

Further classes of materials and applications

building & construction materials
carbon structures based materials
nanomaterials
apparel & textiles
paper

wood: see Biomass course prof. Zanetti/Tondi

Further classes of materials and applications

1- surface effects

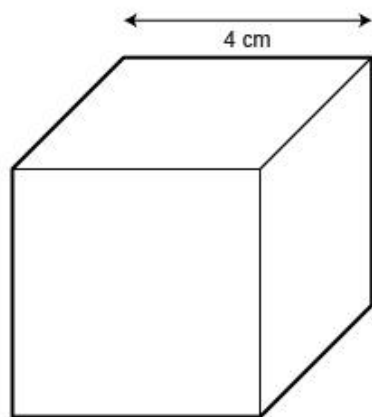
2- quantum size confinement effect

Further classes of materials and applications

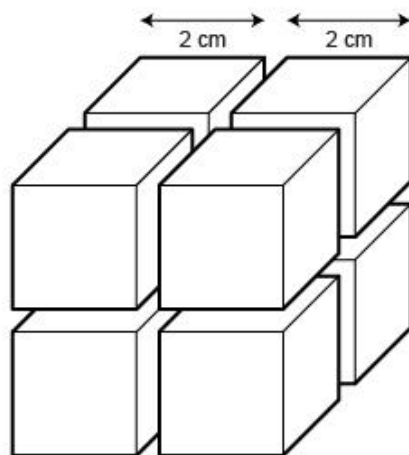
1- surface effects

2- quantum size confinement effect

Size and surface



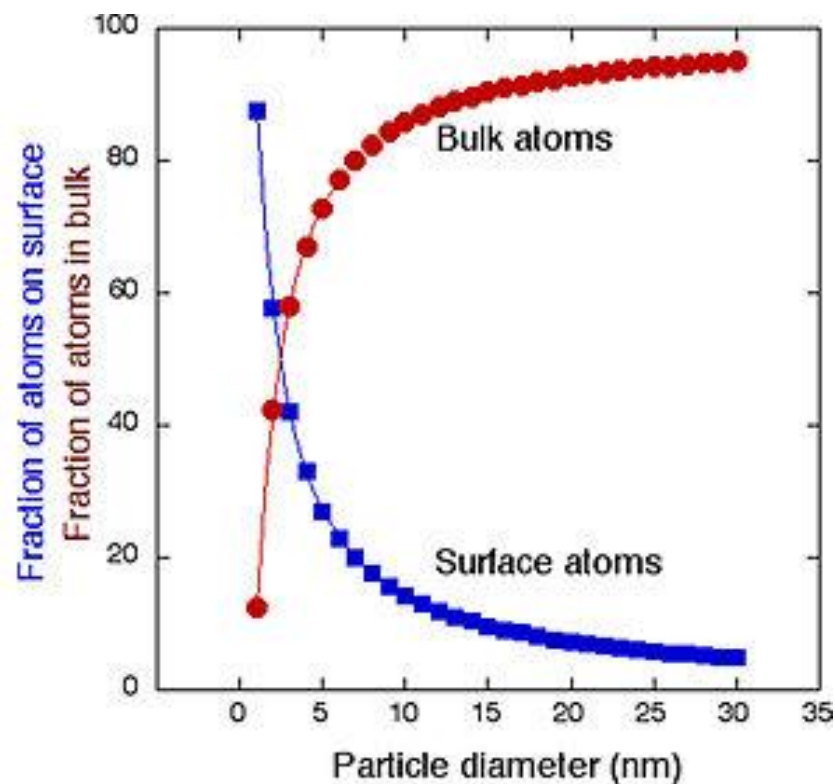
Surface area
= (4 cm x 4 cm x 6 faces) = 96 cm²



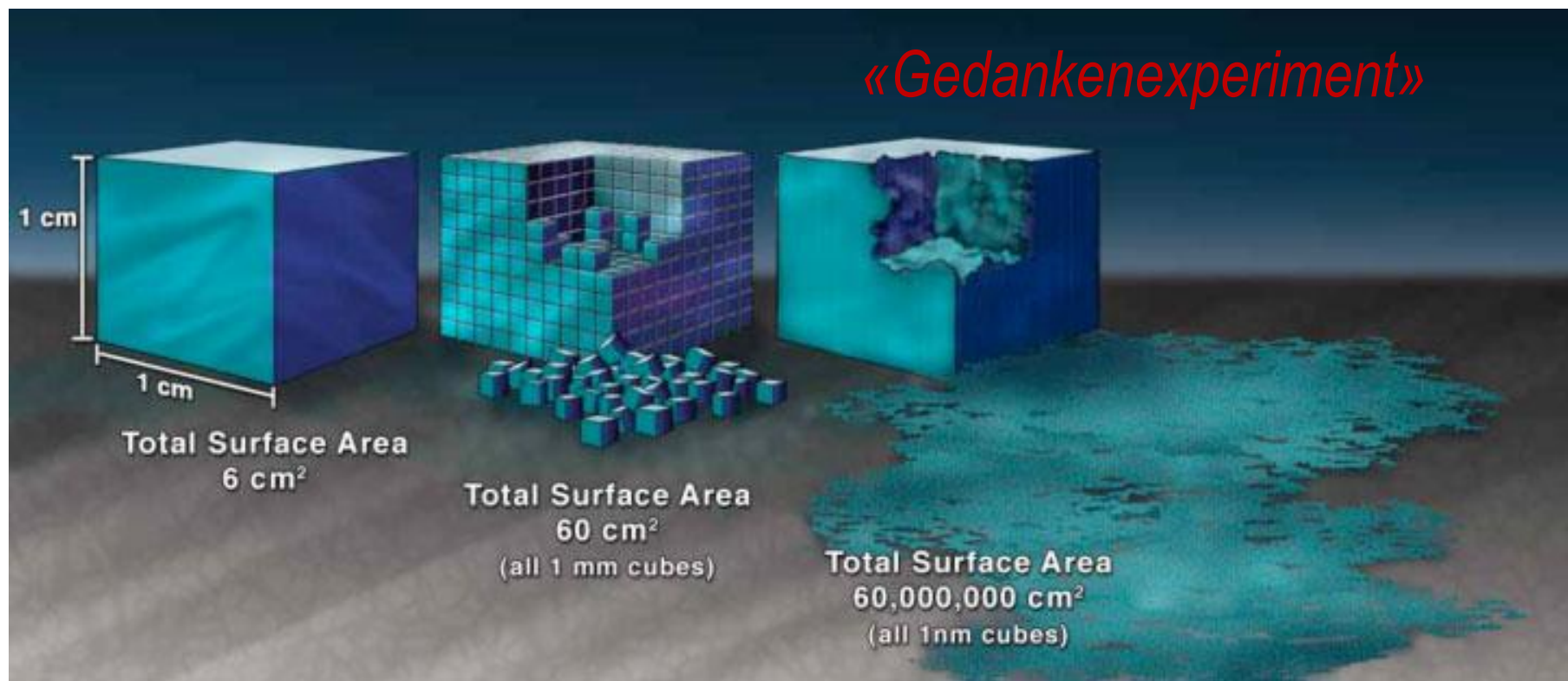
Surface area of one cube
= (2 cm x 2 cm) x 6 faces = 24 cm²

Total surface area
= 24 cm² x 8 cubes = 192 cm²

«Gedankenexperiment»



chemwiki.ucdavis.edu



A solid cube of a material 1 cm on a side has 6 square centimeters of surface. But if that volume of 1 cubic centimeter were filled with cubes 1 mm on a side, that would be 1,000 millimeter-sized cubes ($10 \times 10 \times 10$), each one of which has a surface area of 6 square millimeters, for a total surface area of 60 square centimeters. When the 1 cubic centimeter is filled with micrometer-sized cubes—a trillion (10^{12}) of them, each with a surface area of 6 square micrometers—the total surface area amounts to 6 square meters. And when that single cubic centimeter of volume is filled with 1-nanometer-sized cubes— 10^{21} of them, each with an area of 6 square nanometers—their total surface area comes to 6,000 square meters.

<https://www.nano.gov/nanotech-101/special>

- density remains constant (not true at atomic dimensions)
- properties are different from the bulk

Full-shell "magic number" clusters								
Number of shells	1	2	3	4	5	10	20	21
Number of atoms in cluster (N_{at})	13	55	147	309	561	3871	28741	33153
Percentage of surface atoms (P_s)	92.3	76.4	62.6	52.4	44.9	25.9	13.92	13.31

pubs.rsc.org

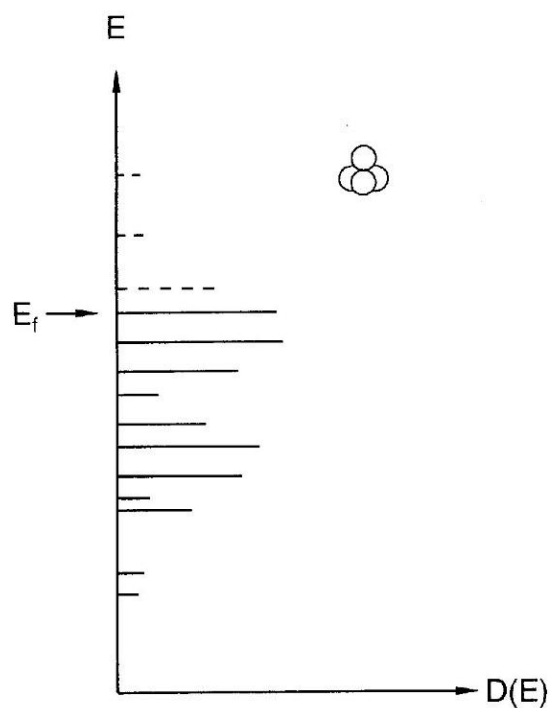
1- size effects

2- quantum size confinement effect

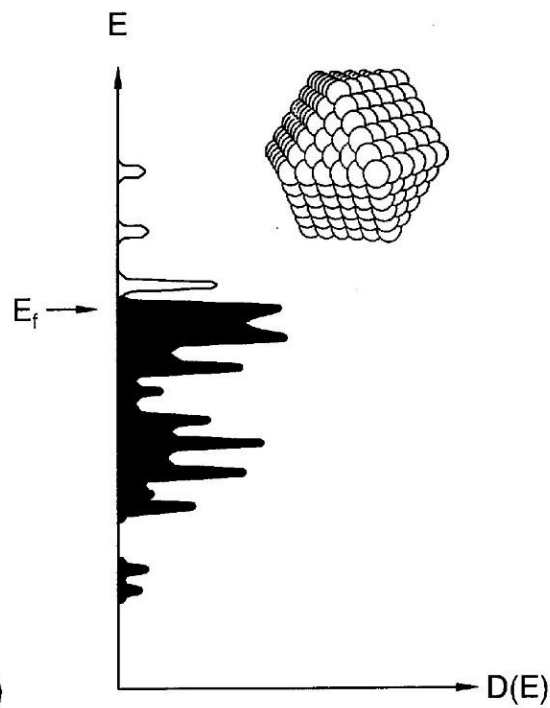
Quantum confinement effect (QCE), an essential physical phenomenon of semiconductors when the size becomes comparable to the exciton Bohr radius*, typically results in **quite different physical properties of low-dimensional materials from their bulk counterparts** and can be exploited to enhance the device performance in various optoelectronic and other functional applications.

