I U P A C

Advancing Worldwide Chemistry

Daniel BERNARD

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Nanomaterials as Chemicals

Daniel BERNARD

—————————

Comité National de la Chimie

IUPAC Advancing Worldwide Chemistry

What is called Nanomaterials ?

Do we need different definitions for Nanomaterials ?

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Nanotechnologies

➢ include, for ISO TC 229, either or both of the following:

1. **Understanding and control of matter and processes at the nanoscale,** typically, but not exclusively, below 100 nanometres in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications,

2. **Utilizing the properties of nanoscale materials that differ from the properties of individual atoms, molecules, and bulk matter,** to **create improved materials,** devices, and systems that exploit these new properties.

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Materials structured at the nanoscale

- **Nanomaterial**
  Material with <u>any external</u> dimension in the nanoscale, or having <u>internal</u> structure, or <u>surface</u> structure <u>in the nanoscale,</u>

- **Nano-object**
  Material with <u>one</u>, <u>two</u> or <u>three</u> external dimensions <u>in the nanoscale,</u>

- **Nanostructured material,**
  Material having <u>internal</u> nanostructure or <u>surface</u> nanostructure,

- **Manufactured nanomaterial,**
  Nanomaterial <u>intentionally produced</u> for commercial purpose to have <u>specific properties or specific composition,</u>

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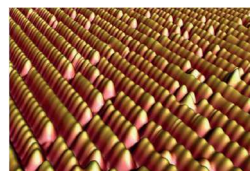
Nanoscale

size range from approximately 1 nm to 100 nm

1/ Properties that are not extrapolations from a larger size will <u>typically, but not exclusively,</u> be exhibited in this size range. For such properties the size limits are considered <u>approximate</u>.

2/ The lower limit in this definition (approximately 1 nm) is introduced to <u>avoid single and small groups of atoms from being designated as nano-objects</u> or elements of nanostructures, which might be implied by the absence of a lower limit.
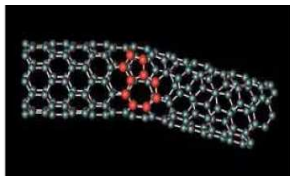
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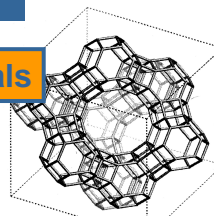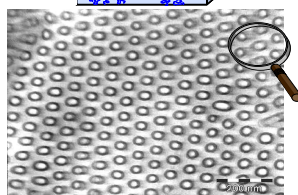ICSU-CODATA; 23-24 february 2012 –D.Bernard

Nanomaterials

Nanostructured materials
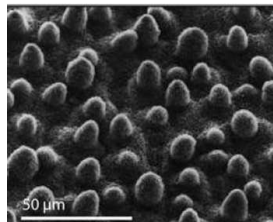
Nanostructured surfaces

Nano-objects

Block Polymers
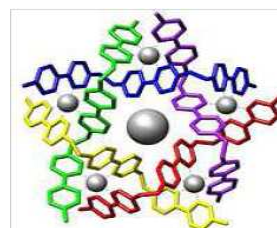
PS PB PMMA
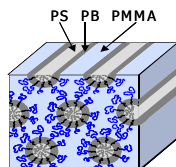
Nanoporous materials

Nanotubes

Supramolecular structures

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OECD WP Manufactured Nanomaterials

Gold nanoparticles

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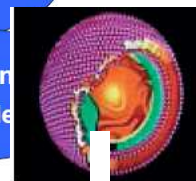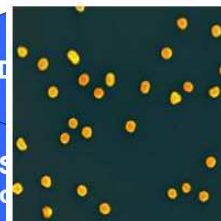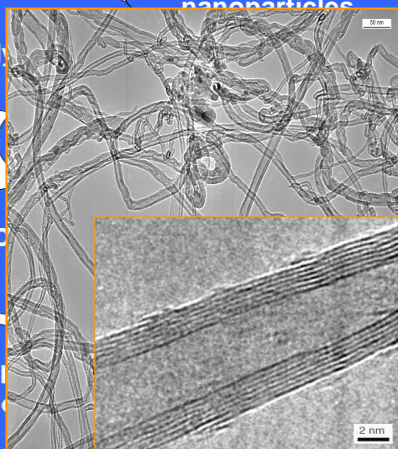
Carbon

