL	27	5,68
1.	25	5,25
	2	0,42
TIVE	72	15,13
aintenance & Accessories	72	15,13
CROSS CUTTING	66	13,87
1.Coatings	39	8,19
2. Others	27	5,67
ELECTRONIC & COMPUTERS	6	1,26
FOOD & DRINK	27	5,67
1.Supplements	25	5,25
2. Others	2	0,42
PRODUCTS FOR CHILDREN	18	3,78
HEALTH & FITNESS	199	41,81
1.Clothing	36	7,56
2.Personal care	136	28,57
3.Sporting goods	27	5,67
HOME & GARDEN	60	12,61
1.Cleaning	28	5,88
2.Construction materials	11	2,31
3.Others	22	4,62
TOTAL	**475**	

Results

From this updated inventory, we can see the following trends:

- While the number of products claiming to contain nanomaterials that we found increased considerably (475 in 2010 / 151 in 2009), the proportion of products per category stayed basically the same, with health and fitness products topping the chart.

- Most of the products available in 2009 are still available in 2010 as only 4% of products we investigated are not available anymore.

- Some of the nano-claims relating to a specific product can be found on an online shop, while they are absent from the website of the brand itself.

These trends are not necessarily a general rule and apply only to the products that we found.

http://www.euractiv.com/en/food/nanotech-presence-consumer-goods-growing-news-499152
http://pr.euractiv.com/press-release/anecbeuc-inventory-exposes-game-roulette-16047
http://www.anec.org/attachments/ANEC%20BEUC%20leaflet%20on%20nano%20inventory_How%20much%20nano%20do%20we%20buy.pdf

Laponite (Rockwood Company)

One Particle : Multiple uses on market

Figure 1. Schéma d'un film de Laponite

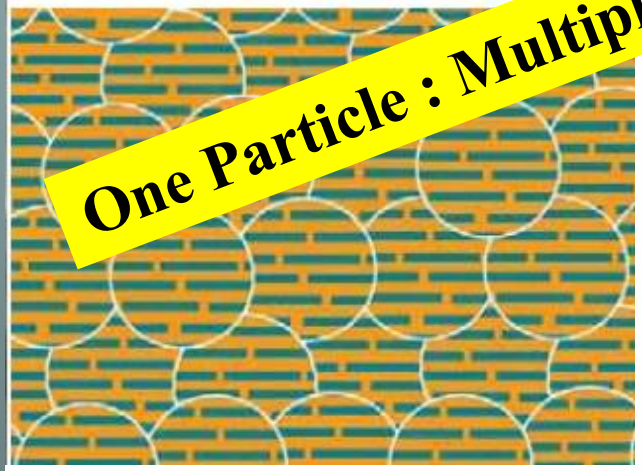


Figure 1. Schéma d'un domaine de Laponite

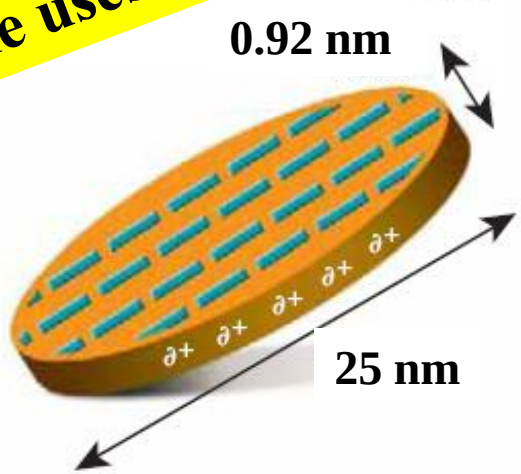


Figure 1. Diagramme de production

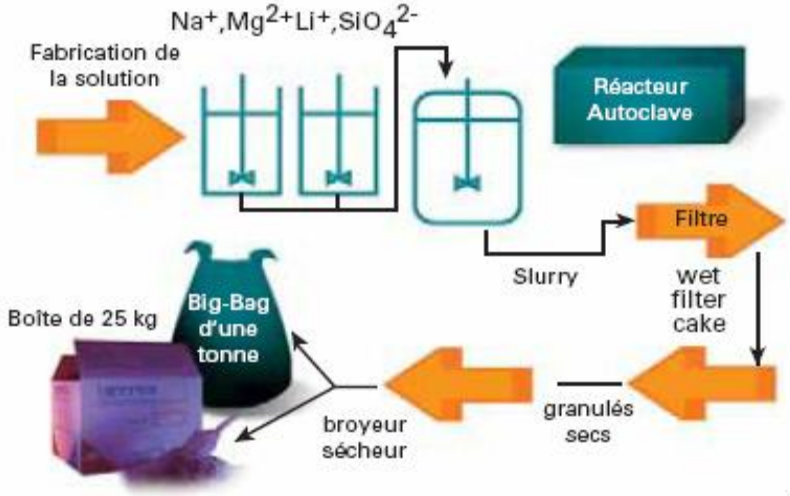
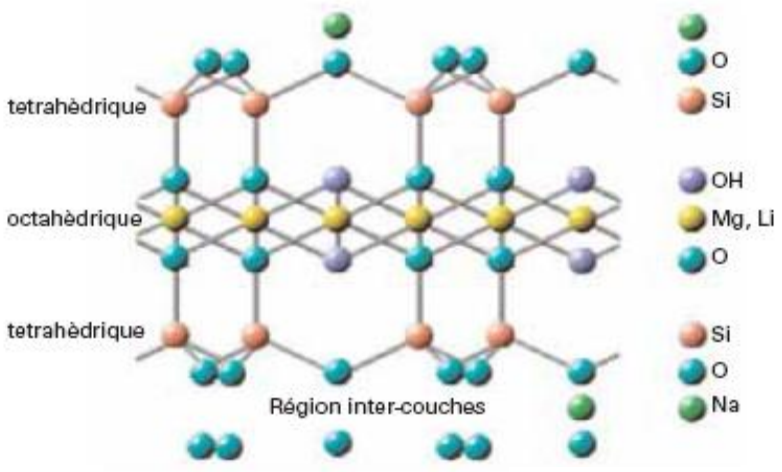


Figure 2. Structure



http://www.laponite.com

Applications de Laponite (source : Rockwood)

One Particle : Multiple uses on market

HealthCare

Produits de soins perso
- produits de beauté
- systèmes d'é… émulsifia…
- pâte …
- … peau
- …ants et a…
- …ongles
- …pooings

Surface Coatings

…ts de surface
- …s pour la décoration et …rchitecture
- revêtements à effets de structure
- peintures multicolores "… …ans eau"
- peintures ind… …t finition
- revêtements … …vernis
- revêtements in… …et de protection
- revêtement stabilisateur de rouille
- alkydes réductibles dans l'eau
- teintures pour bois
- vernis pour bois
- encres d'imprimerie
- peintures pour enfants et artistes
- Suspensions de pigments

House Products

Produits ménagers
- nettoyants pour fours et dégraissants
- produits d'entretien à l'eau de Javel gélifiés
- nettoyants applicables par pulvérisatio…
- détergents en tablettes
- shampooings pour mo… …tes
- produits de nettoya… …cides et alcalins
- produits d… …ces dur…
- désodorisa…
- détergents l… …ave-vaisselle
- produits antis… …s
- agents anti-redéposition

Papers Films Polymers

Papier et films polymère
- revêtements antistatiques
- papier et film d'impression électrographique
- films barrières in…
- revêtements …
- enduits …
- en… imp… …ère
- appr…
- papier… …iaux pour l'industrie
- microparticule pour systèmes de rétention et drainage

Building

Produits pour bâtiment
- plâtres et pâtes de c…
- retardateurs de …
- suspensions … …nt du bois
- colles à bois
- colles à carrelage

Agriculture

Agriculture
- gels pour la germination de graines
- gels pour enracinement de plantes
- concentrés fluidifiables agrochimiques - herbicides, pesticides
- suspensions d'oligo-…

Rockwood me… …isposition des formulatio… …pes pouvant servir d'exemples pour une large gamme de produits.

General Industry

Industrie générale
- suspensions de démoul… …e
- jouets d'enfants
- adjuvants de f…
- pâtes de …
- fluides de …
- céramiques …
- glaçures céra… …es
- revêtements de fonderie
- latex d'élastomère
- fluides électro-rhéologiques

http://www.laponite.com

i) Définitions, Markets, Properties, Applications
Définitions, Prospectives, Propriétés, Applications

► **ii) Real Risks, Perceptual Risks, Regulations**
Risques réels, perçus, réglementation

iii) NP Hazard (Eco/Toxicity)
Nanotoxicité

iv) Benefits / Risks analyses

Ten Toxic Warnings

1/ 1997 – Titanium dioxide//zinc oxide nanoparticles from sunscreen are f… free radicals in skin cells,damaging DNA.(Oxford University and Montreal Univ… inaro et al .

2/ March 2002 – Researchers from the Center for Biolo… chnology (CBEN,Rice University,Houston)report to US EPA t… te in the organs of lab animals and are taken up by cell… *taken up by cells.That sets off alarms.If bacteria can tak… nanomaterials into the f…*

3/ March 2003 – Researc… eport that studies on effects of nanotubes on the lung… an quartz dust.Scientists from DuPont Haskell laborat… ings on nanotube toxicity. *"The message is clear.Peo… t be highly toxic."* – Dr.Robert Hunter (NASA … earcher)

4/ M… es first scientific literature survey on nanoparticle toxicity by toxico… rd.Dr.Howard concludes that the smaller the particle,thé higher its likely tox… particles have various routes into the body and across membranes such as the blood b… . Full hazard assessments should be performed to establish the safety of species of particle … manufacturing is licensed.We are dealing with a potentially hazardous process." – Dr.Vyvyan Howard

ONGs Alert (2000's)

Papers Not Reproduced - Papers Not Confirmed

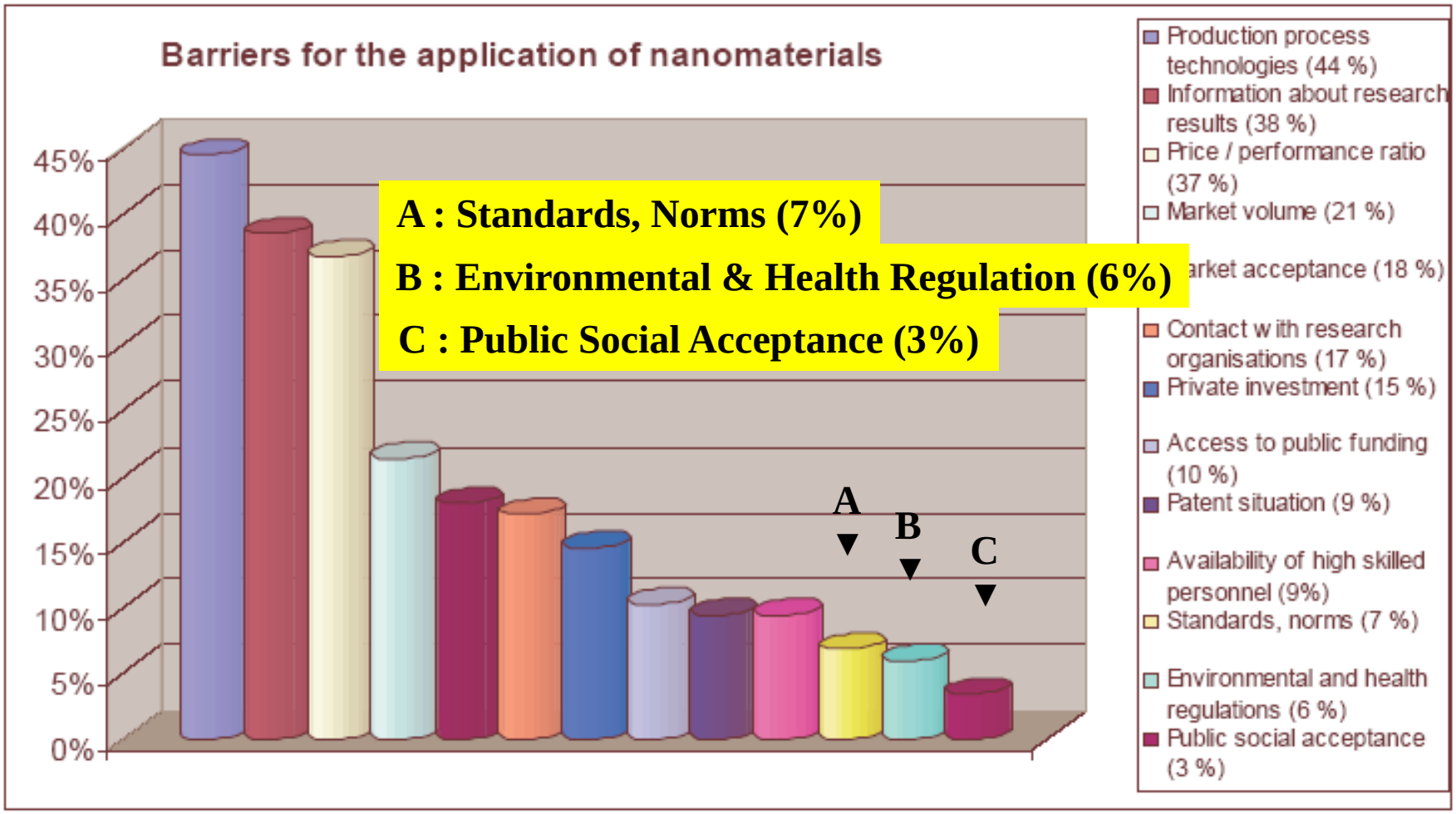
To be analysed in the present knowledge

But Pertinent Addressed Questions !!