*Exciton Bohr radius is the separation between electron and hole in an electron-hole pair.

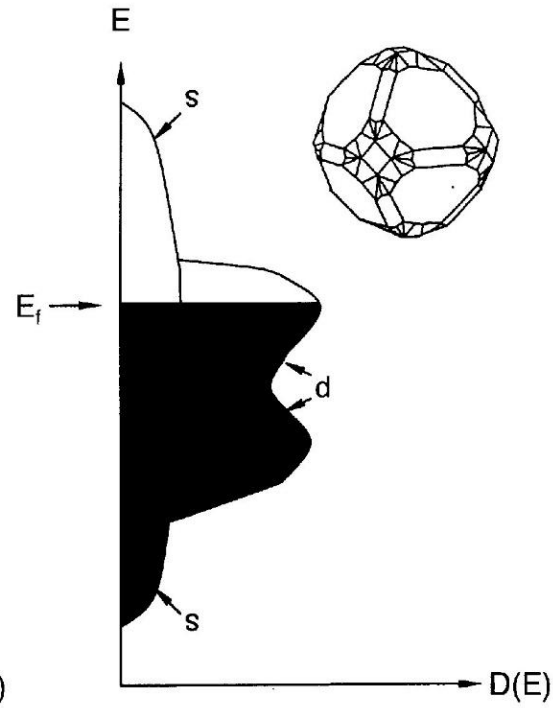
Size matters



a
Molecular Cluster

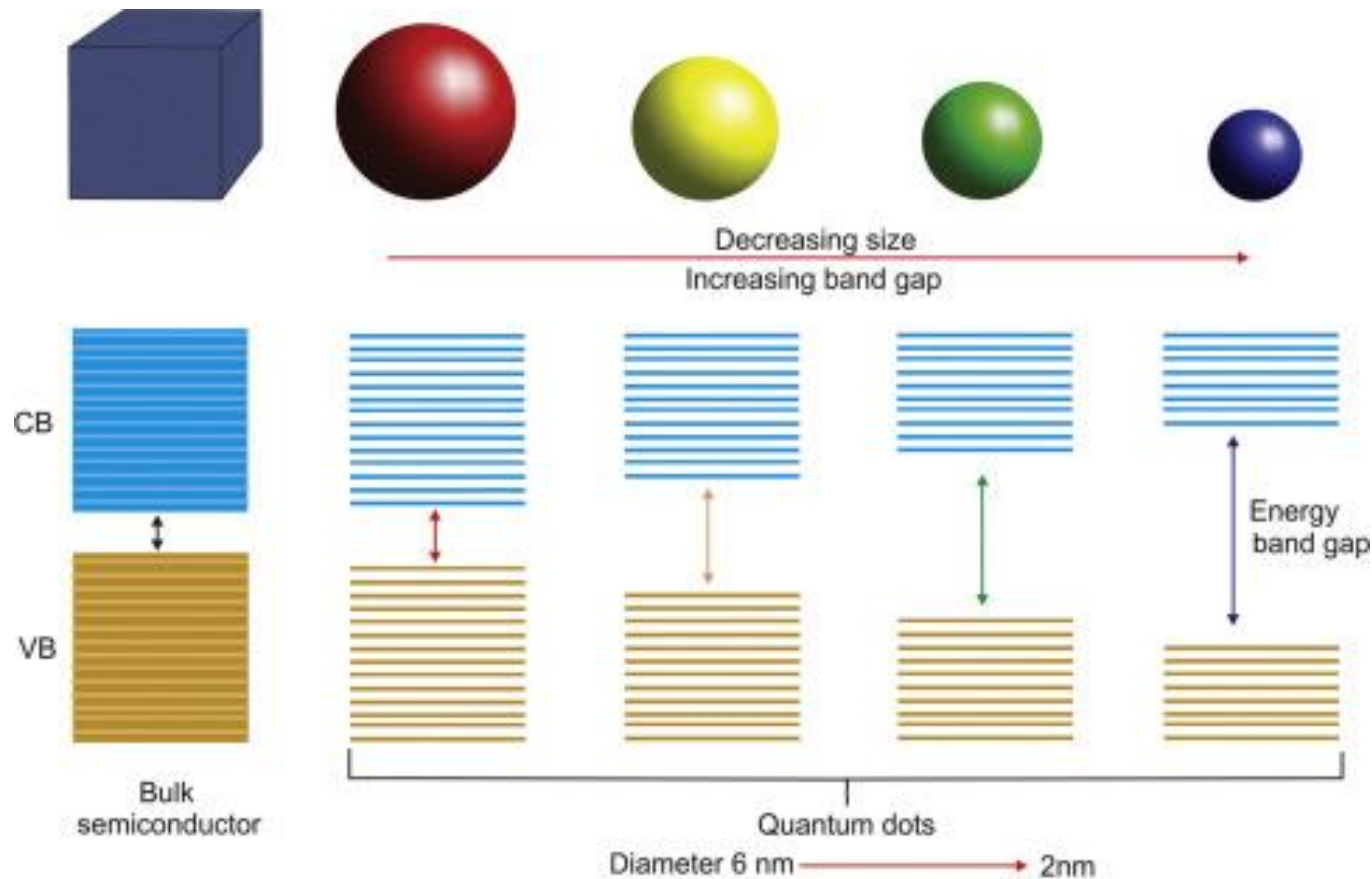


b
Large Cluster



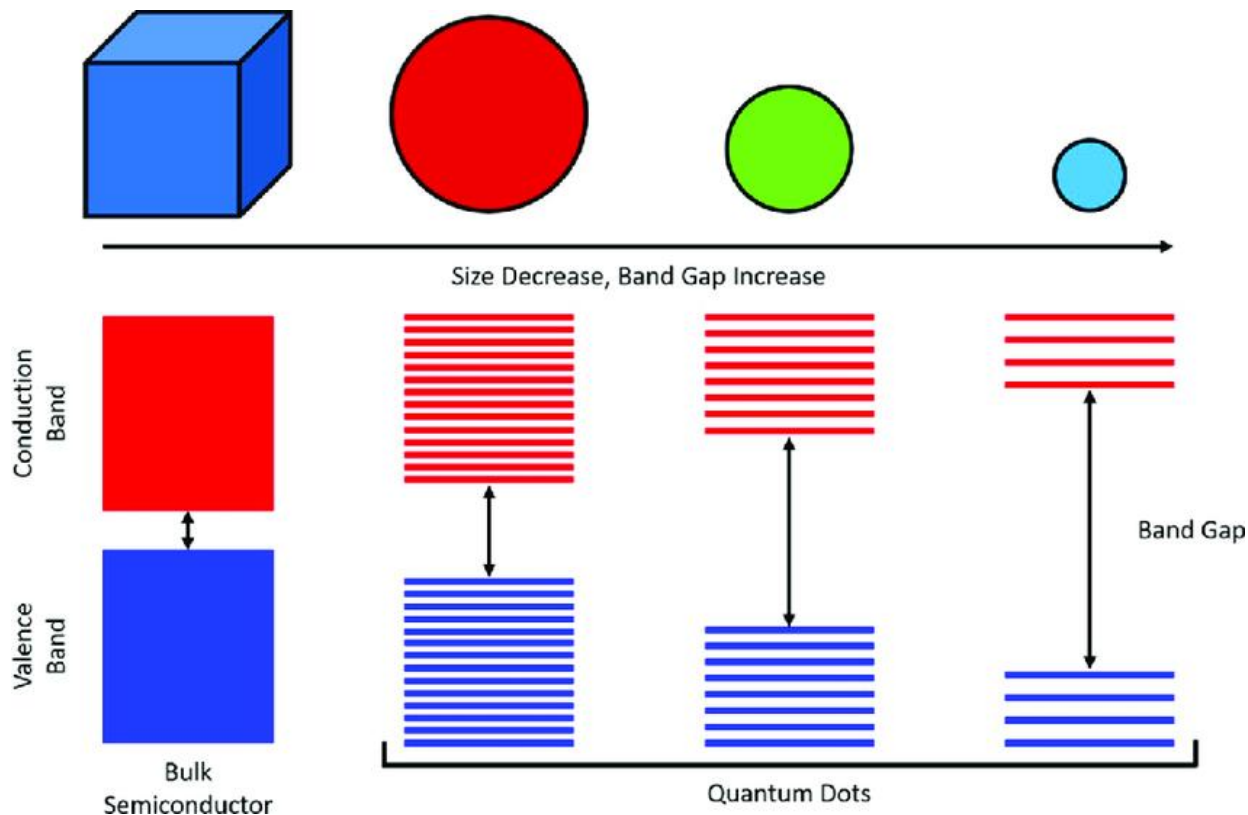
c
Metal

Quantum confinement



<https://www.sciencedirect.com/topics/engineering/quantum-confinement-effect#:~:text=The%20quantum%20confinement%20effect%20is%20observed%20when%20the,material%20properties%2C%20namely%2C%20on%20the%20Bohr%20radius%20aB.>

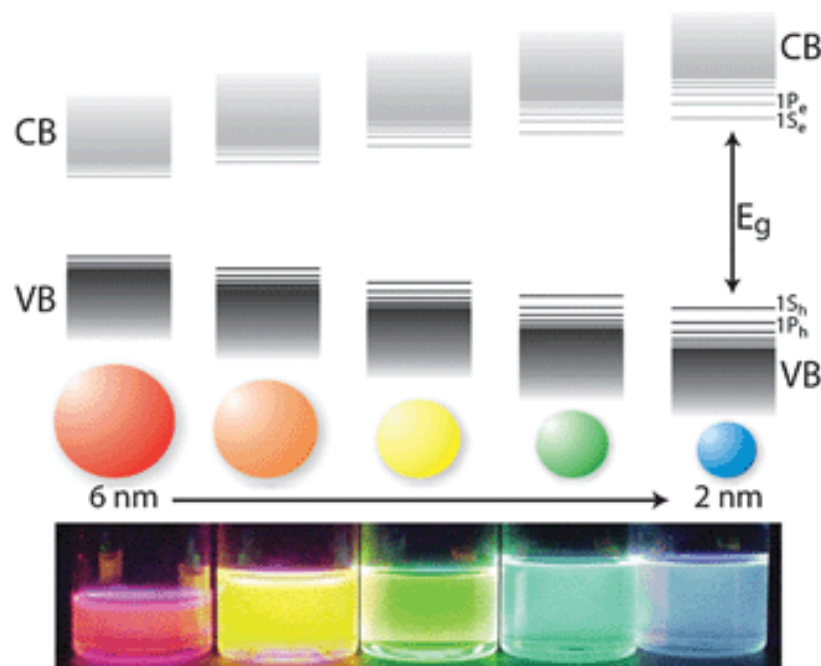
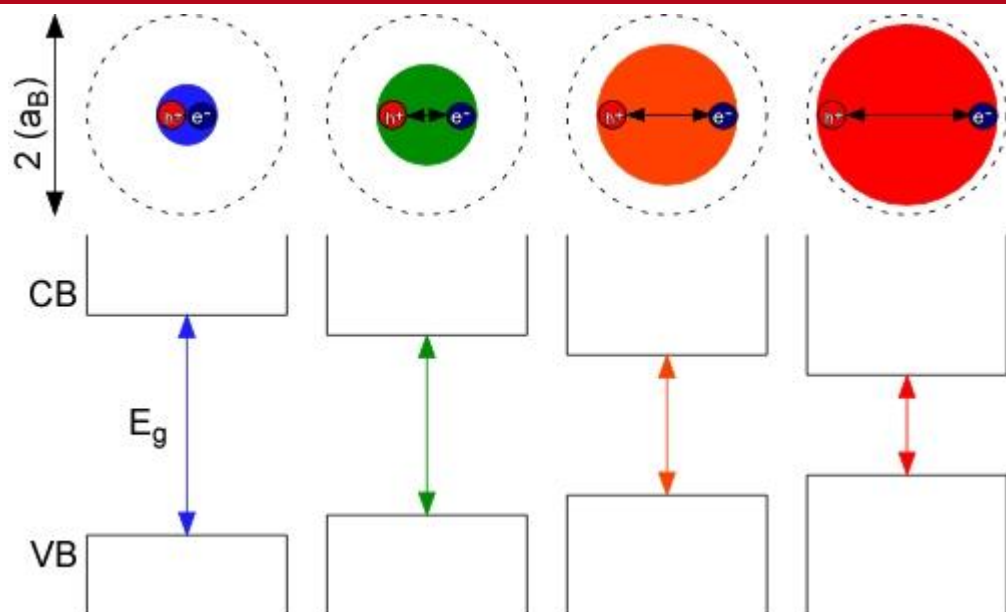
Quantum confinement



In solid-state physics, for the insulators and semiconductors, a band gap energy generally refers to the difference of energy between the top of the valence band and the bottom of the conduction band. It is closely related to the HOMO/LUMO gap in chemistry. Band gap energy (E_g) is a major factor determining the electrical conductivity of material.