Diamond

Graphite

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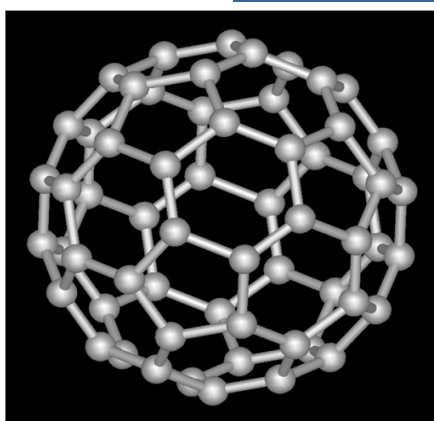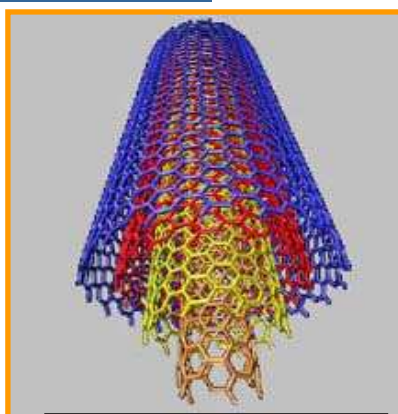
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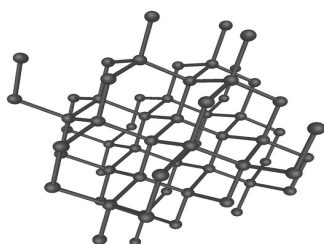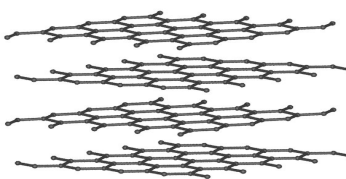
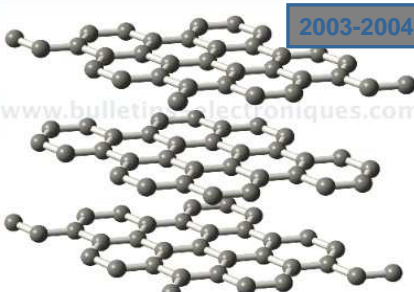**Nanocarbon**

Fullerene C60
R.Smalley,H.Kroto,
R.Curl (1985)

Carbon Nanotubes,
S.Ijima (1991), *yes
but* M.Endo (1976)

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2003-2004

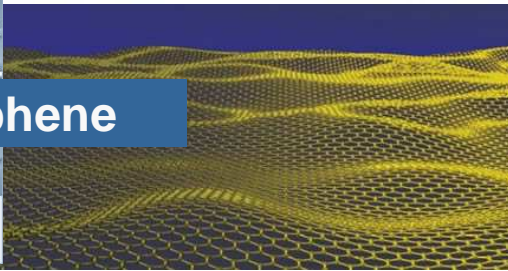2010 Nobel Prize in Physic

Andre Geim   Konstantin Novoselov

Graphene
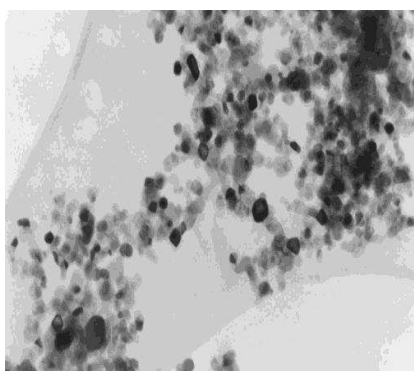
Image par microscopie électronique à balayage d'une feuille de graphène froissée sur wafer de silicium
www.bulletins–electroniques.com/actualites/42147.htm
Crédits : K.S. Novoselov, Université de Manchester
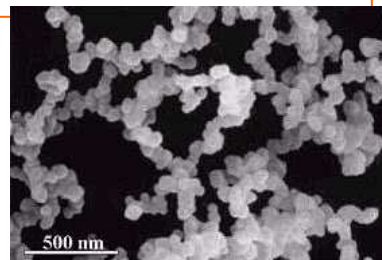
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Commercial nanomaterials

• Doped titaniana nanoparticles used in sunscreen to give UV protection and safeguard against free radical damage
• Titania blocks the damaging UV and a special dopant stops free radicals from being formed

Nanoparticles of cerium oxide used in diesel fuel at ~ 5ppm to eliminate soot and improve fuel efficiency