Do we know relevant Information on Nano-(eco)Toxicity ?

From ETC Group

Barriers for the applications of Nanomaterials

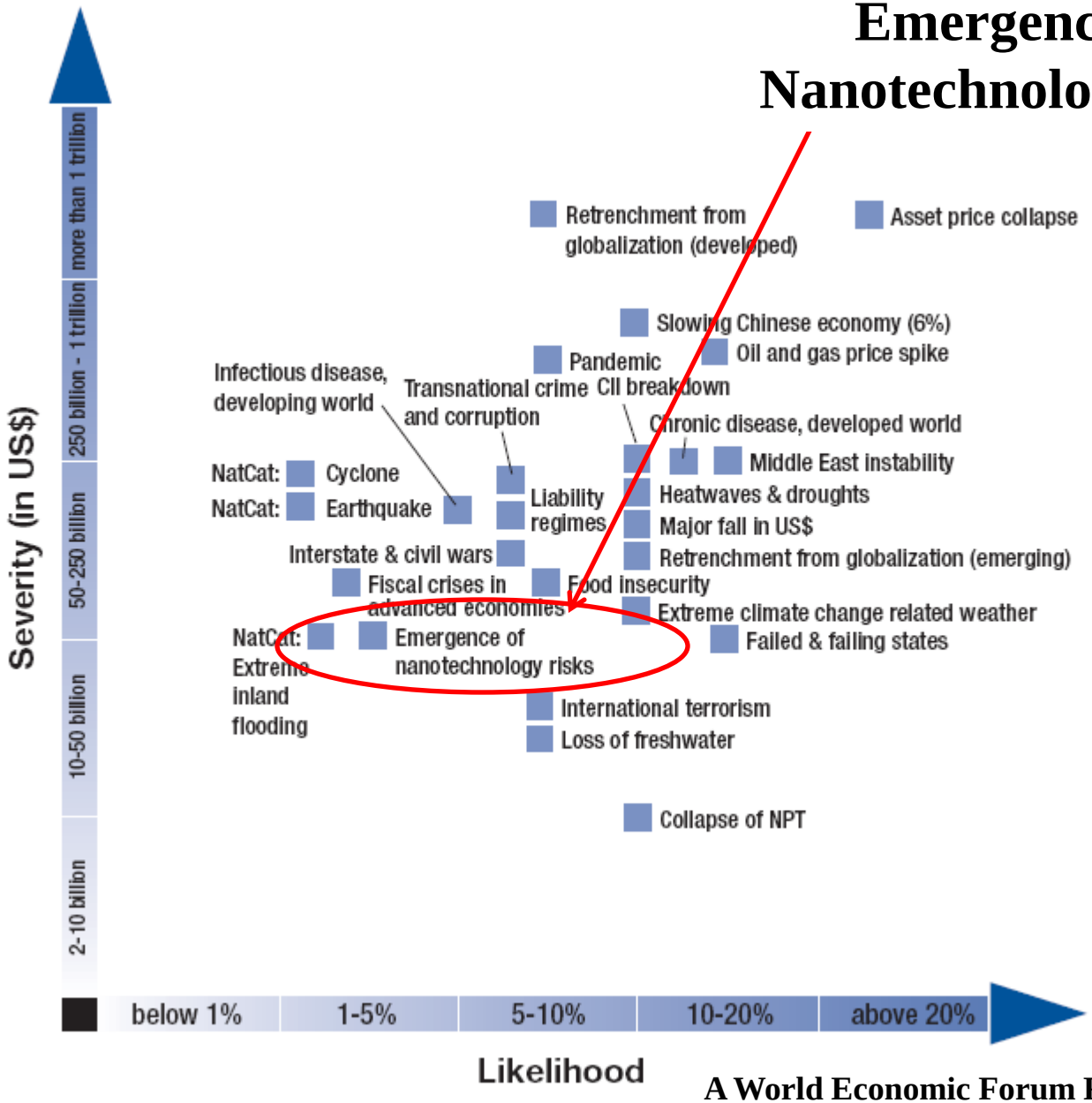


« Public social acceptance (3%), « standards, norms », environmental & health regulations (7%) are not considered as important barriers for the applications of nanomaterials by SMEs. This shows that there is a lack of conscience / awareness on the potential risks of such aspects for thé nanomaterials branche among SMEs.

NanoRoad SME (Juillet 2005)

The 26 Core Global Risks: Likelihood with Severity by Economic Loss

Emergence of Nanotechnology Risks



A World Economic Forum Report – Davos - 2008

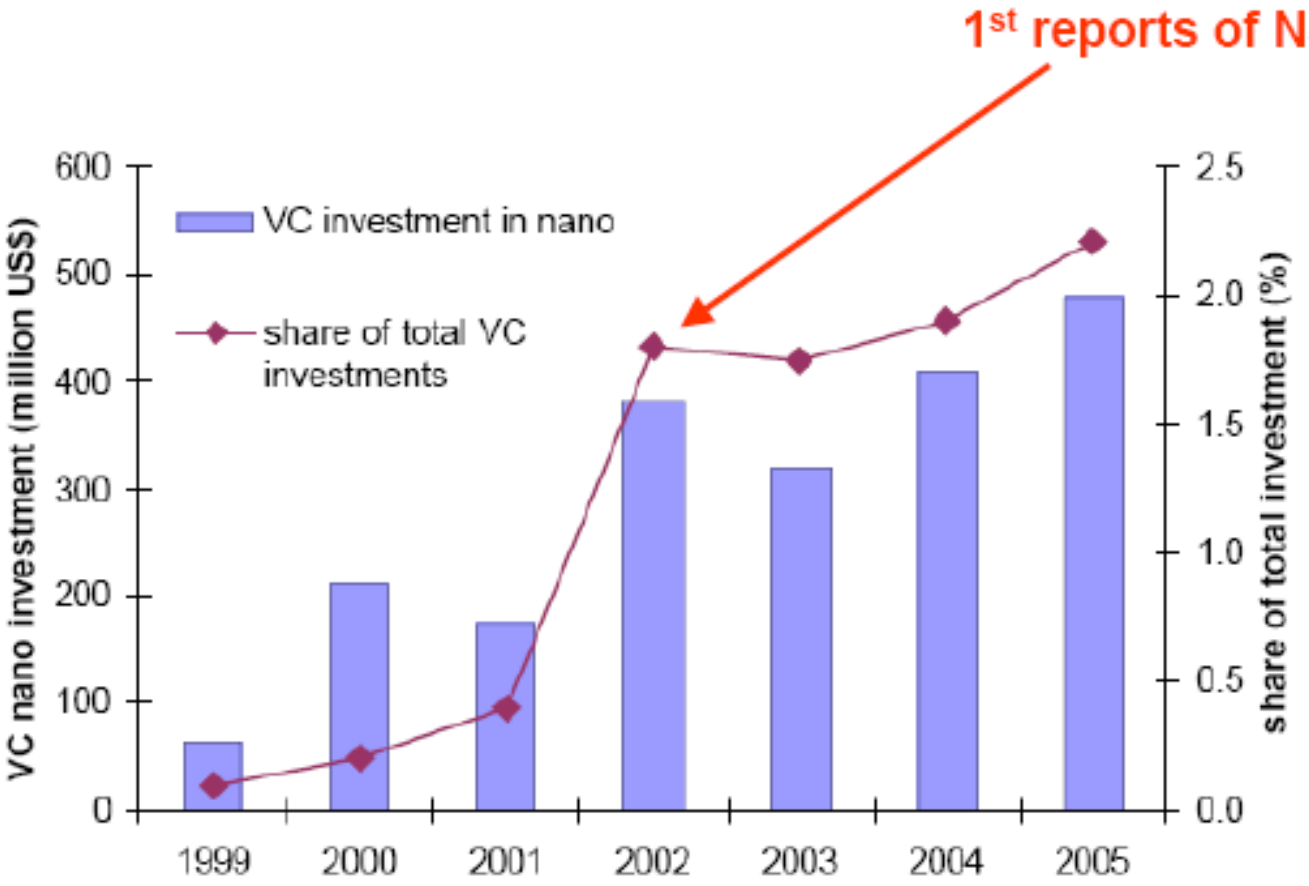


Figure 8: Venture Capital funding worldwide in nano, in absolute numbers and as share. Sources: 1999-2003: Anquetil (2005), 2004/2005: Lux Research, 2006, PriceWaterhouseCoopers 2006

Source : Kenneth Dawson - Nano Impact Net (23 Mars 2009)
http://www.nanoimpactnet.eu/object_binary/o2906_09-03-23-Topic2_Dawson.pdf

Jun 9 2008 : Nanomaterials Mitsui temporarily stops MWNT shipments over perceptual EHS worries

http://64.233.183.104/search?q=cache:1HepRVRPt2oJ:pv2.luxresearchinc.com/+mitsui+nanotube+lux+research&hl=fr&ct=clnk&cd=3&gl=fr

Cancer linked to fibres in tennis racquets / Daily Telegraph (20 Mai 2008)

By Kate Devlin, Medical Correspondent

Last Updated: 11:14PM BST 20/05/2008

Tiny fibres used in tennis racquets, bicycle frames and some electronic equipment could be as dangerous to inhale as asbestos, experts warned on Tuesday.

A new study has linked the fibres, carbon nanotubes, with mesothelioma, a cancer of the lung lining.

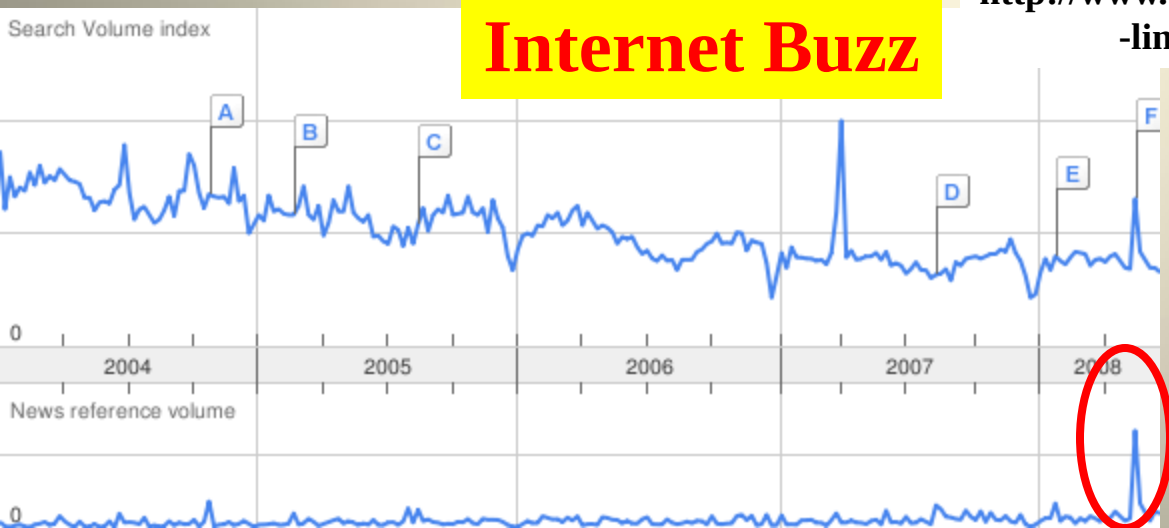
Thousands of Britons have died after contact with asbestos, which can trigger the disease.