Source: <https://www.sciencedirect.com/topics/engineering/band-gap-energy>

Quantum confinement



CRITICAL REVIEW

www.rsc.org/csr | Chemical Society Reviews

Synthesis and properties of colloidal heteronanocrystals†

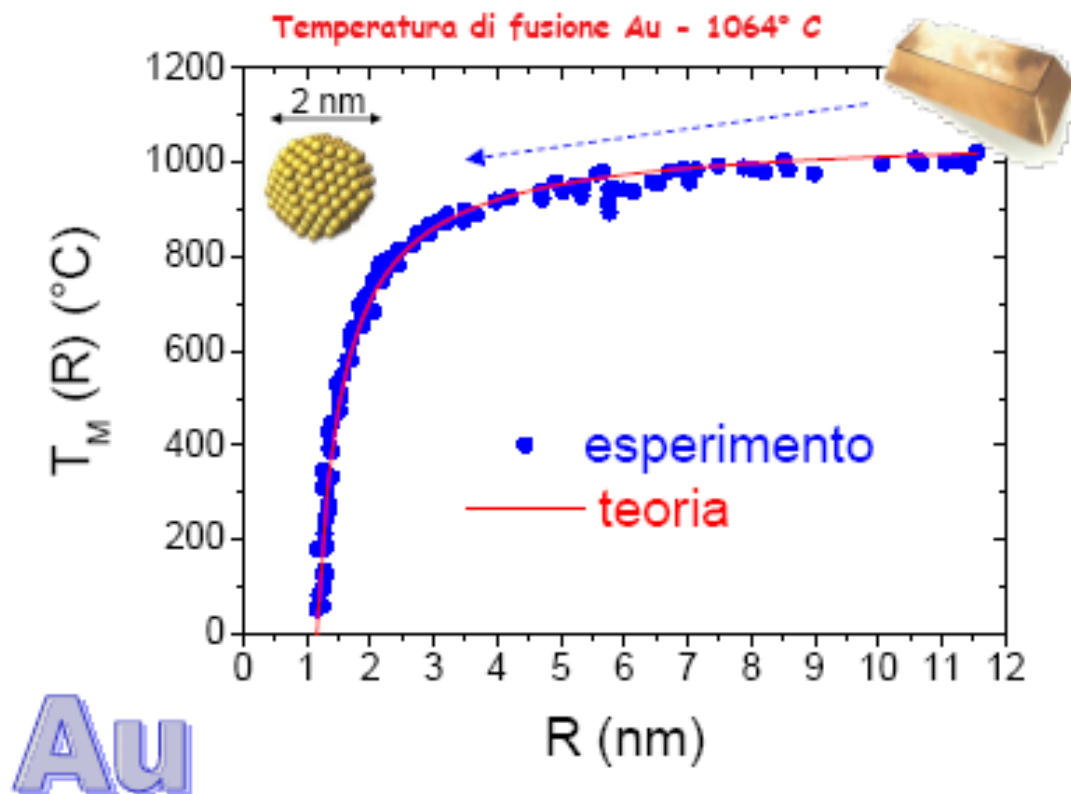
Celso de Mello Donegá*

Received 27th July 2010

DOI: 10.1039/c0cs00055h

The **quantum confinement effect is observed** when the size of the particle is too small to be comparable to the wavelength of the electron. Obviously, the confinement of an electron and hole in nanocrystals significantly depends on the material properties, namely, on the Bohr radius.

Schematic representation of the quantum confinement effect on the energy level structure of a semiconductor material. The picture shows colloidal suspensions of CdSe NCs of different sizes under UV excitation.



The Lindemann criterion states that a crystal melts when the *mean* thermal displacement of the atoms (δ) gets larger than a certain fraction of the interatomic distance.

Surface atoms have smaller coordination numbers and thus a 2-4 fold higher displacement (δ_s) than the atoms in the bulk (δ_v). When a particle gets smaller, the portion of surface atoms gets higher, and thus the mean δ increases. The melting point is therefore only a constant as long as the portion of surface atoms can be neglected.

U. Schubert, N. Hüsing
Synthesis of Inorganic Materials
Wiley VCH

Lindemann criterion

The average amplitude of thermal vibrations increases when the temperature of the solid increases. At some point the amplitude of vibration becomes so large that the atoms start to invade the space of their nearest neighbors and disturb them and the melting process initiates. Quantitative calculations based on the model are not easy, hence Lindemann offered a simple criterion: melting might be expected when the root mean vibration amplitude $(\langle u^2 \rangle)^{1/2}$ exceeds a certain threshold value (namely when the amplitude reaches at least 10% of the nearest neighbor distance).



Silberkolloid
silver colloid



Goldkolloid
gold colloid



What is Nano-Aurum?

Nanoskaliges gold, also gold colloid mentioned, is one since years well-known, often described and sagenumworbene ruby-red liquid. It consists of pure gold and water and is that that it possesses harmony, success, luck and satisfaction to bring, against bad jets and influences protect, in addition, for the healing of different diseases and physical defects be helpful. Nano-Aurum, our nano-gold, contains gold particles with a diameter of approximately 10 Nm. The irradiation of light on the gold particles energizes collective electron movements on the surface of the particles, so-called Plasmonen. The Plasmonenresonanz of our nano-gold particles produces the ruby-red color.

Size matters



Gold nanoparticles
(gold colloidal sol)

Silver nanoparticles
(silver colloidal sol)

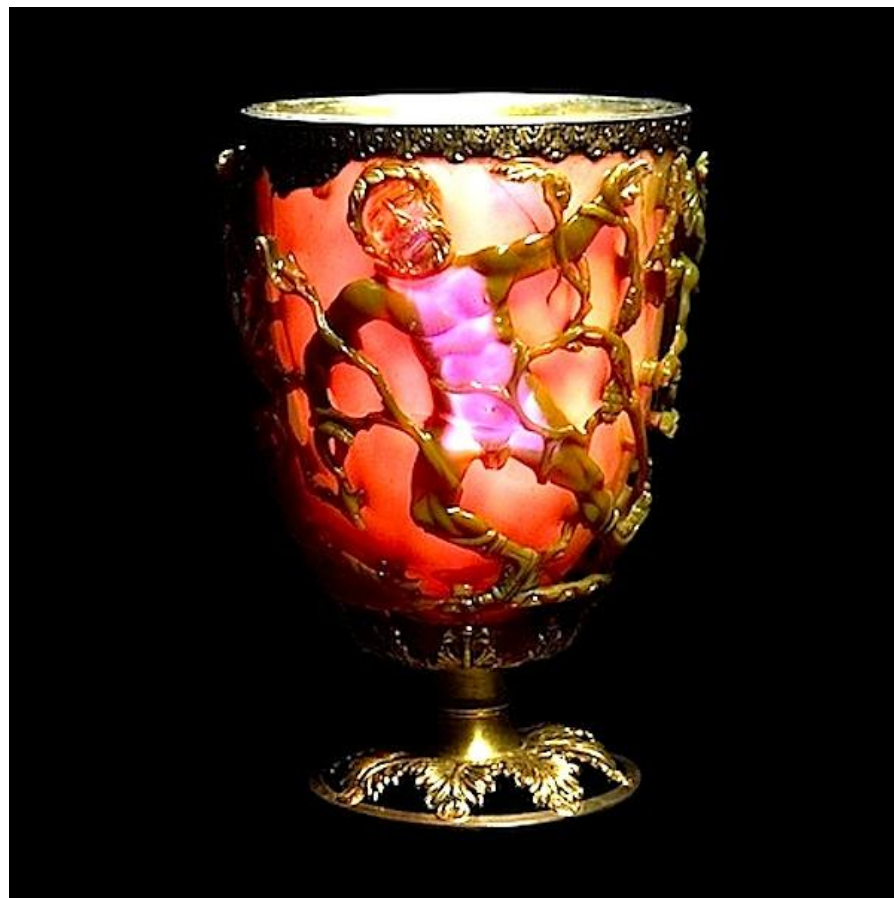


The Lycurgus Cup

Late Roman, 4th century AD

Probably made in Rome

This extraordinary cup is the only complete example of a very special type of glass, known as dichroic, which changes colour when held up to the light. The opaque green cup turns to a glowing translucent red when light is shone through it. The glass contains tiny amounts of colloidal gold and silver, which give it these unusual optical properties.