500 nm

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Water Purification using sunlight

Installation in Spain 13

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Buildings and public works

**Self cleaning concrete incorporating
nano- titanium dioxyde
Jubilee church(Roma)**

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Nano-silver as biocide

nAg washing machine

nAg shampoo

nAg air dryer

nAg tooth brush
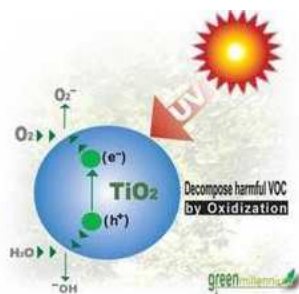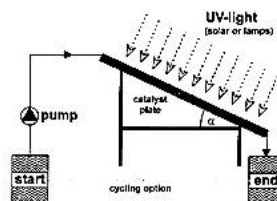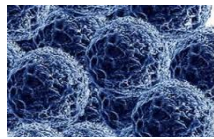
nano silver powder
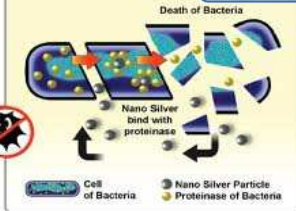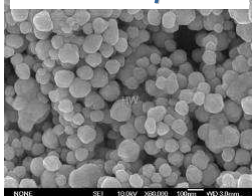
nAg towel

nAg socks

nAg key-board cover

Environmental clean-up with nanoparticles

Contaminant Source

Injection of Iron Nanoparticles

Transformation of Fertilizers (e.g., NO_3^-)

Dechlorination of Organic Solvent (e.g., CCl_4, C_2Cl_4)

Detoxification of Pesticides (e.g., Lindane, DDT)

Immobilization of Metals (e.g., Pb, Cr, As)

Zhang (2003) J Nanoparticle Research vol 5, p 323

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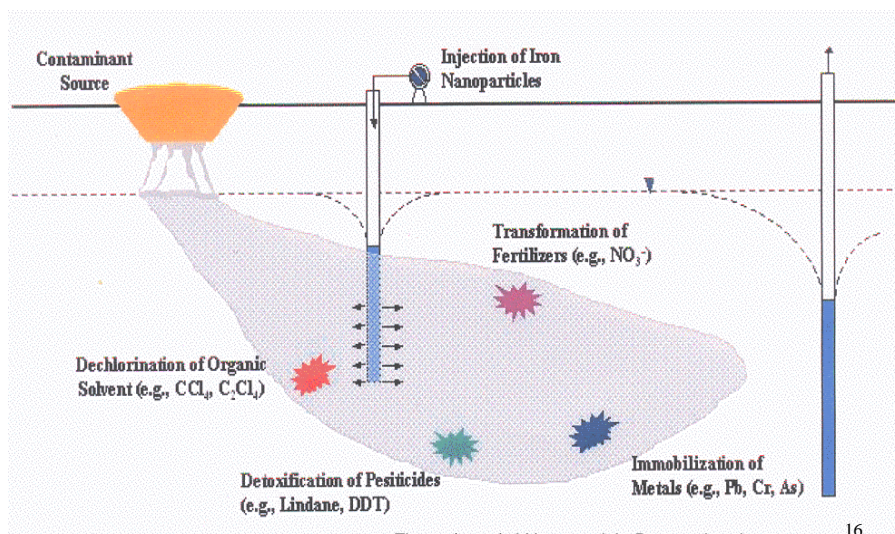
Polymeric structuration at the nanoscale using block copolymers

- **Anionic polymerization of methacrylates : SBM copolymers**
  (Poly Styrene-*b*-Polybutadiene −*b* −PMMA)

  PS   PB   PMMA
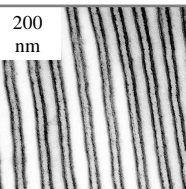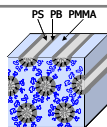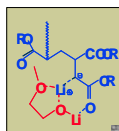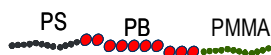
- **Nitroxyde mediated radical polymerization**
  - Functional acrylic and methacrylic block copolymers

  PMMA   PBuA   PMMA

200 nm
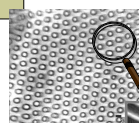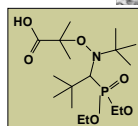
Nanostructured phases obtained with block copolymers