Carbon nanotubes, which are about 1/50,000th the size of a human hair, are extremely strong and able to transmit electricity.

They have been used in around a dozen products including tennis racquets, baseball bats and electronics but experts predict their use will significantly increase in coming decades

http://www.telegraph.co.uk/news/uknews/1996820/Cancer-linked-to-fibres-in-tennis-racquets.html

Internet Buzz



Google Trends

◄ **Carbon nanotubes mimic asbestos in early study**

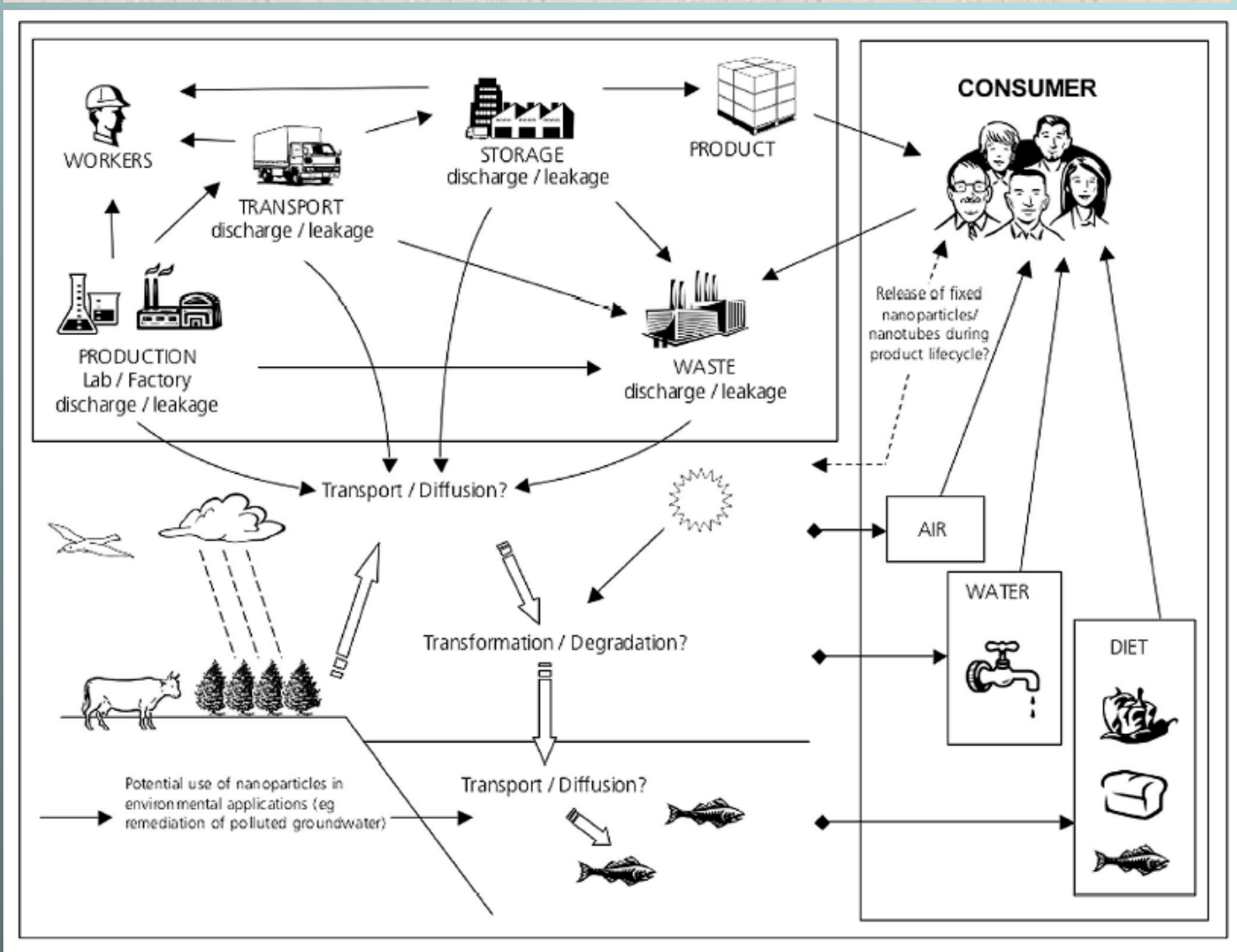
i) Définitions, Markets, Properties, Applications
Définitions, Prospectives, Propriétés, Applications

ii) Real Risks, Perceptual Risks, Regulations
Risques réels, perçus, réglementation

► **iii) NP Hazard (Eco/Toxicity)**
Nanotoxicité

iv) Benefits / Risks analyses

De la Particule Primaire à l'Environnement (Japon)



Some possible exposure routes for nanoparticles and nanotubes based on current and potential future applications. Very little is known about exposure routes for nanoparticles and nanotubes and this figure should be considered with this in mind (Adapted from National Institute for Resources and Environment, Japan http://www.nire.go.jp/eco_tec_e/hyouka_e.htm).

L'air viennois très pollué

http://www.lefigaro.fr/flash-actu/2010/04/20/97001-20100420FILWWW00518-l-air-viennois-tres-pollue.php

AFP - 20/04/2010 |

Un taux de nano-particules trois fois supérieur à la moyenne a été relevé dans l'air de Vienne samedi et dimanche par des physiciens de l'université de la capitale autrichienne, alors que le nuage de cendres du volcan islandais Eyjafjöll traversait le pays.

Vienna – Volcano -> 3 x nanoparticle level

Steam, rocks and ash are thrown out of an erupting volcano near Eyjafjallajokull, Iceland April 19, 2010.

Credit: Reuters/Lucas Jackson

Mother Nature has a way of reminding us who is in charge!

http://www.helsinki.fi/henvi/research/presentations10/ScienceDay2010/Karn.pdf

Risk = Hazard (Toxicity - ????) x Exposition

- La notion de risque repose sur deux éléments : le danger *et* l'exposition

et

=

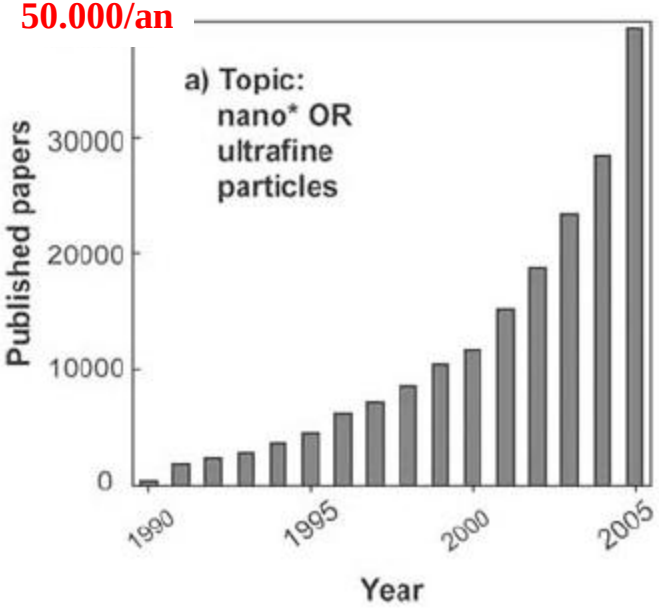
- La connaissance de ces deux éléments est essentielle pour évaluer et maîtriser le risque.

Nanomaterials

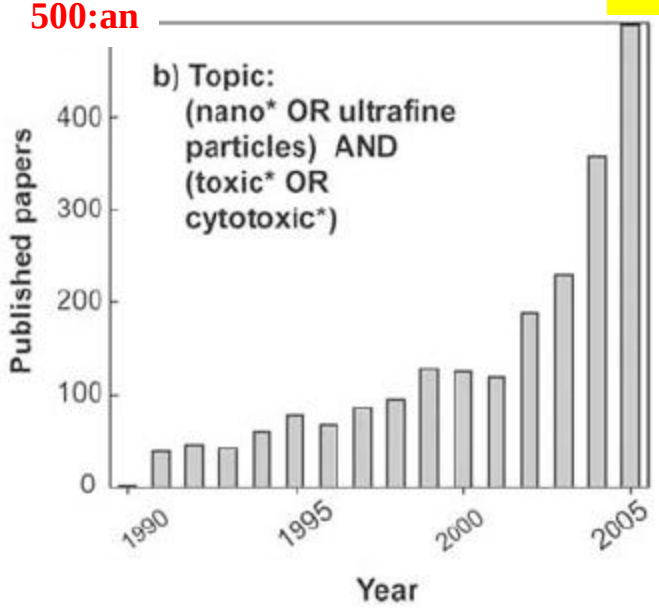
nanoToxicity

> 1.000 en 2009

50.000/an



500:an



Statistics on scientific articles published on (a) nanomaterials and (b) their toxicity (ISI Web of Science).

The number of publications on the **topic of nanomaterials** has increased at an almost exponential rate since the early 1990s, **reaching about 40,000 in the year 2005** as indicated by a search on ISI Web of Knowledge database [29]. There is also a notable rise in the number of publications discussing their toxicity, particularly in the past two years. The total number of papers on **toxicity,** however, remains low compared to the total number of publications on nanomaterials, with only around **500 publications in the year 2005**.

C. Buzea, I.. I. Pacheco Blandino, K. Robbie Biointerphases vol. 2, issue 4 (2007) pages MR17 - MR172

1990 – 2010 : 270 different nanotechnology titles have been published, with at least 142 still in current production - a dozen new titles in the pipelines

http://www.nature.com/nnano/journal/vaop/ncurrent/full/nnano.2010.216.html

Virtual Journal of NanoEHS

Recent enhancements:

- More user-friendly interface
- Powerful ICON database remains the engine beneath the hood

Coming soon:

- Backgrounders on key literature
- Summaries of significant papers
- Guest editorials on breaking topics
- Post actual papers

CBEN

http://icon.rice.edu/virtualjournal.cfm

ICON

Eco – Toxicité

26 (!!!) ecotoxicological published works

Fullerenes : 7 - TiO2 : 6

CNT : 5 - Au : 2 - Ag : 2 - ZnO : 2

Ecotoxicity and analysis of nanomaterials in the aquatic environment

Marinella Farré, Krisztina Gajda-Schrantz, Lina Kantiani & Damià Barceló

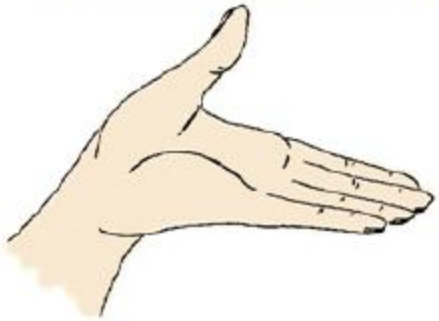
Anal Bioanal Chem (2009) 393:81–95

Material	Test species	Effect measured	Remarks	Measurements	References
Ag NPs	Zebrafish embryos				[102]
Ag NPs	Zebrafish embryos			Hatch rate decreased in the nAg-exposed groups (10 and 20 ng/L)	[103]
Fullerene C_{60}	*P. putida* *B. subtilis*	composition and behaviour		Growth-inhibiting concentrations at 0.5 mg/L *P. putida* and 0.75 mg/L *B. subtilis*	[23]
TiO_2 NPs	*Oncorhynchus mykiss*	Oxidative stress, physiological effects			[91]
Au NPs	*D. magna*	Intake		Retention in gut	[104]
Au NPs	Human cells	Cell death within 12 h		EC_{50}=30–56	[105]
CNTs lysophophatidyl choline-coated SWCNTs	*D. magna*	Biomodification of carbon-based nanomaterials through digestion		e with natural lipid sted and modified	[77]
Cu NPs	Zebrafish	Acute toxicity and gill injury	Soluble NP		[93]
DWCNTs	*X. laevis*	Acute toxicity and genotoxicity		bserved 0 mg/L	[86]
Fullerene C_{60}	*D. magna*	Acute toxicity		n)	[88]
Fullerene C_{60}	*D. magna*			llerene produced e toxicity	[141]
Fullerene C_{60}	*D. m*			sed heart rate	[142]
Fullerene C_{60}					[21]
Fullerene C_{60}				L (stirring) d exposure concentrations tested Effects were observed for *D. magna*	[143]
Fullerenes C_{60}, C_{70}, $C_{60}(OH)_{24}$				200 µg/L of C_{60} and C_{70} induced malformations, pericardial edema and mortality. $C_{60}(OH)_{24}$ was less toxic than C_{60}	[123]
SWCNTs		and gical effects	Sodium dodecyl sulphate	Respiratory toxicity and possible neurotoxic effects	[84]
SWCNTs		Mortality, development and reproduction	Oxidation and dispersion in water	36% mortality at 10 mg/L	[81]
SWCNTs		Development of embryos	Several conditions were tested		[80]
TiO_2-coated NPs	*D. magna*	Acute toxicity		EC_{50}>100 mg/L	[144]
TiO_2 NPs	*D. magna*	Acute toxicity	Solvent (THF) and sonication	EC_{50}=not achieved	[88]
TiO_2 NPs	*D. magna*	Acute toxicity	Sonication	Increase of immobilization of *D. magna* when stimulated with light	[89]
TiO_2 NPs	*D. magna*	Acute toxicity	Shaking	TiO_2 produced 40% mortality at 20 mg/L	[90]
TiO_2 NPs	*D. magna*	Acute toxicity		Nontoxic	[94]
	T. platyurus				
ZnO NPs	*D. magna*	Acute toxicity		3.2 mg/L	[94]
	V. fischeri			1.9 mg/L	
	T. platyurus			2.1 mg/L	
ZnO NPs	*P. subcapitata*	Acute toxicity		EC_{50}=60 µg/L	[81]