<http://www.britishmuseum.org/>

The main parameters of interest with respect to nanoparticle safety are:

Physical properties

Size, shape, specific surface area, aspect ratio

Agglomeration/aggregation state

Size distribution

Surface morphology/topography

Structure, including crystallinity and defect structure

Solubility

Chemical properties

Structural formula/molecular structure

Composition of nanomaterial (including degree of purity, known impurities or additives)

Phase identity

Surface chemistry (composition, charge, tension, reactive sites, physical structure, photocatalytic properties, zeta potential)

Hydrophilicity/lipophilicity

https://ec.europa.eu/health/scientific_committees/opinions_layman/nanomaterials/en/l-3/2.htm

EU definition of nanomaterial

The European Parliament in its resolution of 24 April 2009 on regulatory aspects of nanomaterials called, inter alia, for the **introduction of a comprehensive science-based definition of nanomaterials in Union legislation.**

The International Organisation for Standardisation defines the term ‘nanomaterial’ as ‘material with any external dimensions in the nanoscale or having internal structure or surface structure in the nanoscale’. The term ‘nanoscale’ is defined as **size range from approximately 1 nm to 100 nm.**

L 275/38

EN

Official Journal of the European Union

20.10.2011

RECOMMENDATIONS

COMMISSION RECOMMENDATION

of 18 October 2011

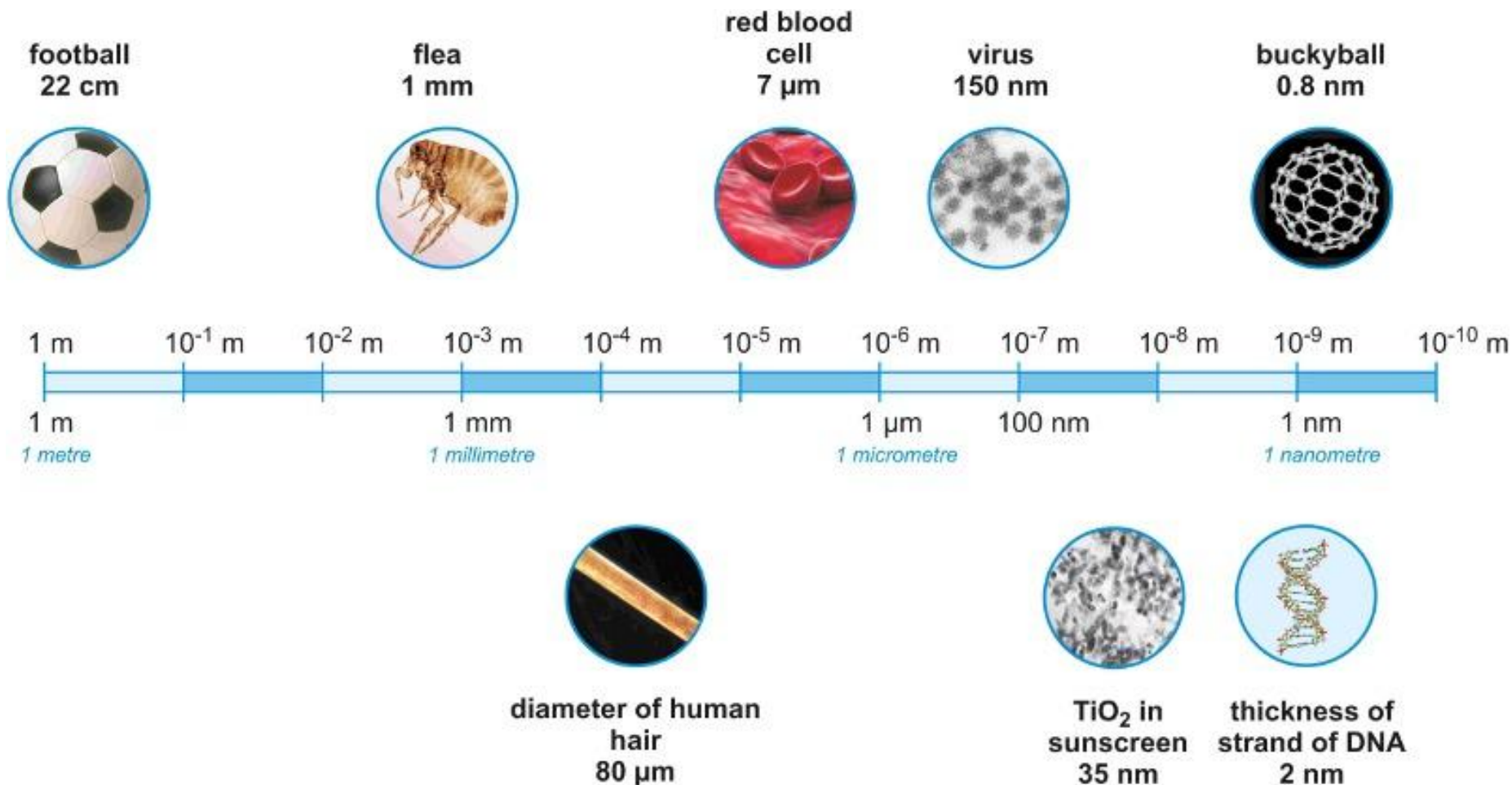
on the definition of nanomaterial

(Text with EEA relevance)

(2011/696/EU)

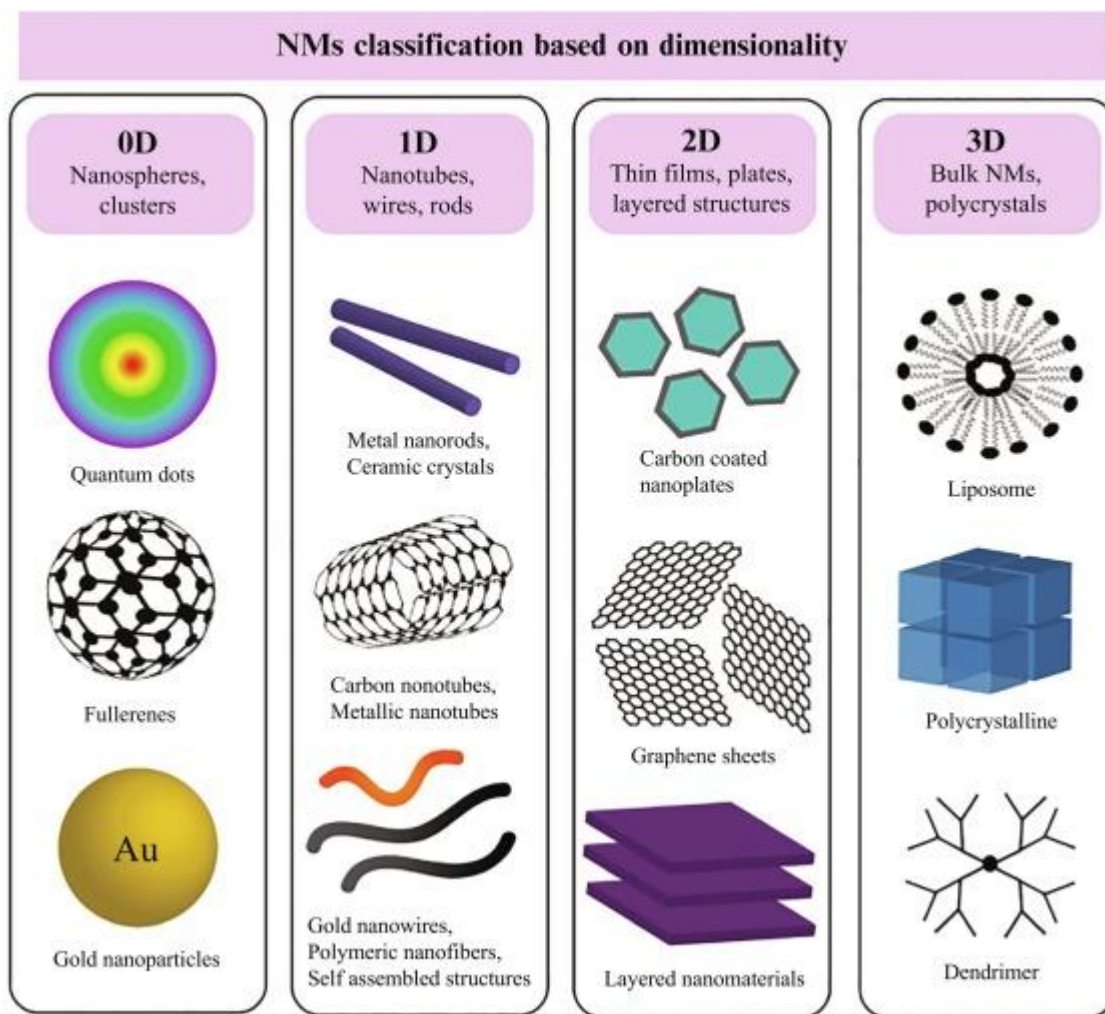
<https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011H0696&from=EN>

Size of nanomaterial



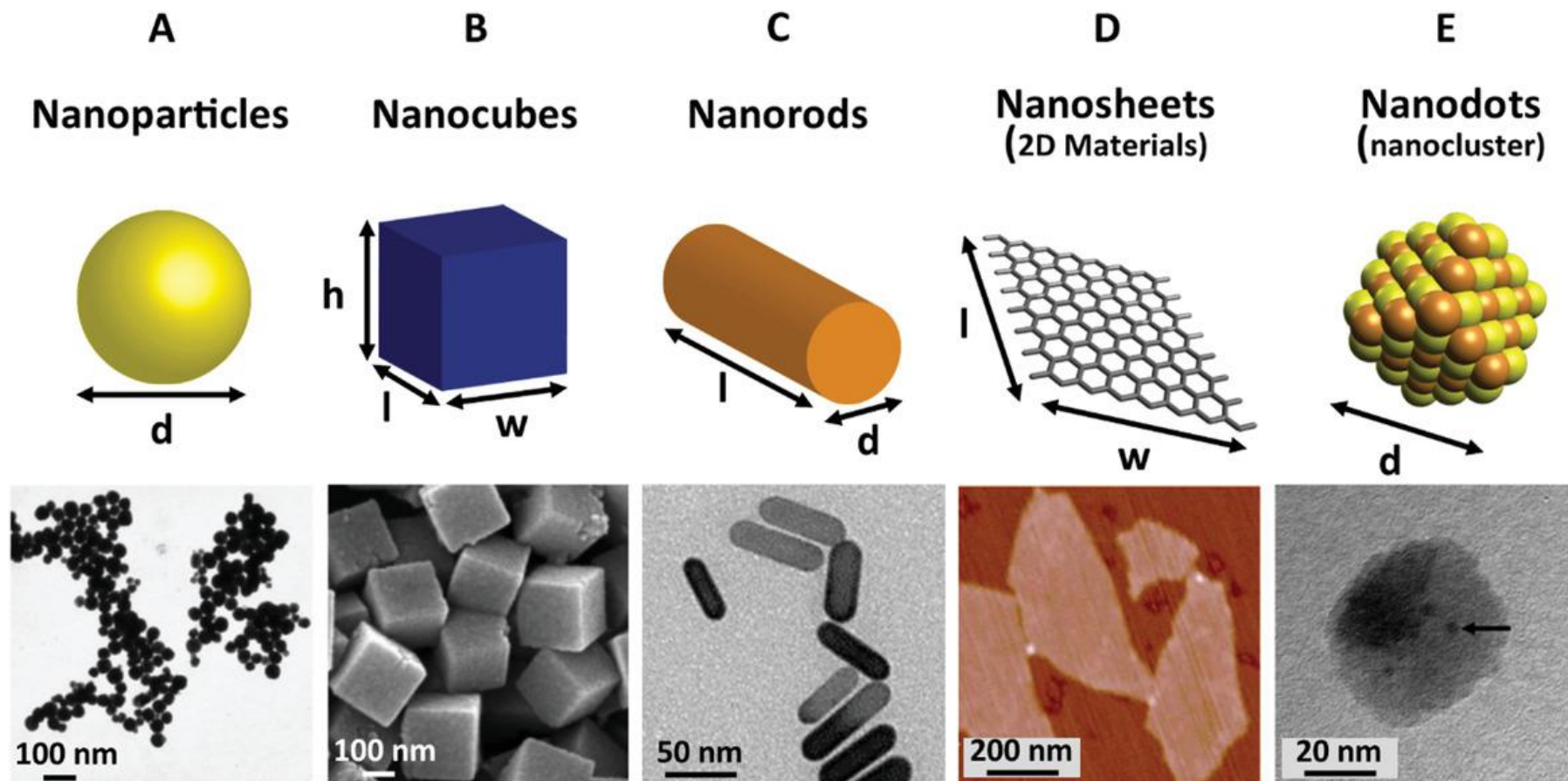
<https://www.essentialchemicalindustry.org/materials-and-applications/nanomaterials.html>