500 nm
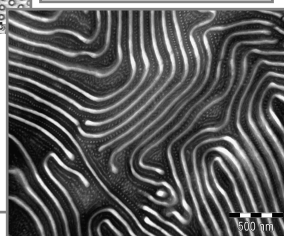
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Micro and ultra filtration membrane for water purification

Hydrophilic Polymer

PVDF

10 nm

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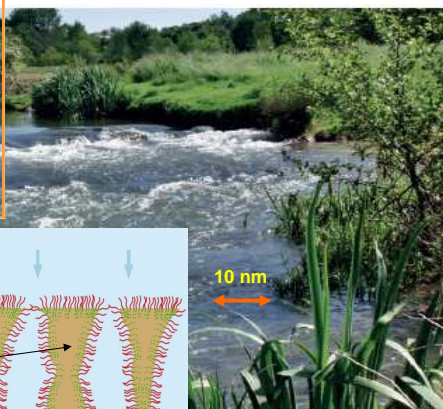
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Coatings and surface treatment

Glass coating

Self cleaning surfaces

Paints

Anti scratch coating

Technical Textiles Membranes 19

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Nanocomposites for aerospace industry

Multifunctional nanocomposites

- Lightened aerostructure,
- Conductive nanocomposites,
- Active materials (probe, actuators,.),

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Carbon Dioxide Capture and Utilization

- Current CO_2 capture media only perform a single function, i.e. CO_2 separation from flue gases. Need to develop:
  - Media and membranes with multifunctional and size/shape selective nanocages that can capture CO_2 from flue gases and convert it to useable products.
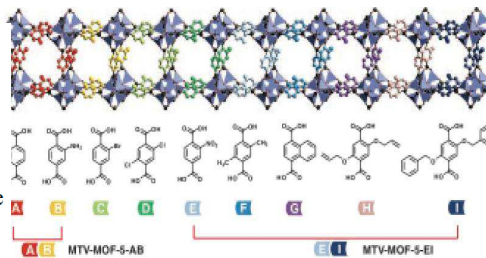
Yaghi et al. Science (2010)**327**, 846

Can CO_2 be then utilized to make fuel (methane) or precursors for chemicals and polymers.

CO_2

+

H_2O

→ **Catalyst** → **Methane Alcohol Olefins**

Sun light
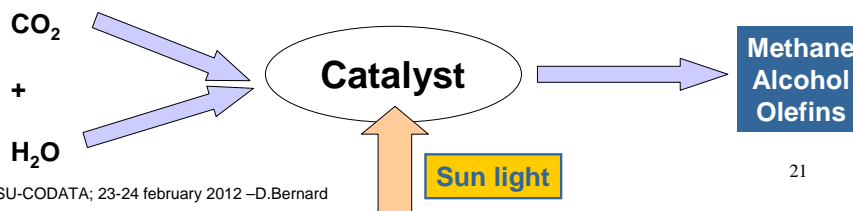
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Alternative energies

Wind mill

Cold light LEDs

Fuel cell Hydrogen storage

Thermal insulation

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Slide 1
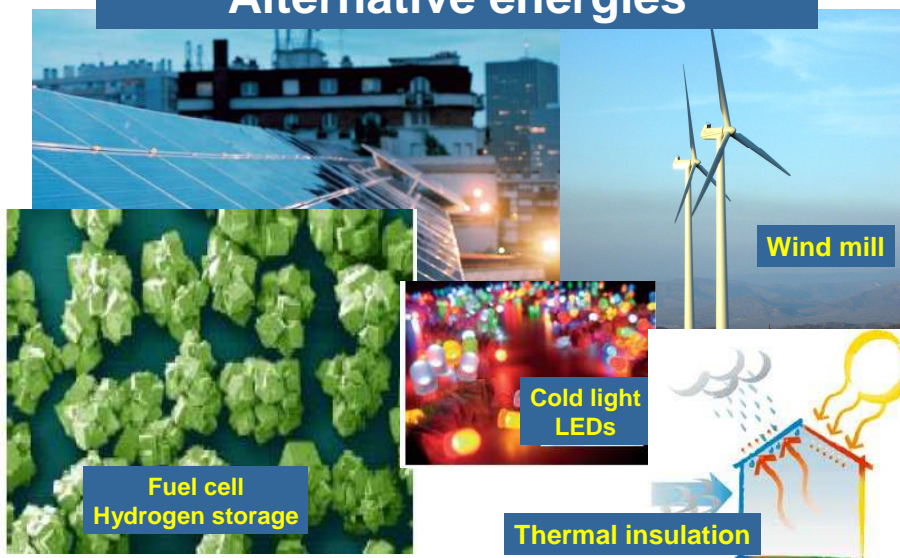
Energy: electrochemical storage