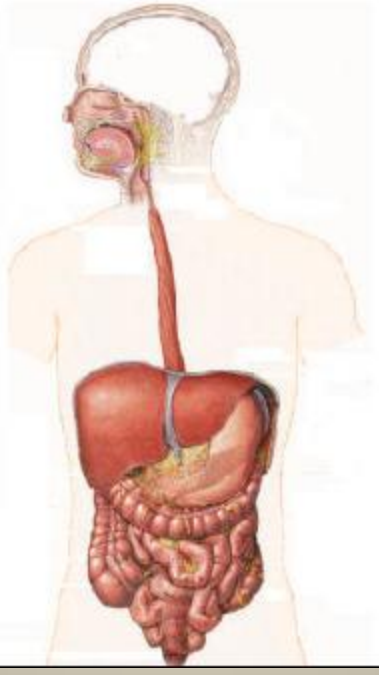
Human Exposure Routes

Inhalation

Dermal absorption

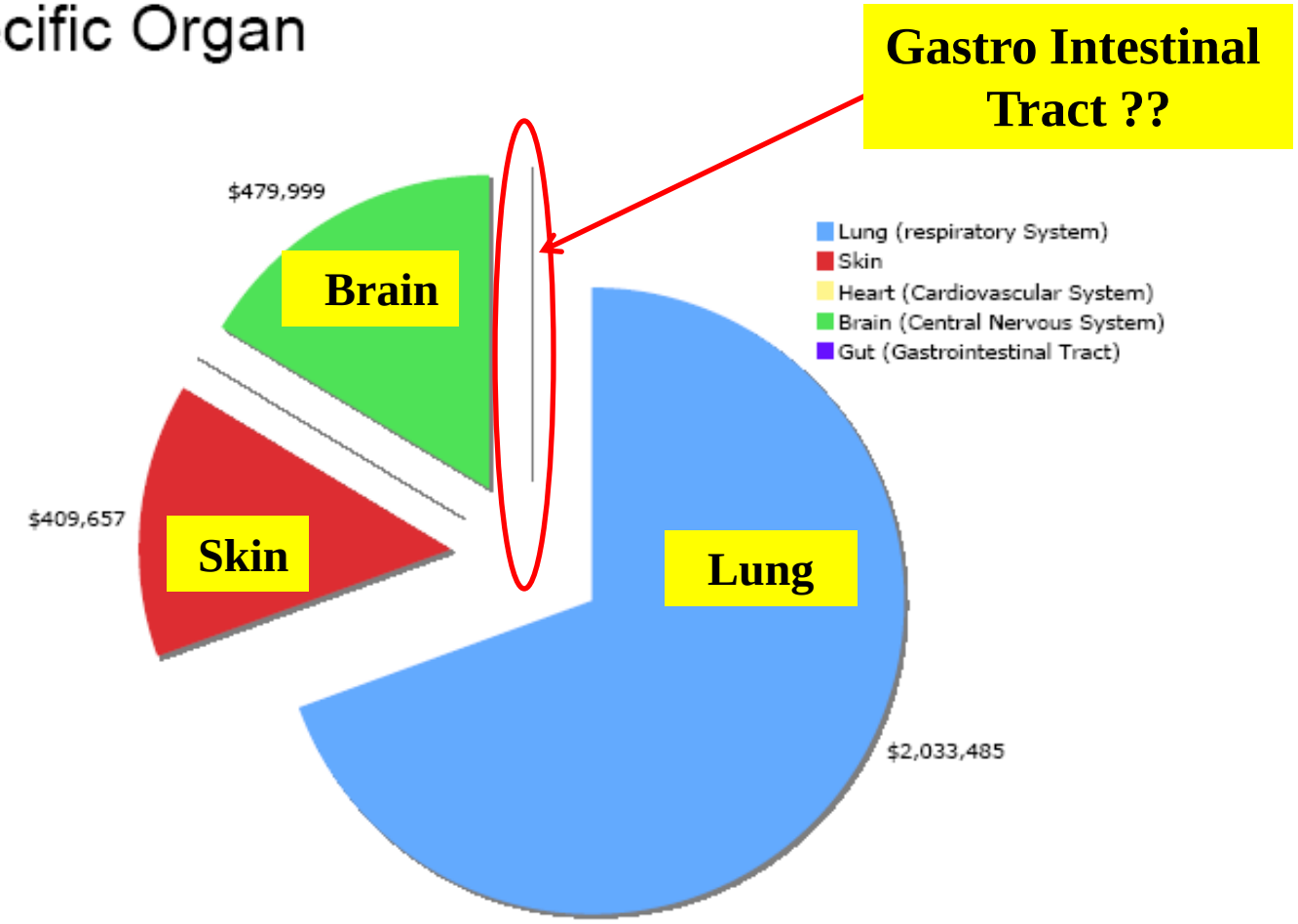


Ingestion



Injection (circulation)

Funding of Highly Relevant Projects on Engineered Nanomaterials Hazard in the United States — By Specific Organ



Nanotoxicology: characterizing the scientific literature, 2000–2007

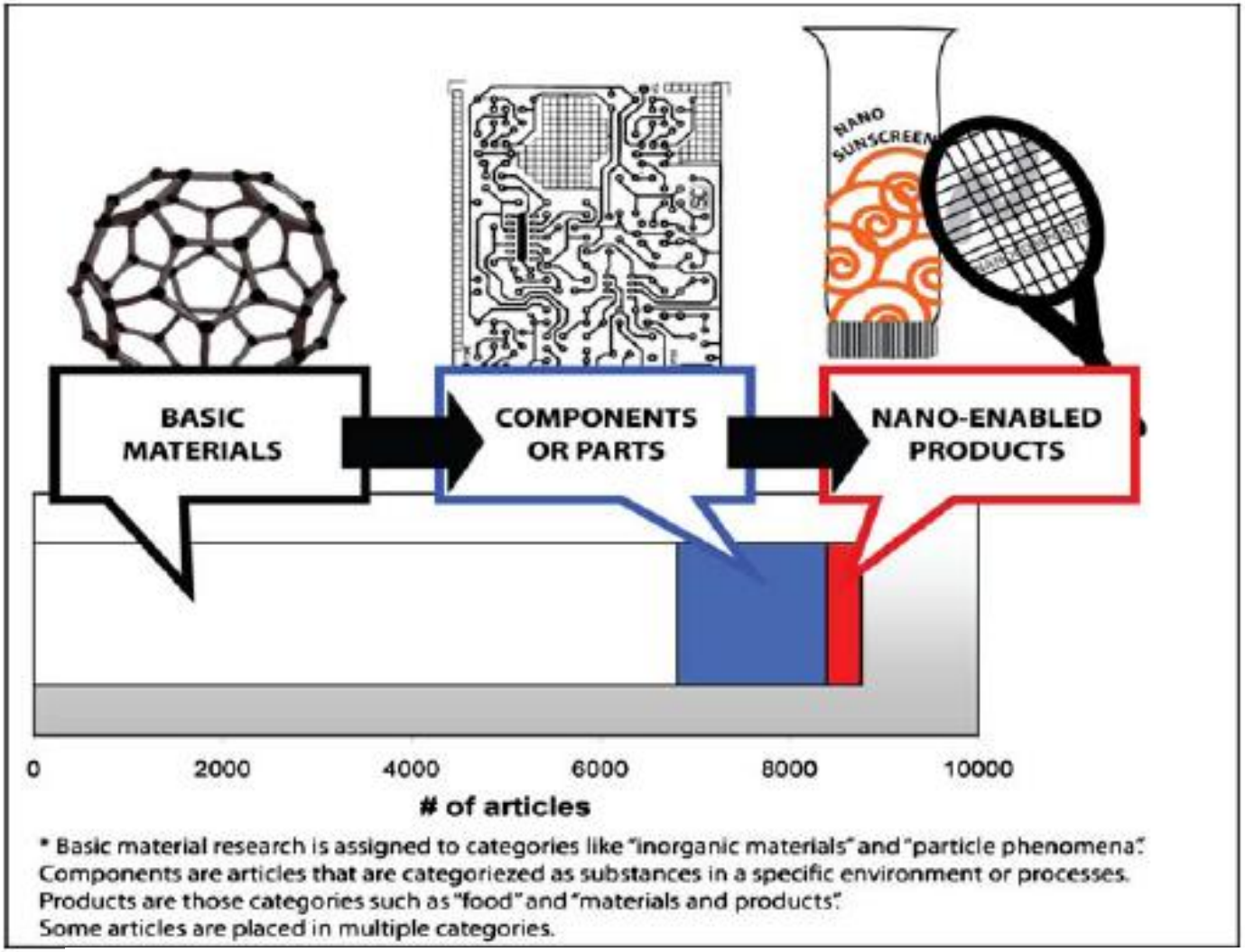


Fig. 5 The number of toxicology articles by stage in life-cycle (Collected from SciFinder)

A. D. Ostrowski, Tyronne Martin, J. Conti, I. Hurt, B. Herr Harthorn - J Nanopart Res (2009) 11:251–257

Calculating the costs of testing for nanotechnology risks 31/03/2009

An editorial in last week's Environmental Science & Technology summarises the findings from a recent paper ("The Impact of Toxicity Testing Costs on Nanomaterial Regulation" by Choi et al.) that explored the efforts required to properly test all nanomaterials that are in the market today. http://pubs.acs.org/doi/full/10.1021/es900758w

If all existing nanomaterials were to be tested for toxicity, it would cost U.S. industries between $249 million and $1.18 billion, but the testing could take as long as 53 years at current levels of investment, according to the first study to estimate the costs and time needed for nanotoxicology testing.

Choi et al., resea … mation on 329 nanotech … on how much money co… ailable, the authors used … ing data on the costs per t… f testing

The authors arg… nd time constraints of tox… eed the most rigorous te… l in the EU's R…

Recherche : Toxicité, Ecotoxicité

OCDE et European Joint Action

➢15 NanoParticules Prioritaires

➢Programme Parrainage → France SiO_2, TiO_2, NTCs, Ag

Produits sur le Marché :

➢Inventaire (Traçabilité !!! & Base de données !!)

➢Evaluation Bénéfices / Risques

➢« Standardisation » Nano Particules

(8 Paramètres Physico-Chimiques → XX paramètres fixes !!))

(Voies d'Exposition ↓ ↓, Dispersion ↓ ↓)

1 June 2010 - Wanted: Nano-Cops The New Haven Independent

(By Jim Motavalli)- Experts on the cutting edge of revolutionary new technology aren't waiting for the government to watch over their booming new industry. They want to band together to start policing themselves. At least some of them do.

They put out a call for nano-cops—people to get in front of the potential health and environmental dangers of nanotechnology, the development of medical,, environmental and consumer super-products from tiny particles with surprisingly powerful properties.

The call went out last week at a gathering in Denver, where some of the world's leading nanotechnology and solar energy experts held a "Nano Renewable Energy Summit."

"There are no good, well-controlled studies to prove the safety of our nanomaterials," Jim Hussey, the CEO of a biomaterials company called NanoInk, said at the summit. "Frankly, we have none. We need to lead the world in environmental health and safety nanotech testing. We either get ahead of this or it will roll over us as an industry."