Nanomaterial dimensionality



<https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011H0696&from=EN>

Nanomaterial morphology



Source of figure: <https://onlinelibrary.wiley.com/doi/full/10.1002/advs.201902913>

Improved properties of nanomaterials

Properties	Examples
Catalytic	Better catalytic efficiency through higher surface-to-volume ratio
Electrical	Increased electrical conductivity in ceramics and magnetic nanocomposites, increased electric resistance in metals
Magnetic	Increased magnetic coercivity up to a critical grain size, superparamagnetic behaviour
Mechanical	Improved hardness and toughness of metals and alloys, ductility and superplasticity of ceramic
Optical	Spectral shift of optical absorption and fluorescence properties, increased quantum efficiency of semiconductor crystals
Sterical	Increased selectivity, hollow spheres for specific drug transportation and controlled release
Biological	Increased permeability through biological barriers (membranes, blood-brain barrier, etc.), improved biocompatibility

Table 3: Adjustable properties of nanomaterials

Applications of nanomaterials

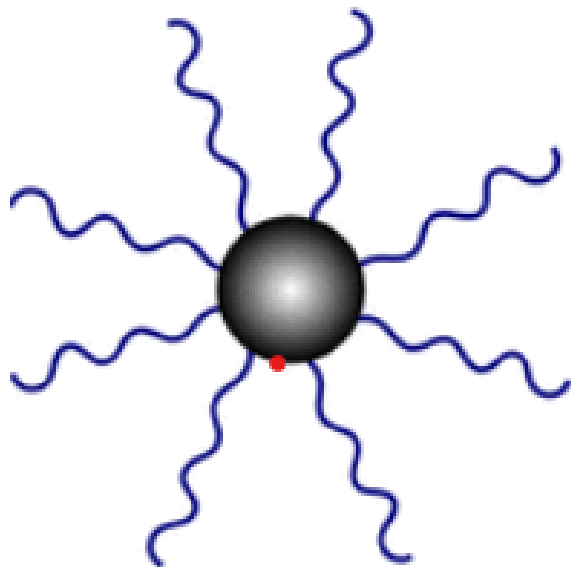
Automotive industry • lightweight construction • painting (fillers, base coat, clear coat) • catalysts • tires (fillers) • sensors • Coatings for wind-screen and car bodies	Chemical industry • fillers for paint systems • coating systems based on nanocomposites • impregnation of papers • switchable adhesives • magnetic fluids	Engineering • wear protection for tools and machines (anti blocking coatings, scratch resistant coatings on plastic parts, etc.) • lubricant-free bearings
Electronic industry • data memory (MRAM, GMR-HD) • displays (OLED, FED) • laser diodes • glass fibres • optical switches • filters (IR-blocking) • conductive, antistatic coatings	Construction • construction materials • thermal insulation • flame retardants • surface-functionalised building materials for wood, floors, stone, facades, tiles, roof tiles, etc. • facade coatings • groove mortar	Medicine • drug delivery systems • active agents • contrast medium • medical rapid tests • prostheses and implants • antimicrobial agents and coatings • agents in cancer therapy

Applications of nanomaterials

Textile/fabrics/non-wovens • surface-processed textiles • smart clothes	Energy • fuel cells • solar cells • batteries • capacitors	Cosmetics • sun protection • lipsticks • skin creams • tooth paste
Food and drinks • package materials • storage life sensors • additives • clarification of fruit juices	Household • ceramic coatings for irons • odors catalyst • cleaner for glass, ceramic, floor, windows	Sports /outdoor • ski wax • antifogging of glasses/goggles • antifouling coatings for ships/boats • reinforced tennis rackets and balls

Table 5: Overview on applications of nanomaterial based products in different areas

Functionalisation: why and how



ALTERNATIVE TERMS

- Derivatization
- Compatibilisation
- Surface modification

FUNCTIONAL UNITS

- Surfactants
- Ligands
- Polymer
- Molecules

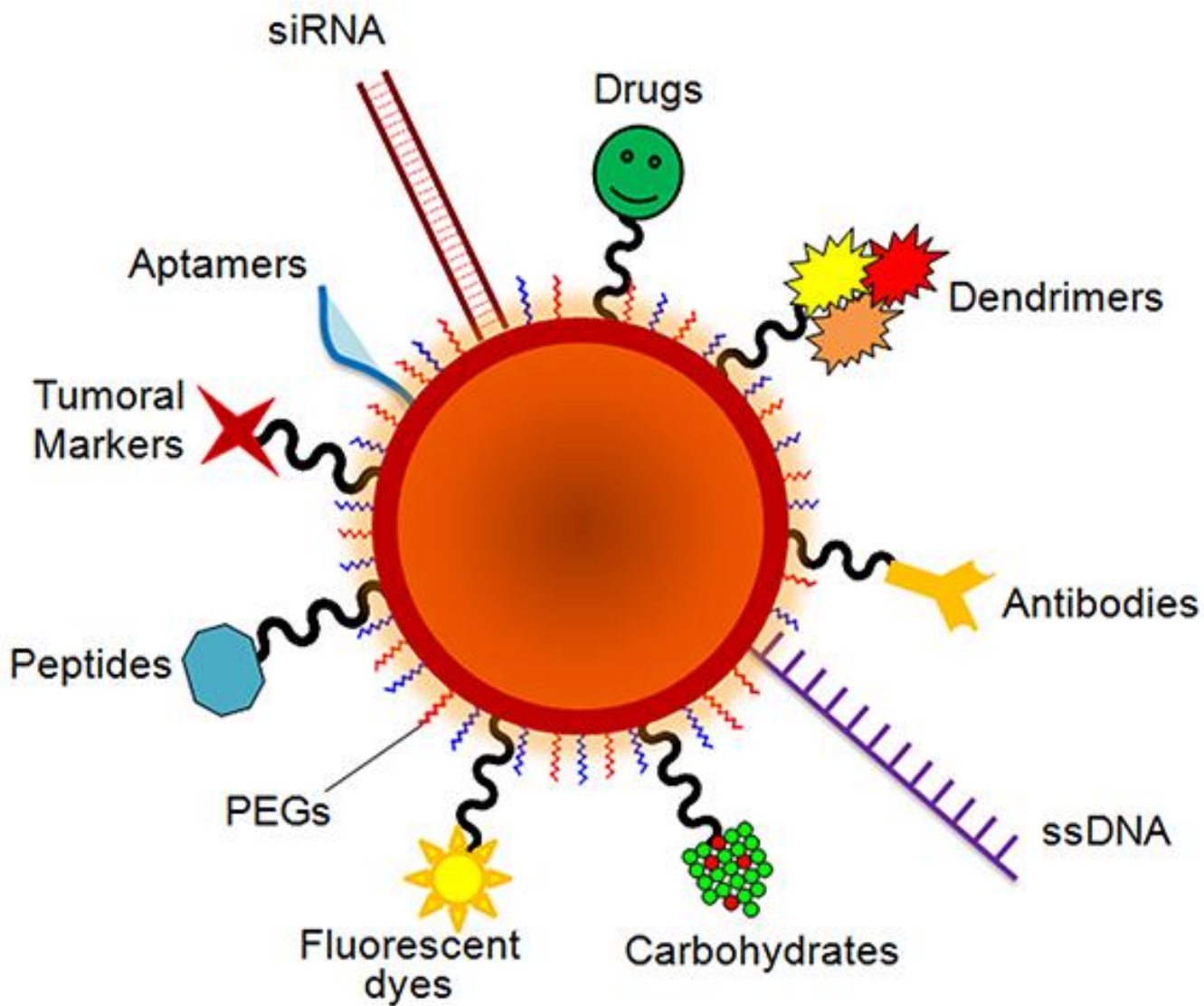
MOTIVATIONS

- for stabilization (steric)
- to enhance solubility
- to improve compatibility (with a polymer host matrix)
- to tune the chemical reactivity (functionalization)
- to influence the physical properties (e. g. hydrophobicity)
- to endow them with biocompatibility
- to enable molecular recognition/stealth properties

METHODS

- direct synthesis in the presence of one or more surface ligands
- ligand exchange
- post-synthesis modification

Functionalisation: biomedicine



Improving compatibility and dispersion in nanocomposites

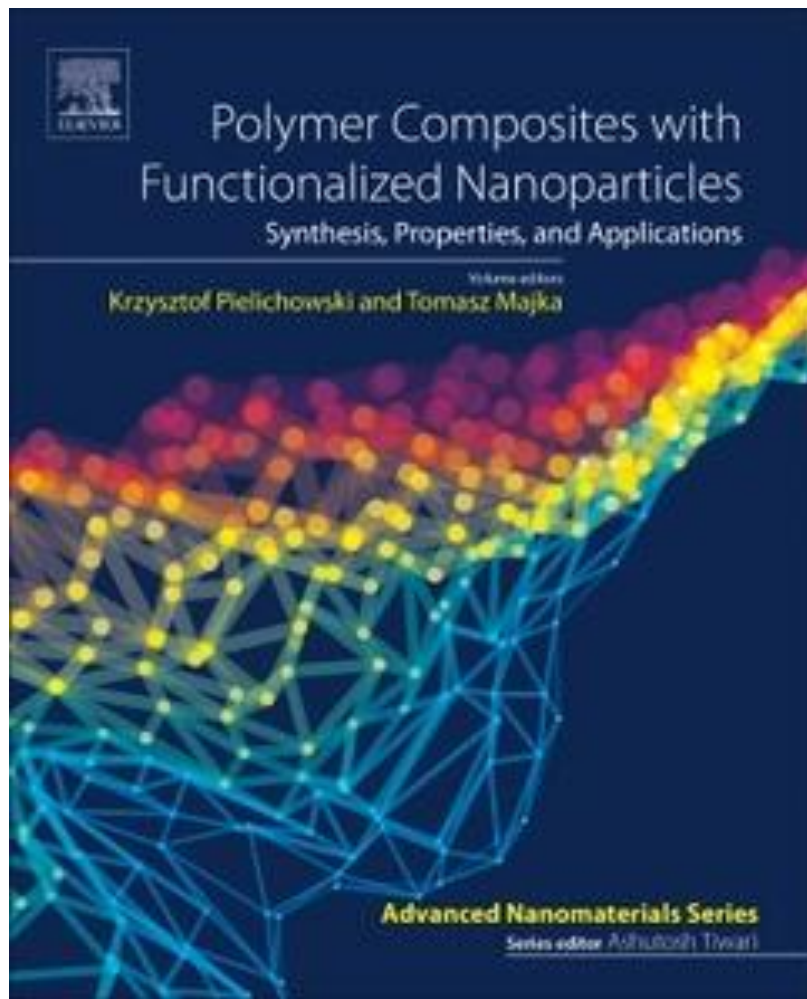
- high filler content is the prerequisite for imparting specific properties to polymeric composite. However, serious mechanical properties degradation occurs in this kind of material due to the **inevitable reduction of material cohesion**
- high loading will deteriorate the mechanical properties because of the inevitable reduction of material cohesion
- introducing a large quantity of fillers into the molten polymer will also drastically change the **rheology behaviour and challenge the following processing**
- external stress field, including extension flow, oscillation shear, and high shear forces, have been developed to improve the dispersion and distribution of fillers, and subsequently obtain high-quality polymer composites
- Rheology* (flow properties) are also dramatically affected by filler-matrix (guest-host) interactions