**Supercapacitors
Lithium-ions batteries**

Power to weight (W/kg)

10^5

10^4

**Capacitors
F-μF
μs-ms**

**Super-capacitors
F-kF
ms-s**

**Batteries
sAh / min**

Charge Q
Electrode area A
Electrode distance d

Electrode | Dielectric | Electrode
(a) Electrostatic

Electrode Electrolyte Separator Electrolyte Electrode
(b) Electrochemical double-layer

1   10 10^2
23
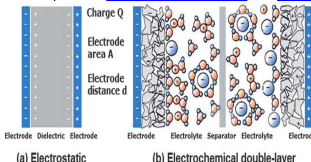
Energy to weight (Wh/kg)

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Slide 2

Enhanced imaging using fluorescently labelled nanoparticles

Cy5.5

Et-O-Si—NH2
APTES

1st Silication of USPIO

Et-O-Si—N—C

1   20
Dye Attachment

2nd Silication

SCION
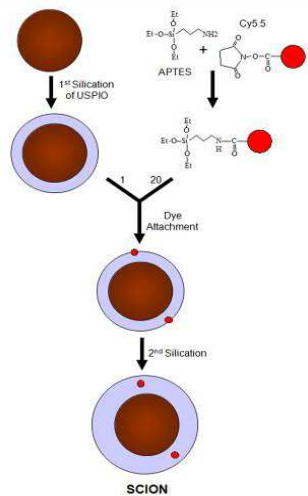
Silica Coated Iron Oxide Nanoparticles

Based on earlier work that makes a dye-doped silica particle around a core of a superparamagnetic iron oxide particle (~9 nm diameter).

Bumbet al. Nanotechnology 19, 335601 (2008)

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Nanomaterials in the past

"LYCURGUS Cup"
(Rome 400 AD)

Dichroïc Glass
- 40 ppm Au and
  300 ppm Ag
- Nanoparticles
  diameter 70 nm
(British Museum)

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Nanomaterials in the past

Carbon nanotubes in Damascus steel
Peter Paufler and al. (Dresde University)
Nature 16.11. 2006

**Damascus cutlass, made by the persian master smith
Assad Allah (XVIth century),
exposed at the historical museum Berne**

[Steel produced in India and imported under the name of wootz – containing with iron, 1,2 % à 1,8 % de C, and some traces of Si, Mn, P and S]

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Slide 1

Nanomaterials uncertainties

➤ **Nanomaterial definition ?**

➤ **Nanomaterial detection/characterization ?**

➤ **Specific regulation for nanomaterials («nano-REACh», US EPA PMN, notification, labelling,..) v.s. chemical substances ?**

➤ **« Specific nanomaterial » risks:**
- Technical and market,
- Health and environment impacts,
- Legal / liability, insurance, financial,
- Ethical, *societal acceptance*,

➤ **« Specific nanomaterial » benefits,**
- Sustainable development (less energy, less raw materials),
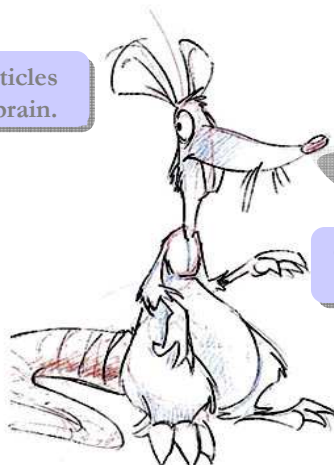- Efficiency / Performance, new functions,

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Slide 2

Nano-objects hazard

Nanoscale particles end up in the brain.

Conventional particles end up in the lungs.

Based on Oberdörster, G., *et al.*, *Inhal. Toxicol.* 16 (6-7), 437-445, 2004.

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Conclusions

Societal perception and impacts of nanomaterials is difficult to predict. Early societal intervention may enable anticipation of positive and negative impacts.

In spite of uncertainties, nanomaterials are an opportunity for the Society and the citizens.
All the stakeholders must collaborate to support a safe and responsible production and uses of nanomaterials for the benefit of all the citizens.

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Thank you for your attention

Questions ?

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