Bipartisan Pressure

Support for nanotechnology is deeply political, and it doesn't necessarily split along clear party lines. For instance, positive votes for basic science research are declining am[illegible]ongressional Republicans, Hussey said.

"We've lost one of the major political parties," he said during a fascinating talk at the summit. "If the Republicans win control over the House or Senate in N[illegible] down basic science research funding."

Many Democrats have questions, too. In fact, U.S. Sen. Frank Lautenberg (D-NJ) just proposed the Safe Chemicals Act of 2010, amendm[illegible]ol Act of 1976 that have alarmed the nanotech industry because they would enforce a new round of expensi[illegible]

But the nanotech industry has more immediate concerns, according to Hussey. In Denver, he pointed to disturbing medi[illegible]elf on environmental health and safety iss[illegible]

The first order of business, he said, is a comprehensive self-funded pro[illegible]

"There are no good, well-controlled studies to prove the safety of our nanomaterials," Hussey sai[illegible] and safety nanotech testing. We either get ahe[illegible]

Nanomaterials, said Hussey, live for a long time in the body, though if they're [illegible]captured and metabolized by the liver.

Of most concern are the smaller 40- to 50-nanometer partic[illegible]

"The physical size of the particle has given it access to the ce[illegible]ell pores and invade the cell nucleus.

nanotech particles demonstrated the greatest abilit[illegible] closed." A 2008 paper in Nature noted that the smaller [illegible]eath)." If you're very technical, you can learn from this recent [illegible]on.

Is there a cancer risk? "T[illegible]t there's no question that they do," Hussey said.

[illegible]genic," he declared. These are significant admissions from an industry that has been on the [illegible]nsive.

"[illegible]pared the current situation to a ringing fire alarm.

Conf[illegible]oasket or one engulfing the whole house," he said. "We don't have the data, but we need it. Reporters are writing [illegible]ve information available. So that puts the burden on us to do those studies in a systematic way."

[illegible]was in line with an earlier talk by Don Ewert, the environmental health and safety manager for OSD BioPharmaceuticals. Ewert also called for self-regulation, but the tone sounded very different to me.

[illegible]ction, Ewert projected a series of articles on nanotech health issues (including a recent three-part series on AOL) and called them "baloney."

Ewert's a[illegible]notech poses no health risk, but that "today we have forensics and toxicology we never had in the time of asbestos [a reference point for some nanotech critics]."

[illegible]He outlined detailed nanotech safety analysis that could result in a risk-factor scale for nanotech products from "risk free" to "do not produce."

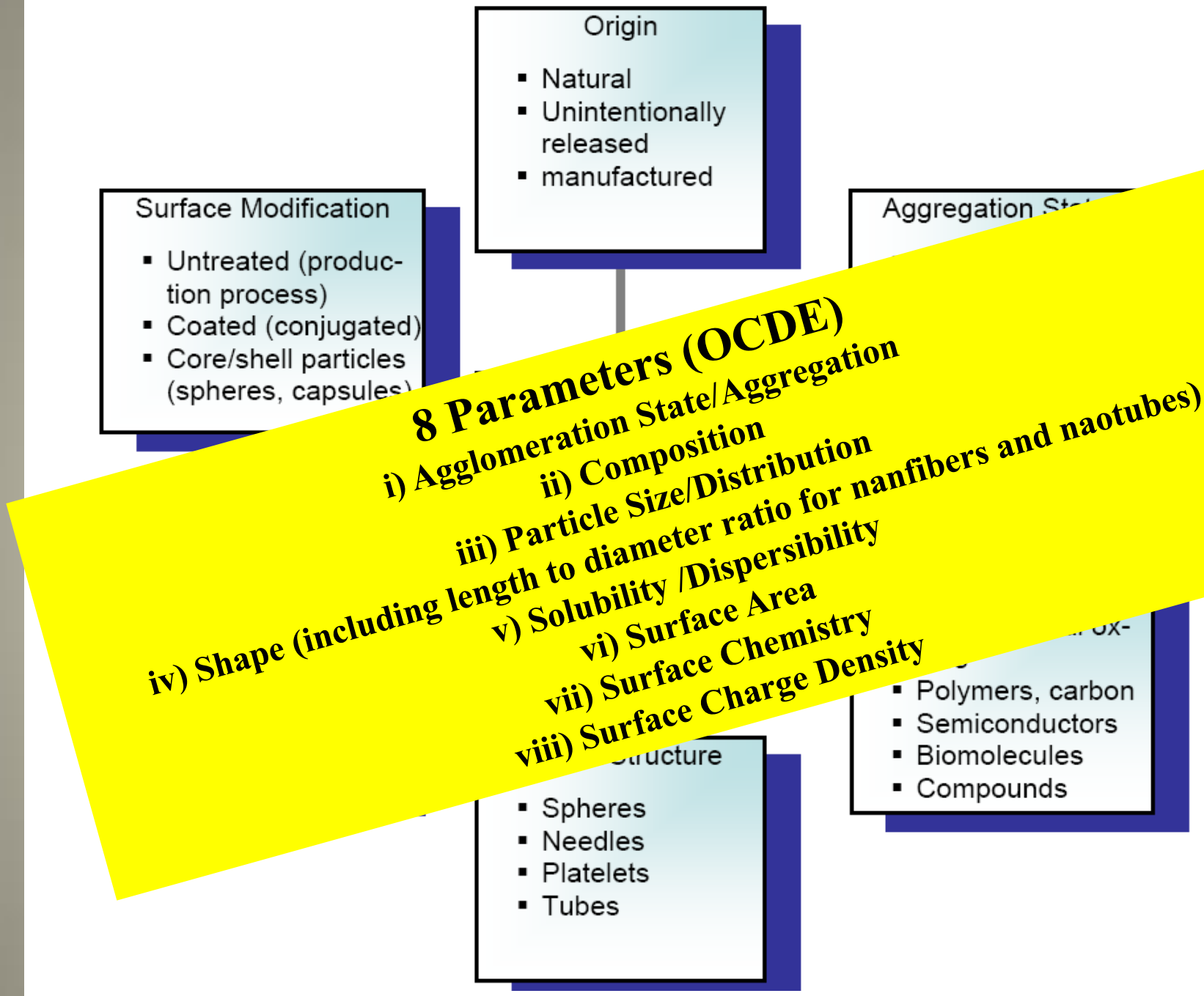
Ewert n[illegible]e need for safe handling protocols for hot-seat substances like carbon nanotubes. As a possible alarm bell for nano advocates, Bayer MaterialScience last November set a low occupational limit for exposure to nanotubes. "It's a mistake to say that nanomaterials are 'safe,' but it's also a mistake to say they are 'dangerous,'" Ewert said. "Can we as an industry manage the risks? Absolutely."

The industry clearly prefers in vitro lab tests over much more expensive in vivo testing using animals, but such reliable cell-based assays that correlate to animal studies are not currently available.

According to Hussey, that testing has long been discussed, but Sen. Lautenberg's bill gives the need to develop dependable protocols new urgency. Full-scale animal testing of just 2,000 substances a year (two percent of the 88,000 chemicals in EPA's inventory) could cost $10 billion a year over many years, Hussey said, and would secondarily require the yearly sacrifice of 200,000 rodents and 20,000 monkeys or dogs.

The reaction in the animal rights community to such an escalation of testing is hard to imagine. But there are other considerations. "It would bankrupt the industry to do that kind of testing," Hussey said

The need to develop dependable protocols new urgency : Full-scale animal testing of just 2,000 substances a year (two percent of the 88,000 chemicals in EPA's inventory) could cost $10 billion a year over many years,[…] and would secondarily require the yearly sacrifice of 200,000 rodents and 20,000 monkeys or dogs.



Source : Future Techonologies Divison of VDI Technologiezentrum GmbH

Table I. Hazard identification scheme illustrating the relevant inherent physical and chemical properties in comparison to each of the categories proposed in Figure 1.

Materials	Categories	Chemical composition	Size	Shape	Crystal structure	Surface area	Surface chemistry	Surface charge	Solubility	Adhesion
Bulk	Ia	+	–	–	–	/	/	/	+	+
Multiphase	Ib	+	+	+	–	+	+	–	+	+
Structured surface	IIa	+	+	+	–	+	+	–	+	+
Film	IIb	+	+	–	–	–	+	–	+	+
Structured film	IIc	+	+	+	–	–	+	–	+	+
Surface bound NPs	IIIa	+	+	+	+	+	+	+		+
NPs suspended in liquids	IIIb	+	+	+	+	+				+
NPs suspended in solids	IIIc	+	+	+						+
Airborne NPs	IIId	+								+

+ Proper… identifica… …azard

80% Publications / Incomplete Physico Chemical Characterization

8 paramèters

→ Non Conclusive (and dispersive) Results

Table II. T… compilation … …lata

				Shape	…ystal structure	Surface area	Surface charge	Surface chemistry	Solubility
Cxx	210	100	17	8	2	6	7	4	7
SWCNT	64	100	45	39	2	14	2	20	–
MWCNT	39	100	56	33	8	23	–	5	–
QDs	73	100	71	10	–	–	27	85	–
N-metals	275	100	96	39	24	33	17	25	4
Others*	304	100	76	12	.3	12	30	26	2

*Others include polymers, in-organic nanoparticles, carbon black, and soot.

(Source : Categorization framework to aid hazard identification of nanomaterials S. F. HANSEN, B. H. LARSEN, S.I. OLSEN, A. BAUN – Nanotoxicology 2007, 18)

afsset

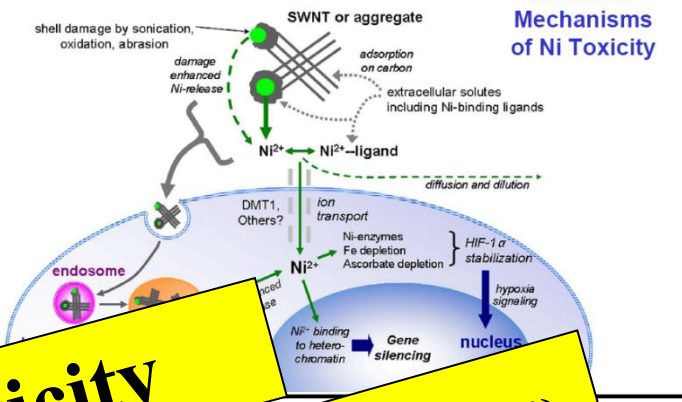
Unstabilised Knowledge !!

Origin
- Natural
- Unintentionally released
- manufactured

Surface Modification
- Untreated (production process)
- Coated (conjugated)
- Core/shell particles (spheres, capsu

Shape/Structure
- Spheres
- Needles
- Platelets
- Tubes

Chemical Composition
- Metals/ metal oxides
- Polymers, carbon
- Semiconductors
- Biomolecules
- Compounds



Nano Toxicity ≠ Micro Toxicity

Specific Toxicity of THE nanoparticle (protocole also !)

Troian Horse « Key – Lock (clé – Serrure) »

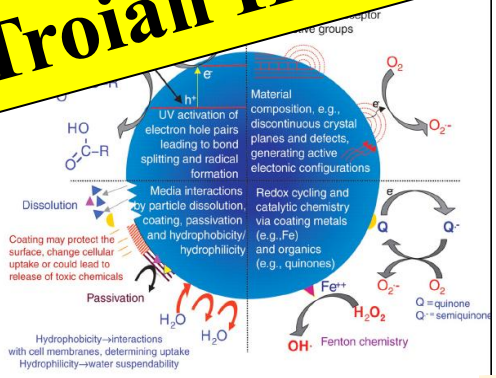
Basi… relevant to toxicity

> Dose

> Size and sha…

> Biopersistence

> Surface chemistry



Surface Reactivity of Nanoparticles
Nel et al. Science 311: 622-627, 2006

Source : Future Techonologies Divison of VDI Technologiezentrum GmbH

Nanoparticles do not exist as single particle entity, they adsorbe things, e.g. proteins

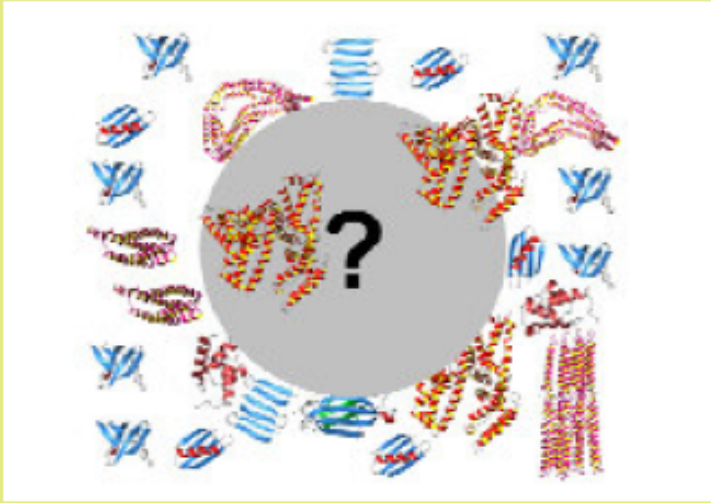
What do we know

- Protein corona is important for biological interactions and cellular recognition
- Corona is not static, proteins get on and off

What do we not know

- Dependence on nanomaterial?
- Dependence on size?
- Dependence on …?