* **Rheology** see next slide

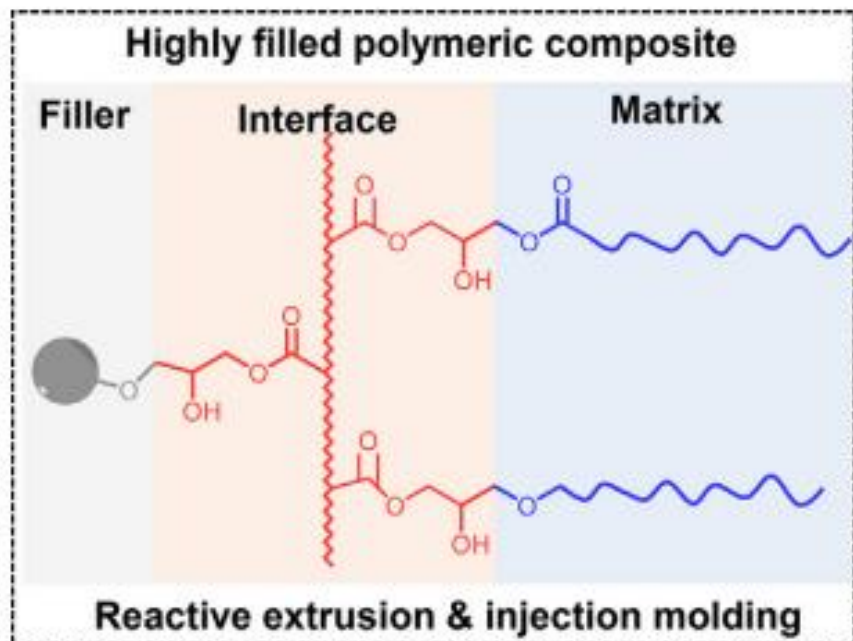
- Rheology is a science that studies **the flow and deformation of objects** under the action of external forces.
- It is a science that is intercrossed between physics, chemistry, medicine, biology, and engineering technology.
- Rheology is the study of the **relationship between deformation and stress over time** caused by various reasons.
- After nearly a century of improvement and development, rheology has been widely used in chemical industry, petroleum, water conservancy, biological engineering, light industry, food, materials, and other disciplines.
- The study of rheology covers almost all substances (i.e., liquids, gases, and solids). Rheology interprets flow as the continuous deformation of an object under constant shear stress over time, so flow is essentially a deformation of a special state.

<https://www.sciencedirect.com/topics/materials-science/rheology>

Improving compatibility and dispersion



Improving compatibility and dispersion



Highly improved toughness

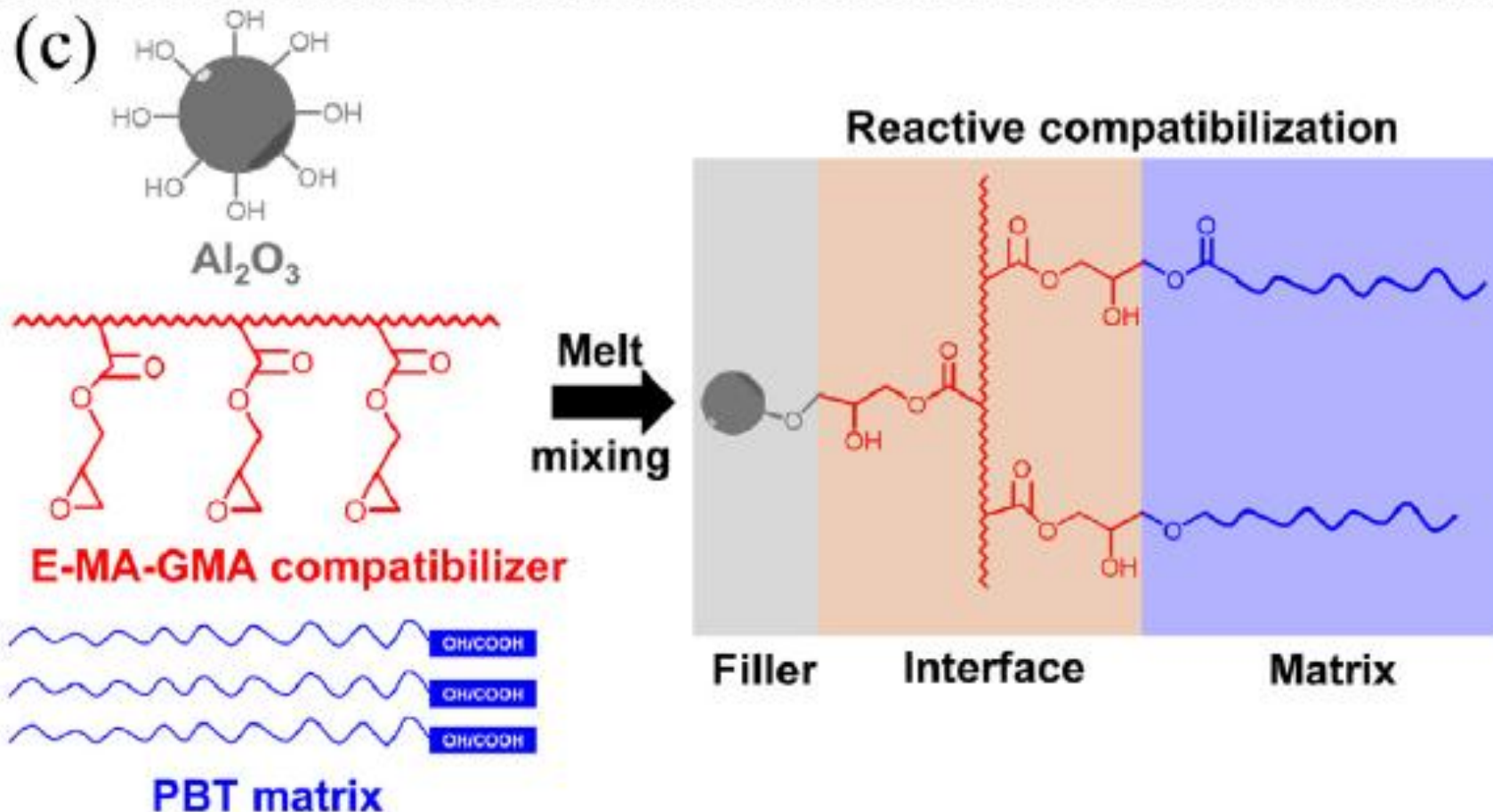
Preserved high thermal conductivity

Percolating network and yield behavior

More stable phase structure

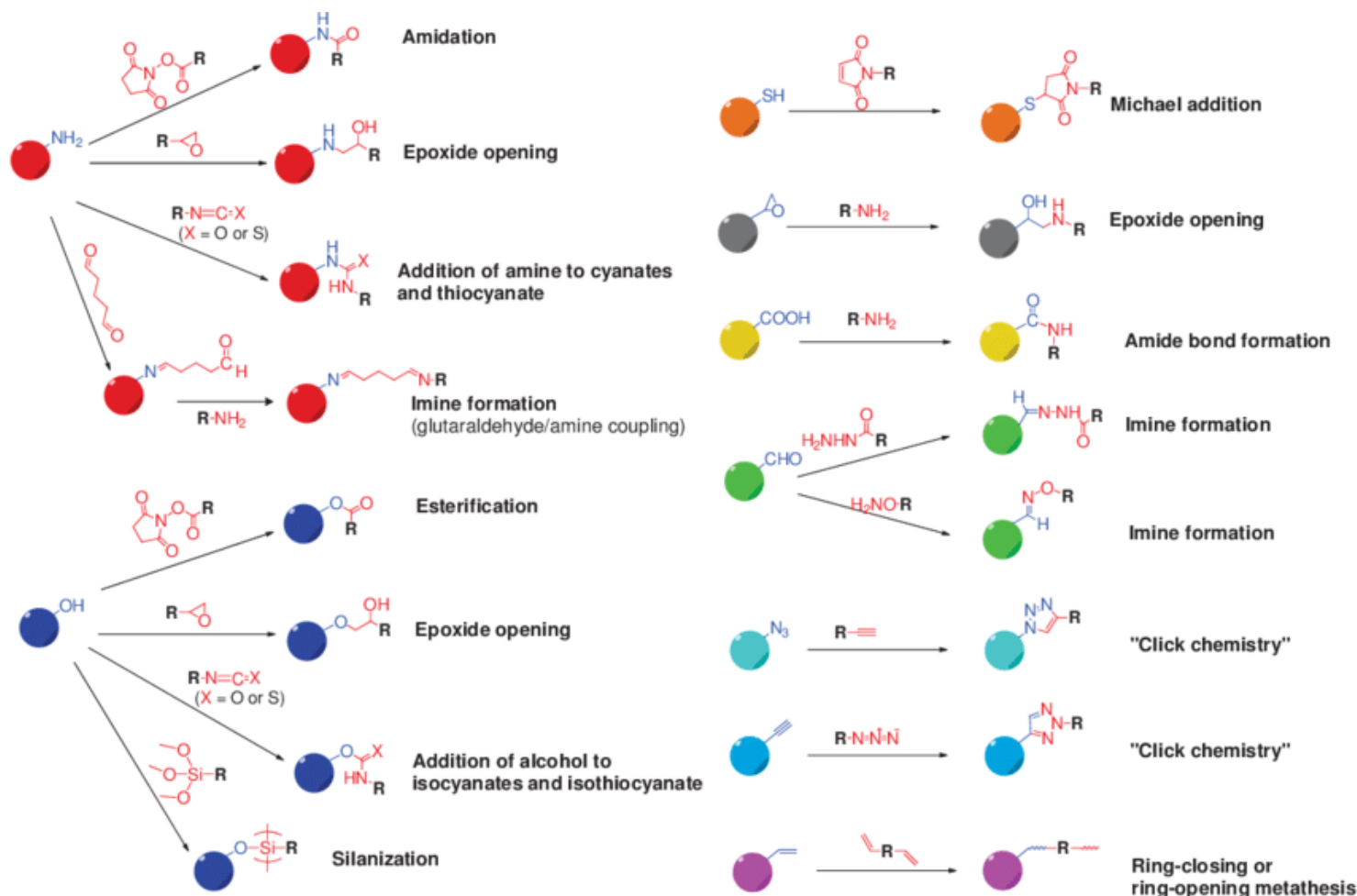
- adding an interfacial **compatibilizer** is a simple and effective method, which could not only strengthen the filler-polymer interfacial interaction, but also improve the matrix property
- avoids leaching, phase separation etc.