Implications for interpretation of testing



EU FP6 project NanoInteract,

courtesy of Prof Kenneth Dawson, UCD, Dublin, Ireland

New research demonstrates that TiO2 nanoparticles can damage brain cells (18/11/2008)

For the first time, researchers have demonstrated that titanium dioxid… particles can directly enter the brain and lead to cell damage. Although the mechanisms involved… gation, these new fin… e concern regarding the potential risk of occupation… licles during… lications.

In the study, which w… Beijing a… were intranasally insti… cles (i.e. 80… r day for 30 days – a tec… with taki… d and assessed to determ… the… markers

…llum …the …t of …und …ys, …or …, …the study

These … …pational exposure to TiO_2 nanoparticles … application.

Placenta Barrier Transfert

Nanoparticles Transferred from Pregnant Mice to Their Offspring Can Damage the Genital and Cranial Nerve Systems

K. Takeda, K. Suzuki,A ki Ishihara,Miyoko Kubo-Irie, Rie Fujimoto,Masako Tabata,Shigeru Oshio,Yoshimasa Nihei,Tomomi Ihara, and Masao Sugamata -

J.Health Sci., 55(1), 95-102, 2009

Nanomaterials are being used increasingly for commercial purposes, yet little is known about the potential health hazards such materials may pose to consumers and workers. Here we show that nano-sized titanium dioxide (TiO_2), which is used widely as a photo-catalyst and in consumer products, administered subcutaneously to pregnant mice is transferred to the offspring and affects the genital and cranial nerve systems of the male offspring. Nanoparticles identified as TiO_2 by energy-dispersive X-ray spectroscopy were found in testis and brain of exposed 6-week-old male mice. In the offspring of TiO_2-injected mice, various functional and pathologic disorders, such as reduced daily sperm production and numerous caspase-3 (a biomarker of apoptosis) positive cells in the olfactory bulb of the brain, were observed. Our findings suggest the need for great caution to handle the nanomaterials for workers and consumers

http://www.safenano.org/SingleNews.aspx?NewsID=535

Risks = Hazard (Toxicity) x Exposition (↓ ↓)

- La notion de risque repose sur deux éléments : le danger *et* l'exposition


et

=


- La connaissance de ces deux éléments est essentielle pour évaluer et maîtriser le risque.




Do Not Forget the Accident Event

Medical surveillance, exposure registries, and epidemiologic research for workers exposed to nanomaterial

There is a growing and coalescing level of evi… materials can…

Nano : à considérer comme potentiellement (!!) Dangereux

to treat engineered nanoparticles "as if" they are hazardous

Risk Control = Exposition Control

…ation, and … of animal studies with … information and demonstrating end effects.

…vidence has been reviewed by numerous organizations that have concluded that there is enough preliminary information

to treat engineered nanoparticles "as if" they are hazardous

(ASCC 2006-IRSST 2006-AFSSET 2006-DOE 2007-BSI 2007-AFSSET 2008,-HCSP 2009-NIOSH 2009)

Clearly, prudent controls should be implemented and more research is needed but at present, there also is sufficient evidence and concern to consider whether there is need for occupational health surveillance of nanomaterials workers and whether formation of exposure registries and conduct of epidemiologic research is appropriate

Douglas B. Trout, Paul A. Schulte (NIOSH – CDCP)
Toxicology (2008), doi:10.1016/j.tox.2009.12.006

Assessment of exposure and health status in workers handling titanium dioxide

Co Présentation Chine / Japon – NanoSafe II – Grenoble Nov. 2008

Weihua Li[1], Ying Liu[1], Qiangyi Wang[2], Gaku Ichihara[3] Takahiro Kobayashi[4], Yuj
Fujitani[5], Uka Cui[3], Natsumi Hata[3], Sahoko Ichihara[6] , Xuncheng Ding[1]

Study of Nanoparticle Emission from Production of Multi Walled Carbon Nanotubes

Su-Jung (Candace) Tsai, Mario Hofmann, Marilyn Hallock , Earl Ada , Jing Kong , Michael Ellenbecker

NanoManufacturing Series – May 2009

Emissions were measured for the production of multi-walled carbon nanotubes under varying operating condi**The study was designed to investigate nanoparticle emissions from the production of carbon nanotube at a univ aboratory. The furnace was located in a laboratory fume hood, and the emissions were measured at the f t and at the researcher's breathing zone..**tions. Significant nanoparticle release was found under er certain operating conditions carbon nanotubes were found in the exhaust as well. Due to th fume hood, no particles were found in the researcher's

In January 2009 the state of California asked all manufact ns and release from their facilities, including fate and transpo have not been extensively characterized. The laboratory produ vapor deposition was studied to evaluate and characterize the na or diameters from 5 nm to 20 µm were measured using the Fast M izer; the particles released from the furnace were found to b elemental composition of the released nanoparticles were c icroscopy and energy dispersive spectroscopy. Different operat on the number and morphology of aerosol particles, and the n noparticle aerosols were measured in the exhaust and CNT on particles in clusters were found.

The increase in concentration compared to the background exceeded 10^6 particle/cm^3 and mostly the particle diameters were generally less than 100 nm.

Differen changed the morphology of aerosol particles formed during production of multi-walled carbon nanotube ing condition of using a lower injector temperature during production results in the mutual benefits of enhanced production yield and reduced filament formation during production.

This study demonstrated that large quantities of spherical carbon nanoparticles can be found in the exhaust from carbon nanotube furnaces. That results in the potential for significant exposure to production personnel and the general public. It is essential that steps be taken to control these exposures.

WorkPlace Guideline

Direction Générale du Travail
Circulaire du 18 Février 2008

Les nanomatériaux, sécurité au travail
AFSSET juillet 2008

Guide de bonnes pratiques favorisant la gestion des risques reliés aux nanoparticules de synthèse
IRSST Québec – Novembre 2008

Avis du Haut Conseil à la Santé Publique
relatif à la sécurité des travailleurs lors de l'exposition aux nanotubes de carbone - 7 Janvier 2009

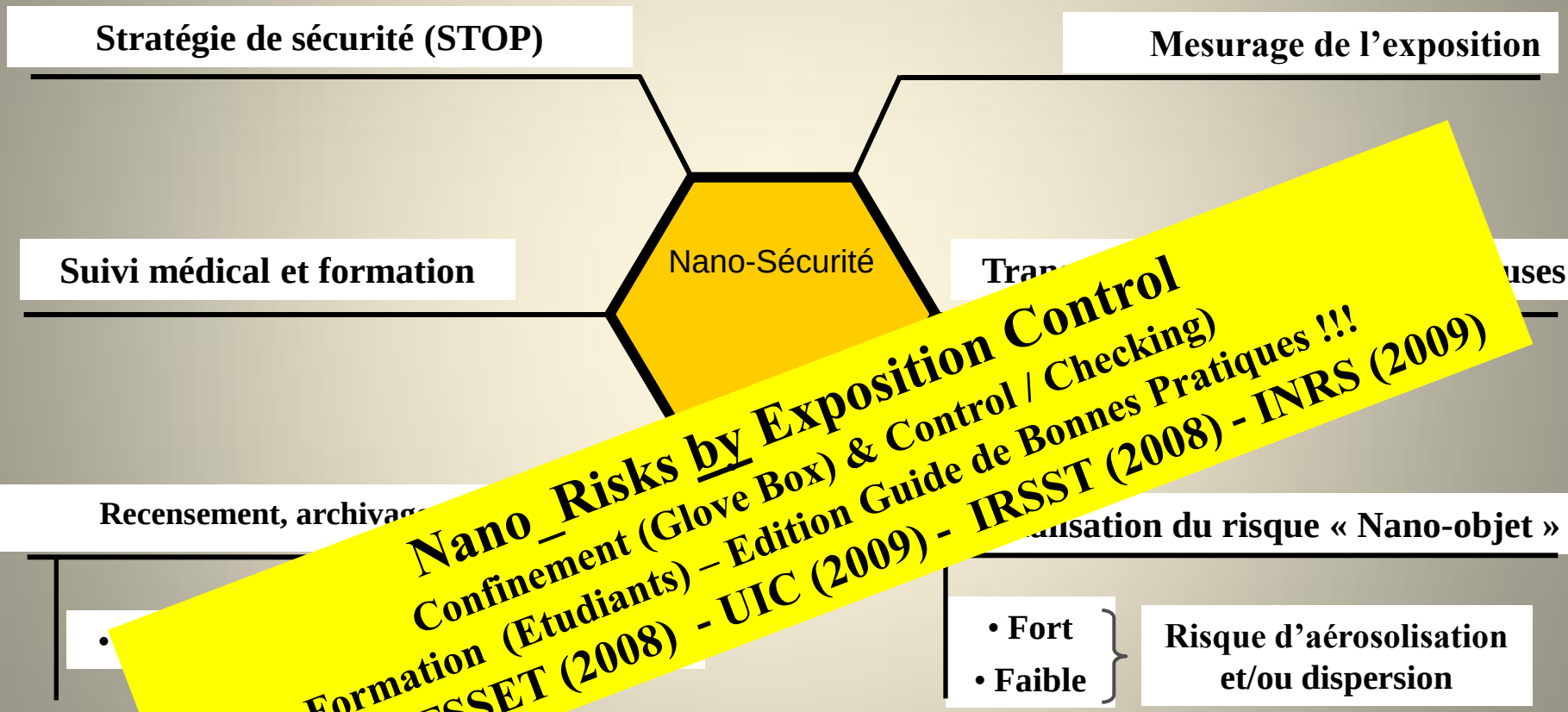
Guide de bonnes pratiques - Nanomatériaux et HSE
Union des Industries Chimiques – Mars 2009

- Reviews of Nano Health & Safety Protocols and Good Practices (13)
- Universities & research center protocols (19)
- Companies protocols & practices (17)
- Governmental Perspectives (21)
- Union Perspectives (4)
http://www.nanoceo.net/nanorisks/OHS-Protocols-Best-Practices

France

Nano Security Elements

Rapport Nanomatériaux et sécurité au travail, Afsset, 2008



Nano_Risks by Exposition Control
Confinement (Glove Box) & Control / Checking)
Formation (Etudiants) – Edition Guide de Bonnes Pratiques !!!
≠ Guides AFSSET (2008) - UIC (2009) - IRSST (2008) - INRS (2009)

afsset
agence française de sécurité sanitaire de l'environnement et du travail

Hazard Categories in BSI PD6699-2:2007

Nanomaterial Category	Benchmark Exposure Level
Fibrous *high aspect ratio insoluble NMs (ratio > 3:1 and length > 5000 nm)*	0.01 fiber/cm^3 *(1/10 of asbestos PEL)*
CMAR *NMs classified in its larger particle form as carcinogenic, mutagenic, asthmagenic or reproductive toxin*	0.1 x OEL (bulk) *(increased solubility)*
Insoluble	0.066 x OEL (bulk) *(based on NIOSH CIB on TiO2)*
Soluble	0.5 x OEL

Nanotubes

www.bsi-global.com/en/Standards-and-Publications/Industry-Sectors/Nanotechnologies/

http://www.nhsf2009.org/presentations/Murashov_NHSF_UNIT1.pdf

Occupational Exposure Limit (OEL) for Baytubes defined by Bayer Material Science (Décembre 2009)

http://www.baytubes.com/news_and_services/news_091126_oel.