Improving compatibility and dispersion



Source of the picture: Influence of reactive compatibilization on the mechanical, thermal and rheological properties of highly filled PBT/ Al_2O_3 composites, Materials and Design 196 (2020) 109175. PBT: Polybutylene terephthalate

Functionalisation strategies



Source of the picture: Froimowicz, P. & Muñoz-Espí, R. & Landfester, K. & Musyanovych, A. & Crespy, D.. (2013). Surface-Functionalized Particles: From their Design and Synthesis to Materials Science and Bio-Applications. Current Organic Chemistry. 17. 900

Functionalisation strategies

Ligand	Substrate	Ligand Attached to Substrate	Reaction
			Michael Addition
			Epoxide Opening
			Amidation
			Amide Bond Formation
			Amide Bond Formation
			Imine Formation

			Imine Formation
			Click Chemistry
			Addition of Amine to Cyanates
			Ring-Closing or Ring-Opening Metathesis
			Diels-Alder Reaction

Vol. 44, No. 10 ■ 2011 ■ 925-935 ■ ACCOUNTS OF CHEMICAL RESEARCH ■

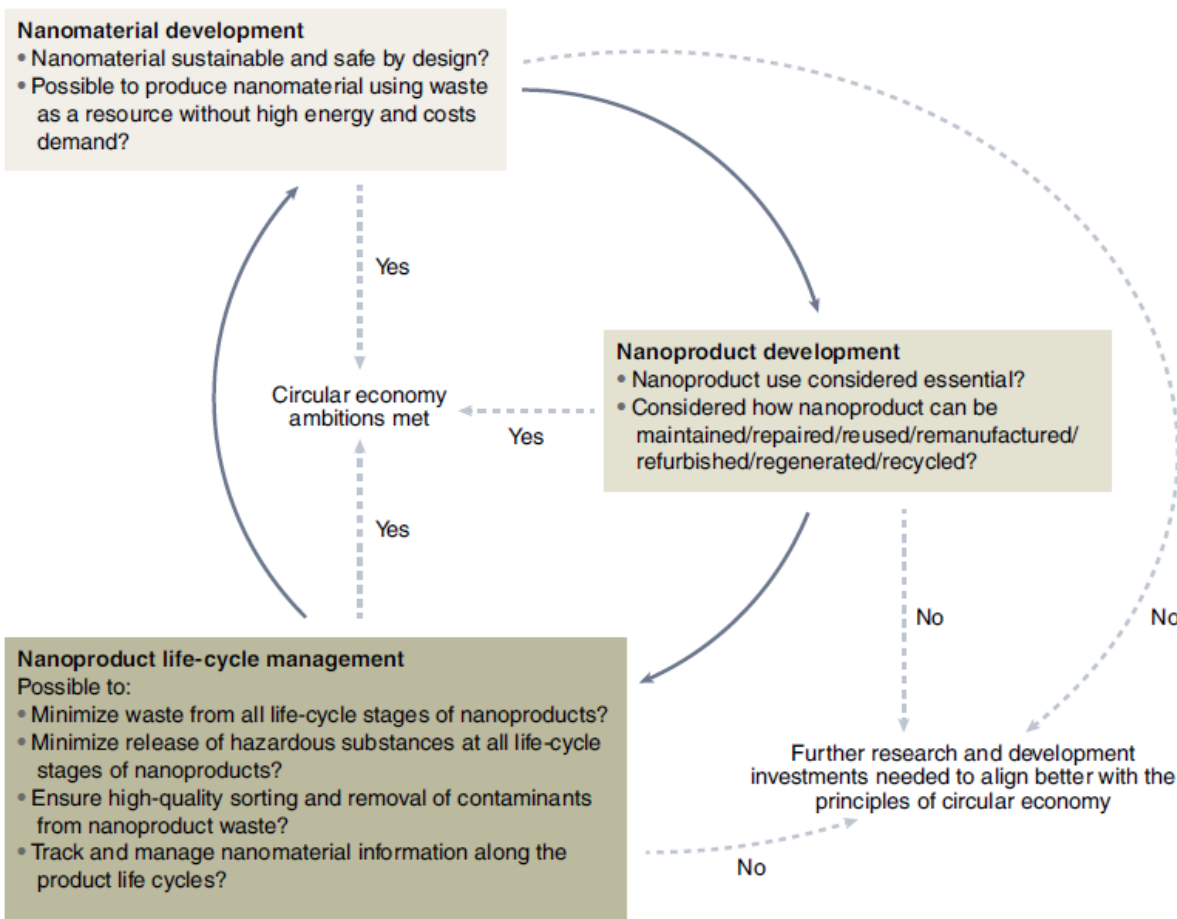
comment Check for updates

Nanotechnology meets circular economy

The transition from a linear 'take-make-dispose' economy to a circular economy is gaining momentum. Although there are many opportunities for using nanotechnology to enable circularity, the knowledge gaps related to (eco-) toxicological hazards and the presence of nanomaterials in waste streams constitute significant challenges.

Steffen Foss Hansen, Rickard Arvidsson, Maria Bille Nielsen, Oliver Foss Hessner Hansen, Lauge Peter Westergaard Clausen, Anders Baun and Alessio Boldrin

Nature Nanotechnology | VOL 17 | July 2022 | 682–685 |
www.nature.com/naturenanotechnology

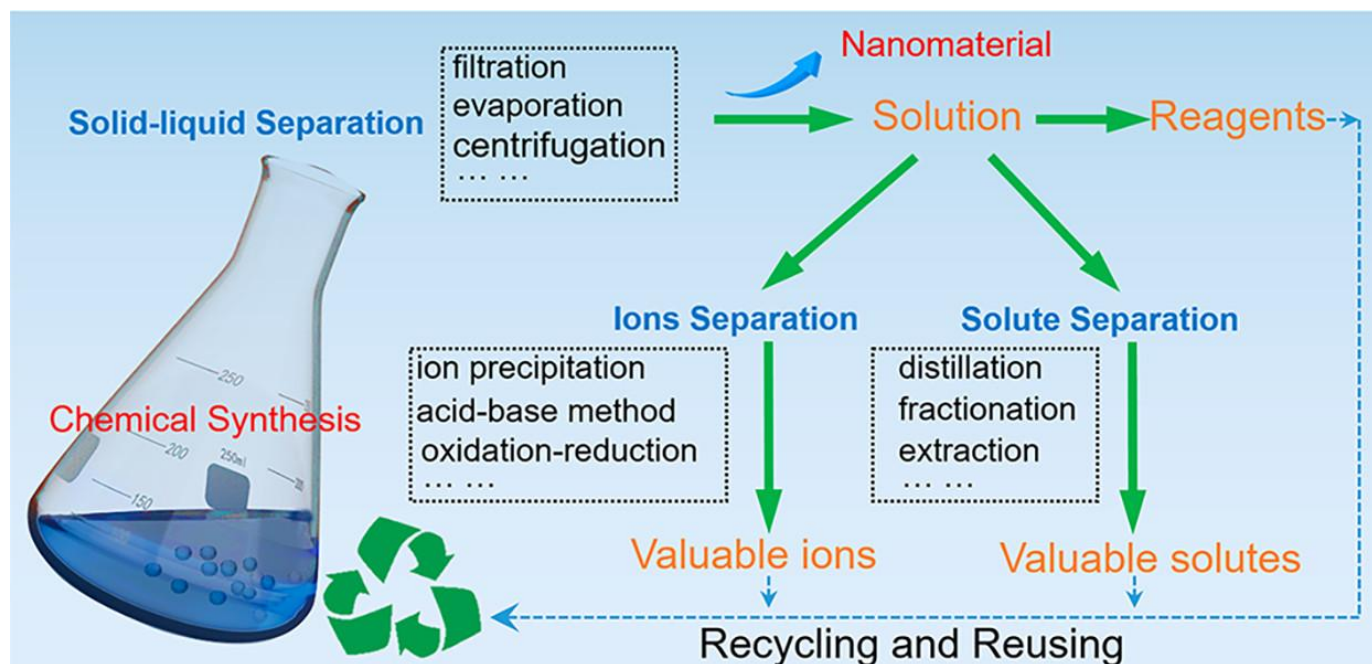


Critical questions to be addressed for nanomaterials in a circular economy from development, over nanoproduct development, to nanoproduct life-cycle management.

Nanotechnology can only be used to meet the circular economy ambitions **if the development of nanomaterials and nanoproducts are sustainable and safe along the life-cycle of the nanoproducts**. This includes considerations of whether the use of the nanoproducts are essential, minimizing waste and tracking and managing nanomaterial information. Further research and development might be needed to ensure that the development of nanoproducts are aligned with the principles of circular economy

Recycling of nanomaterials

If nanomaterials are to be recycled, they first need **to be recovered from the waste**. Some studies have recovered inorganic nanoparticles from complex liquid mixtures using centrifugation or solvent evaporation, which have high energy and economic costs. Methods using **magnetic fields, thermoresponsive materials, molecular antisolvents and nanostructured colloidal solvents** are cheaper, faster and less energy intensive



Safe and sustainable by design

- The (eco)toxicological hazard profiles of many nanomaterials are challenging to establish.
- Recently, the EC revised the information requirements that manufacturers and importers must provide for nanomaterials under the EU's chemical legislation.
- The minimum characterization information includes particle number size distribution, surface functionalization, shape, aspect ratio, specific surface area and exposure estimates for all life-cycle stages.
- While this will help manufacturers, importers and downstream users to document appropriate risk management, it remains uncertain whether and to what extent the interactions between particle characteristics (for example, particle size distribution, surface chemistry and volume specific surface area) affect the overall hazard of a given nanomaterial.
- Future discovery of nanomaterials may be driven by the use of machine learning and artificial intelligence, and safety considerations ought to be built into the machine learning algorithms.
- For this to be possible, considerable amounts of standardized high-quality data are needed in open-access databases that have yet to become available.