Bayer MaterialScience (BMS) has recentl
stewardship program to ensure the safe use of
multi-wall carbon nanotubes, have also been pa
results of sub-chronic inhalation studies sup
Baytubes act like poorly soluble particles. Base
recent repeated inhalation studies BMS just de **pational Exposure Limit (OEL). The OEL was set at 0.0 mg/m³. All relevant information are now included in the updated Safety Data Sheet and will further ensure that our customers work safely with our Baytubes.**

Bayer :
Nanotubes : 50 µg / m³
&
Nanocyl :
Nanotubes : 2.5 µg / m³

The detailed results of the inhalation studies have been recently published in the peer-reviewed journals "Inhalation Toxicology", "Toxicological Sciences" and "Toxicology".

http://nanotech.lawbc.com/2009/12/articles/occupational-health-and-safety/bayer-material-sciences-announces-oel-for-baytubes/

Recommended Exposure Limit for Inhalation of Carbon Nanotubes Proposed by NIOSH

Source:The Bureau of National Affairs' Daily Environment Report

Author:Greg Hellman (7 Dec. 2010)

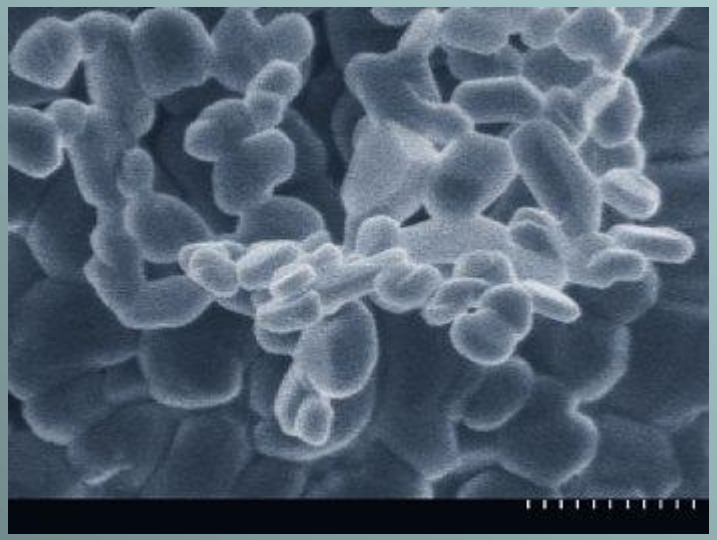
The United States National Institute for Occupational Safety and Health (NIOSH) has proposed a recommended exposure limit of seven micrograms per cubic meter of air for carbon nanotubes and nanofibers, which is the lowest concentration that can be reliably measured. These materials are used in many industries, including electronics, solar cell manufacturing, plastics and pharmaceuticals. NIOSH has observed pulmonary inflammation and fibrosis in animals resulting from exposure to certain nan hn Howard, NIOSH Director, said "[A]s nanotechnology becomes more widely u ness grows, employers, workers, and health and safety professionals all i ures for controlling occupational exposures. These diverse s wardship of nanotechnology is essential for public accept global market." NIOSH said, in the proposal, that employers should i ealth surveillance programs and take other steps to minimize risk, until researchers haracterize the toxicity of carbon nanotubes and nanofibers. James Bonner, an associate professor at North Carolina State University's Environmental and Molecular Toxicology Department, said that NIOSH chose a conservative recommended limit. "I think it's a wise choice. Based on studies with exposure to animals, we and other folks at NIOSH see significant effects at carbon nanotube concentrations above that level," Bonner said. "It's a good place to start because there's a lot of start-up companies dealing with carbon nanotubes." NIOSH will accept public comments on its proposal until February 18, 2011, and will hold a public meeting on February 3, 2011, in Cincinnati, Ohio.

The article can be viewed online at the link below.

http://news.bna.com/deln/DELNWB/split_display.adp?fedfid=18688829&vname=dennotallissues&fn=18688829&jd=a0c5m8y9f9&split=0

NIOSH (December 2010)
Nanotubes & Nanofibres 7 µg / m³

NIOSH: Nano-Titanium Dioxide "A Potential Occupational Carcinogen"



the National Institute for Occupational Safety and Health has concluded that airborne super-small particles of titanium dioxide "should be considered a potential occupational carcinogen."

For airborne titanium dioxide, NIOSH's recommendation is a limit of 2.4 milligrams per cubic meter of air for larger particles, and 0.3 milligrams per cubic meter for air for "ultrafine" or nano-sized particles, defined as under 100 nanometers in size (that figure is the traditional threshold for a substance to be considered a nanoparticle). Those exposures are predicated on a 10-hour day during a 40-hour workweek, according to the recommendations

April 2011
http://www.cdc.gov/niosh/docs/2011-160/pdfs/2011-160.pdf

i) Définitions, Markets, Properties, Applications
Définitions, Prospectives, Propriétés, Applications

ii) Real Risks, Perceptual Risks, Regulations
Risques réels, perçus, réglementation

iii) NP Hazard (Eco/Toxicity)
Nanotoxicité

► iv) Benefits / Risks analyses

Environmental Impacts of Nanosilver

An ICON Backgrounder - M. Kulinowski

Published November 2008

Environmental Contamination

Recommandation de vigilance relative à la sécurité des nanoparticules d'argent

Haut Conseil à la Santé Publique - 12 mars 2010

[…] sur le besoin de recherches portant en particulier sur (i) la mesure du nano Ag ainsi que son devenir dans les aliments, dans l'eau, dans l'air et (ii) une meilleure connaissance de ses effets sur l'homme et l'environnement, notamment sur les conséquences des effets génotoxiques et pro-apoptotiques qu'il pourrait entraîner à long terme en lien avec les différentes structures chimiques que prend le nano Ag dans les produits de consommation

[…] sur l'importance d'une évaluation toxicologique et environnementale avant la mise sur le marché des nouveaux produits sans attendre l'évolution de la réglementation européenne que les autorités françaises sont invitées à impulser, selon les principes fondateurs des dispositifs REACH et biocides.

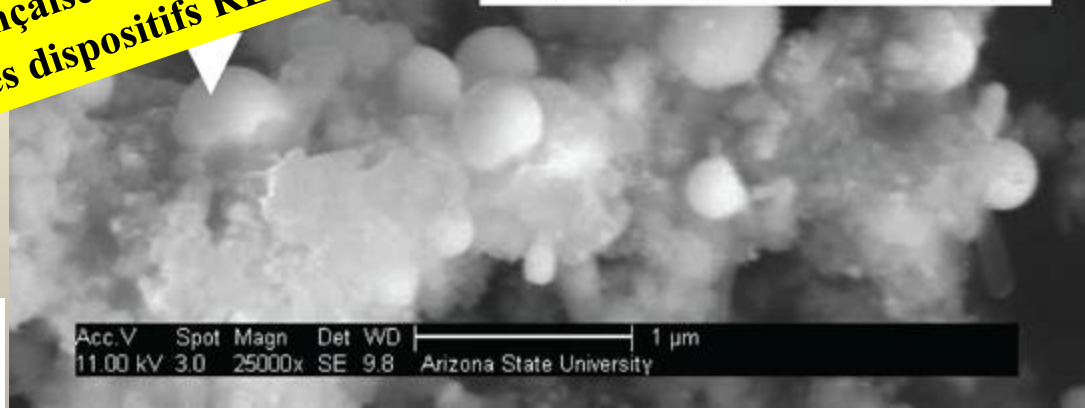


Image of nanosilver particles from socks. Inset demonstrates the particles contain silver

Silver Beware: Antimicrobial Nanoparticles in Soil May Harm Plant Life

Scientific American - Nicholette Zeliadt (**Aout 2010)**

Researchers at **Duke University, United States**, have found that silver nanoparticles negatively impact the growth of plants and kill the soil microbes that sustain such plants. Silver nanoparticles, used for their potent antimicrobial properties, are used in a wide variety of consumer products, such as clothing, hand sanitizers, and water treatment systems. As the nanoparticles make their way into the environment, via wastewater, and eventually in the sludge disposed of as fertilizer, the new study suggests that there are environmental impacts worthy of further investigation. The Duke team applied biosolids and silver nanoparticles to prepared "mesocosms" - fields of plants growing in rubber tubs - and studied the results. According to Ben Colman, a postdoctoral researcher at Duke, "[W]hat we found was actually a little bit surprising. We added lower concentrations [of silver] to a more complex system, but rather than find no measurable effect, **we found that the silver nanoparticles significantly altered the plant growth, microbial biomass and microbial activity."** Colman added that "[T]he exciting part about this work is that we have a chance to get in early on studying what could be a potential problem. Typically, as ecologists we document the effects of things such as DDT after the fact, after it's had widespread effects." The team next plans to investigate the effects of nanoparticles in a controlled wetland ecosystem.

The nanoparticles reduced the growth of one of the tested plant species by 22 percent as compared with silver-free biosolid treatment. Similarly, microbial biomass was reduced by 20 percent.

http://www.scientificamerican.com/article.cfm?id=silver-beware-antimicrobial-nanoparticles-in-soil-may-harm-plant-life

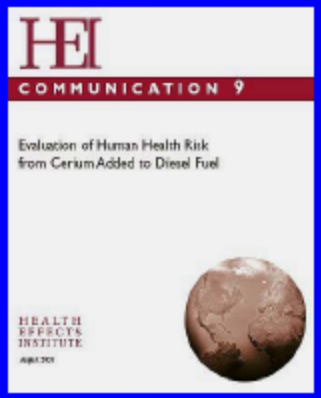
Health Risk Assessment of Nanomaterials

Air Pollution Control: Nano-metals
(Al_2O_3; Transition Metals; CeO_2: 5 - 10nm)

Fuel Additives: Better Fuel Economy and Reduced Emissions

-On and Off Road Diesel\Gas Additive:
  - Oxonica: Envirox® (nano-Cerium Oxide; 10nm);
  - Nanotech Fuel Corporation: Fuel Reformulator
-Dept. of Defense

Air
Environmental Interactions, Transformations, Fate?
Potential Health Effects?



Diesel Exhaust:
↑>50% in each: benzene; 1,3-butadie
↓80% PAHs (Air Toxic)
↓8-20% NOx (NAAQ)
↑50-100% CO (NAAQ)

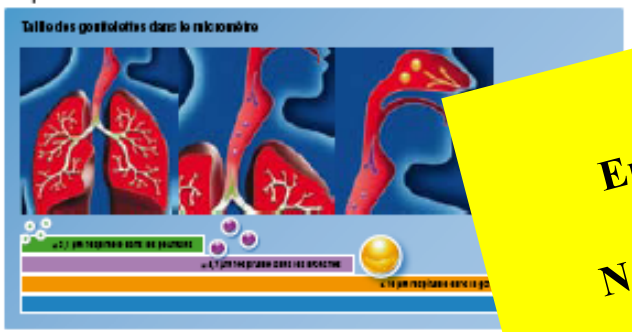
Evaluation of Human Health Risk from Cerium Added to Diesel Fuel (Health Effect Institute 2001)

Communication / Transparence / Informations

Holmenkol (Allemagne)

Il est indubitable que la nanotechnologie a ouvert d'énormes possibilités du point de vue économie et société, mais elle présente toutefois quelques risques. L'étude des risques éventuels a lieu tant au plan national qu'international. Hormis le ministère de l'Education et de la Recherche, de nombreuses entreprises investissent des millions d'euros dans cette recherche. Des leaders allemands en matière de nanotech[illegible] et qui se sont associés dans le forumnano, s'engagent pour [illegible] protection du consommateur.

HOLMENKOL [illegible] intermédiaire de ses partenaires [illegible] (comme Nansafe) pour analyser les risques liés à [illegible] avant leur lancement sur le marché, les produits HOLMENKOL [illegible] soumis à un nombre d'essais internes et externes, ces derniers étant effectués par des laboratoires d'essais. Les nano composants employés chez HOLMENKOL ne sont pas utilisés à l'état pur mais sont intégrés dans une matrice de façon sûre. Il a été prouvé que la taille des gouttelettes des produits pulvérisés est réglée de façon à garantir que les composants pulvérisés ne sont pas respirables dans les poumons.



Après avoir fait évaporer le solvant, les composants sont bien ancrés [illegible] surface traitée. Donc, une émanation de nano particules individuelles [illegible] L'ensemble des nano composants utilisés chez HOLMENKOL ont été et [illegible] à des analyses de toxicologie.

En résumé, les produits HOLMENKOL jouissent d'une quadruple sé[illegible]

1. Il a été prouvé que les composants de départ ne sont pas toxiques.
2. Seuls des nano composants ou nano couches intégrés sont utilisés
3. Il a été prouvé que les gouttelettes des produits pulvérisés ne sont pas respi[illegible]
4. Les nano composants sont fermement ancrés au fond.

Les nano produits HOLMENKOL sont sur le marché depuis des années – et ce sans réclamations.

HYGIENE EFFECT

Les vêtements fonctionnels de sport ne peuvent être lavés qu'à une température de 30°C ou de 40°C. Les protecteurs se lavent uniquement à la main. Le linge n'est pas [illegible]tement propre. La mauvaise odeur n'a pas disparu après lavage. En principe, la [illegible]est inodore, mais une fois décomposée par des bactéries elle prend son odeur [illegible]ristique. L'effet d'hygiène prévient la formation de mauvaises odeurs.

ACTIVE DRY

Les tissus synthétiques hydrofuges ne permettent qu'un mouillage insuffisant. Grâce à l'additif « séchage actif » le tissu peut mieux absorber l'eau, et l'effet de nettoyage ainsi que l'activité respiratoire sont améliorés.

NanoPhase (USA)

Environmental Health and Safety Management Systems :

The Illinois EPA regulates all Nanophase locations. Nanophase complies with the SARA 313 and 312 regulations, and holds all required environmental permits. Nanophase enjoys excellent relations with local, state, and federal regulators.

Nanophase is a proactive health and safety manager and provides monitoring in the production, quality control and research and development area for exposure to particulates, solvents and noises. All of the results have been positive in over five years of testing.

NanoTechnologies & NanoMaterials

Nano - Solutions for Sustainable Development

Conclusion & Perspectives

Yet on Market !

(since many years)

How to Manage Incertitude ?

► **Safe by Design**

(toxicity and/or exposition controls)

► **Safe by Process**

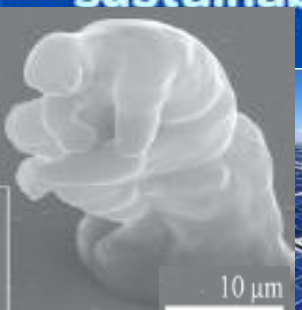
(exposition control)

► **Inventory**

(State Agencies – Not only volountary one)

► **Risk / Benefit ?**

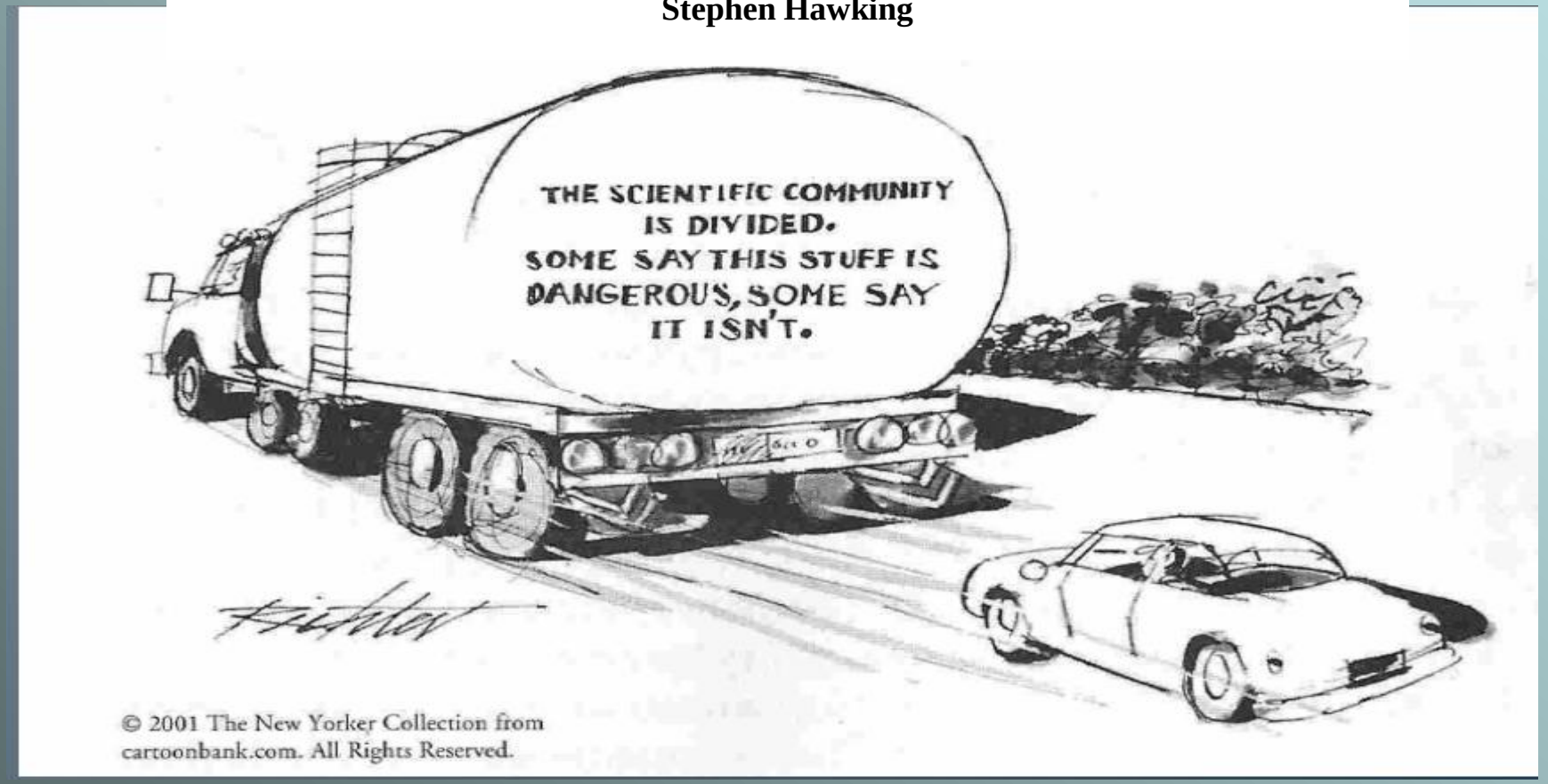
(opened analyses and public discussion)



Eric.Gaffet@utbm.fr

NanoMaterials and Nanotechnologies For a Sustainable Development (Responsible, Safe, Approved)

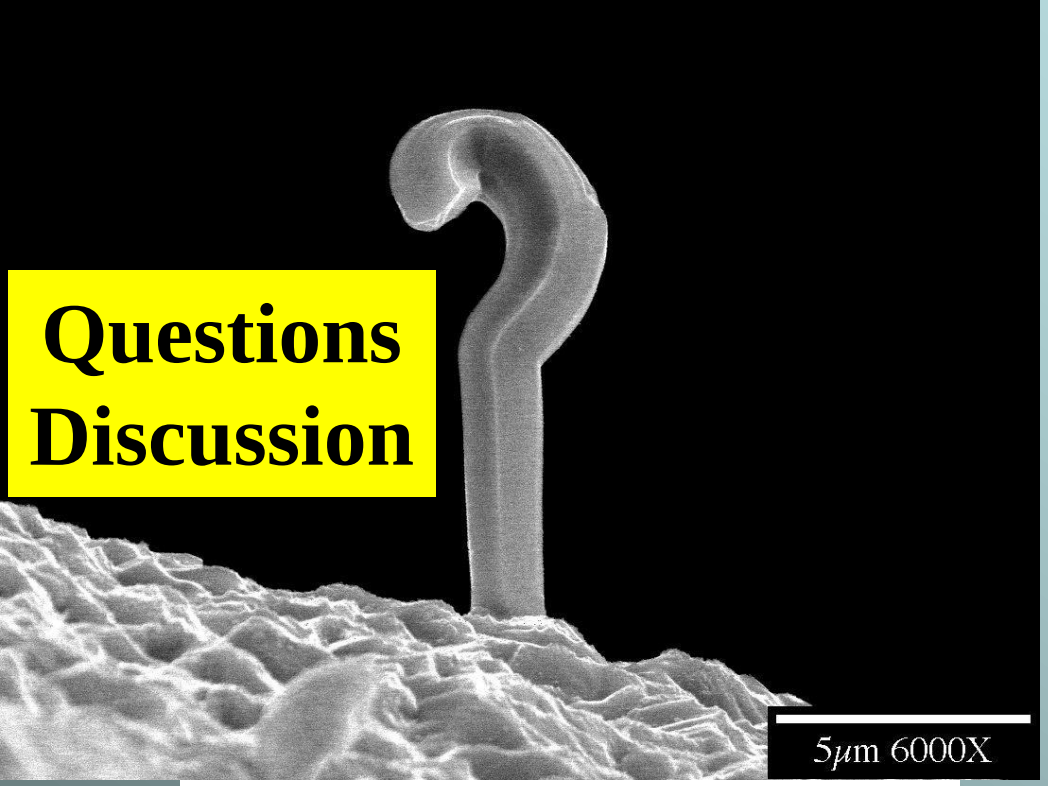
"Today's science fiction is often tomorrow's science fact."
Stephen Hawking



http://www.afsset.fr (pour les rapports AFSSET / nano EHS)
http://www.ecologie.gouv.fr (pour le rapport CPP / Nano)
http://www.nanomateriauxetsecurite.fr (pour les GT nano EHS)

Eric.Gaffet@utbm.fr

Questions Discussion



Tin Whisker (Peter Bush, SUNY at Buffalo)

Eric.Gaffet@utbm.fr

I, Robot
Isaac Asimov (1950)

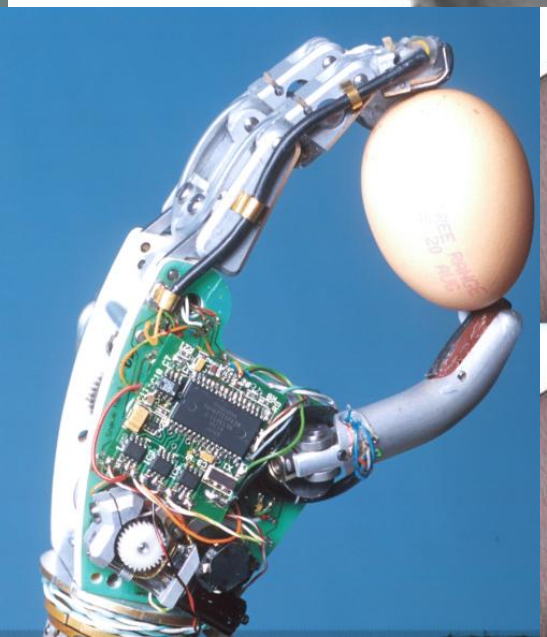
Thank you very much for your attention

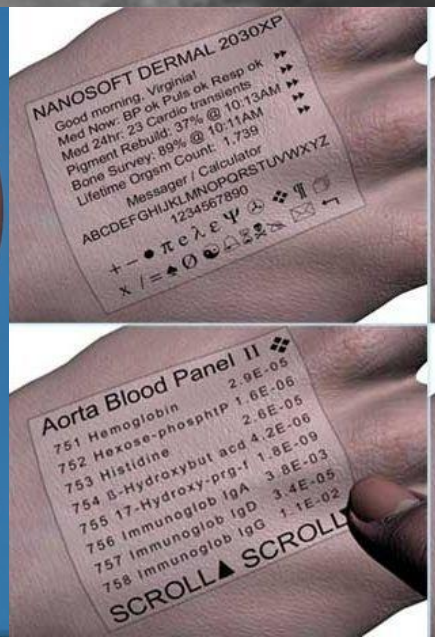
Eric.Gaffet@utbm.fr

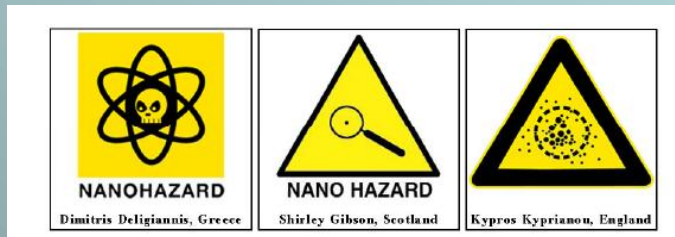
1. **A robot may not injure a human being,**
   or through inaction, allow a human being to come to harm

2. **A robot must obey the orders given it by human beings,**
   except where such orders would conflict with the first law

3. **A robot must protect its own existence,**
   as long as such protection does not conflict with the first or second law







I never came upon any of my discoveries through the process of rational thinking

Albert Einstein

Eric.Gaffet@utbm.fr