Further classes of materials and applications

building & construction materials

carbon structures based materials

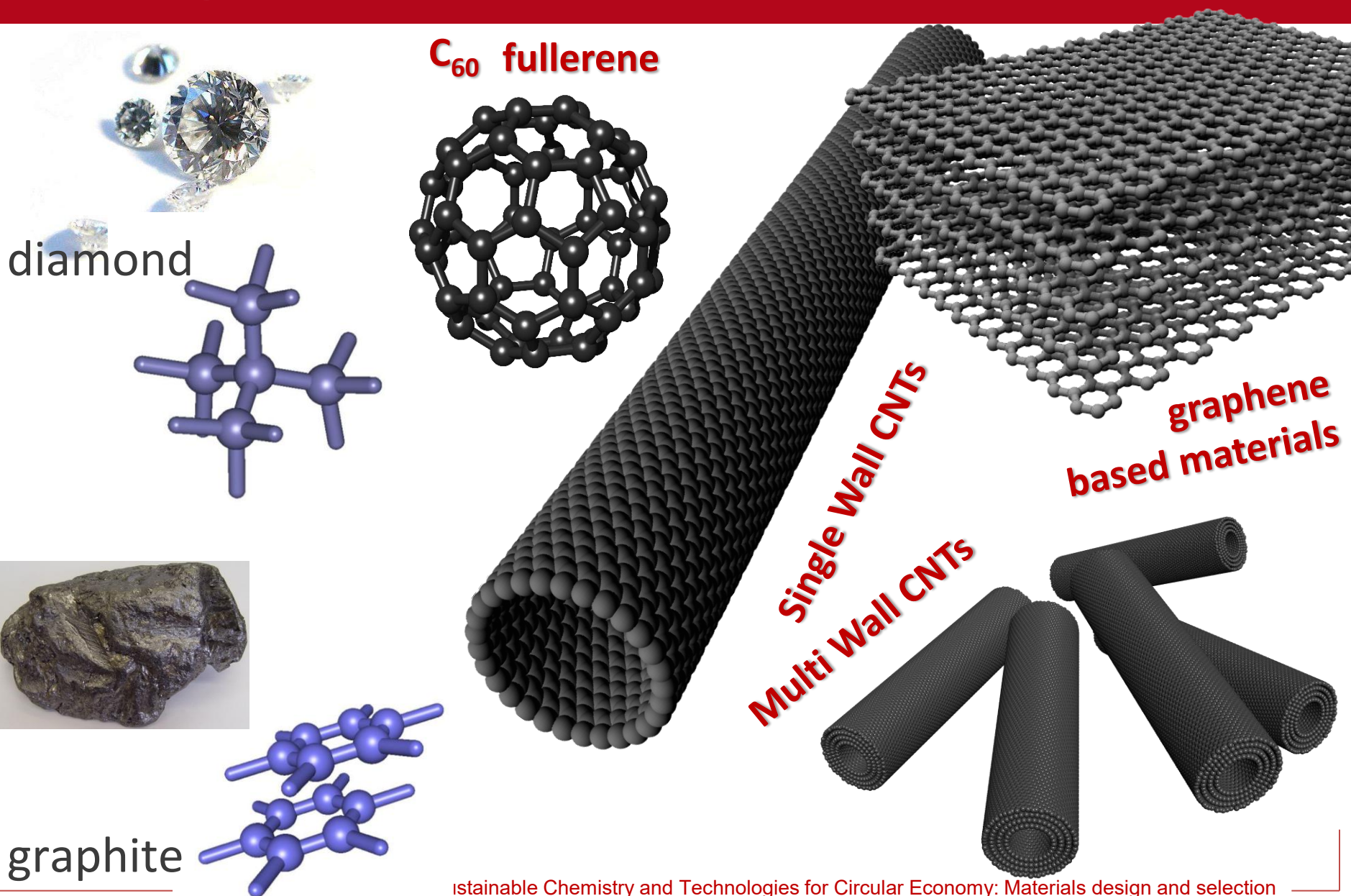
nanomaterials

apparel & textiles

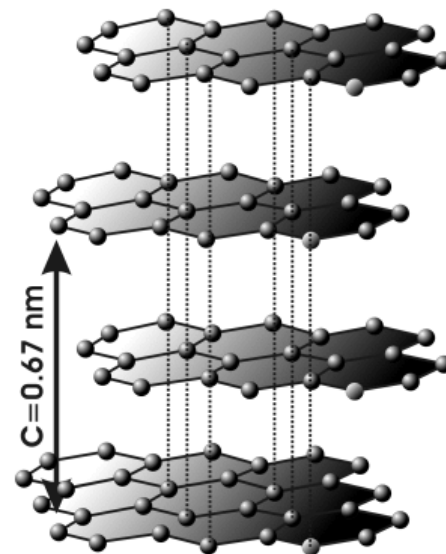
paper

wood: see Biomass course prof. Zanetti/Tondi

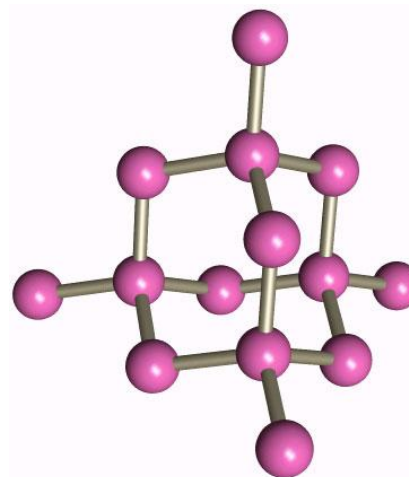
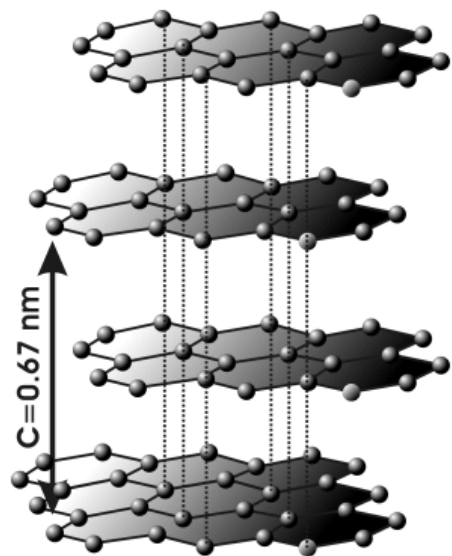
Carbon nanostructures (CNS)



Carbon nanostructures (CNS)



graphite



diamond

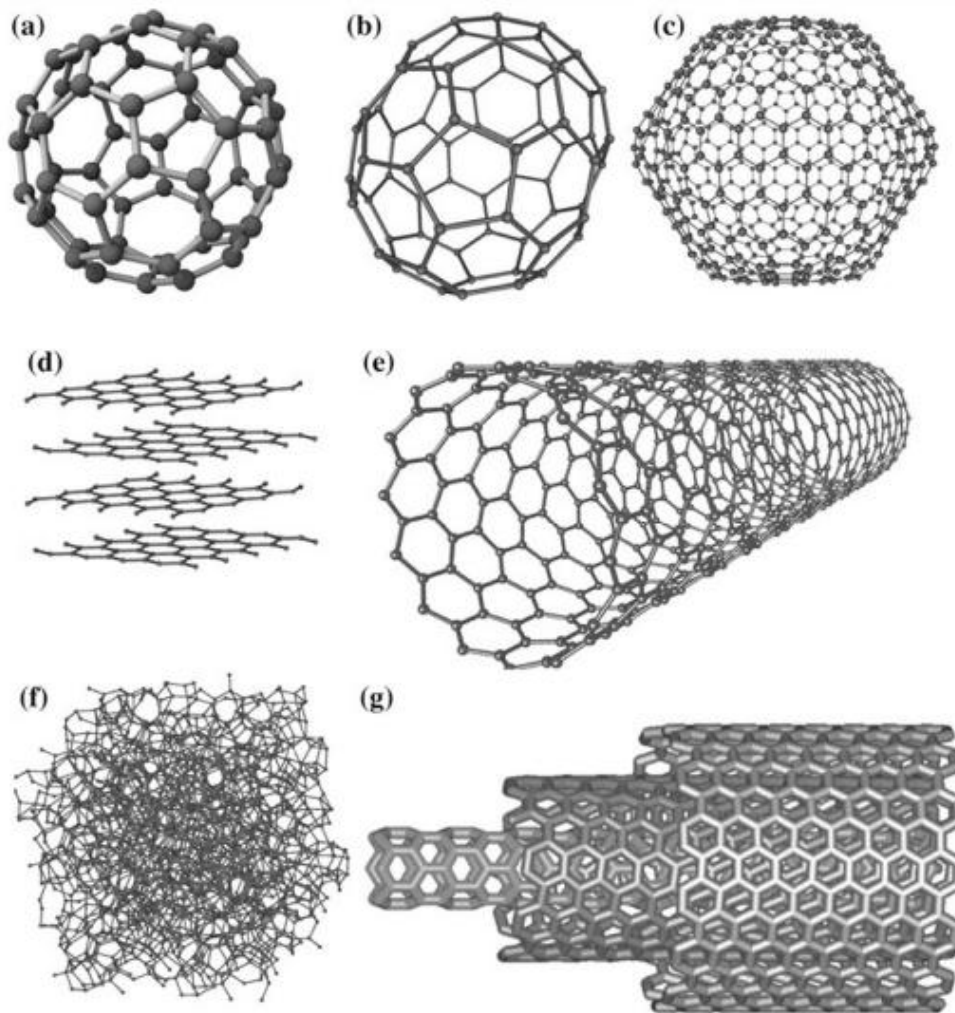
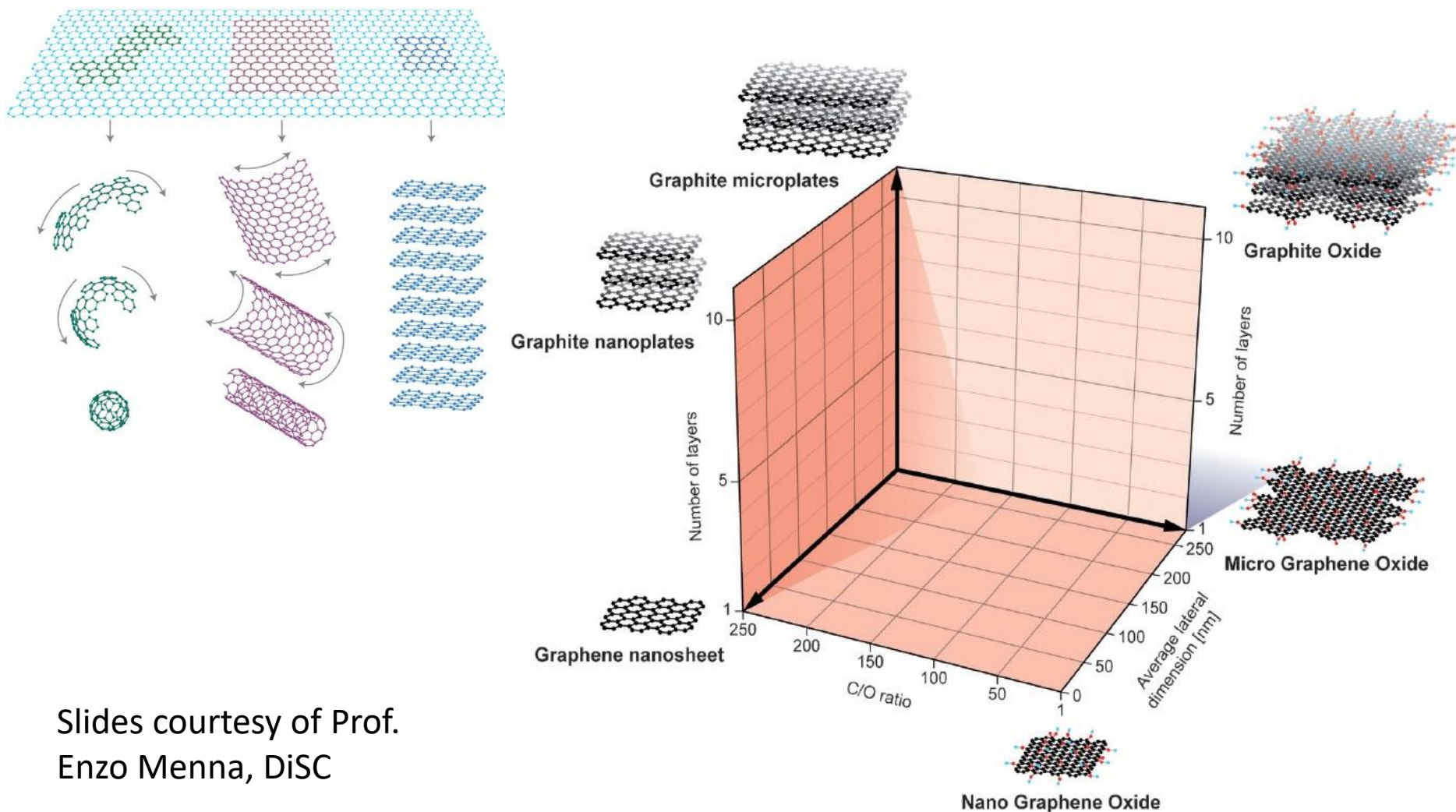


Fig. 3 Carbon allotrope structures in nanoform: (A) fullerene C60; (B) C70; (C) C540; (D) graphite; (E) single-walled carbon nanotube (SWCNT); (F) amorphous carbon; (G) multiwalled carbon nanotube (MWCNT) [10].

Graphene and its derivatives



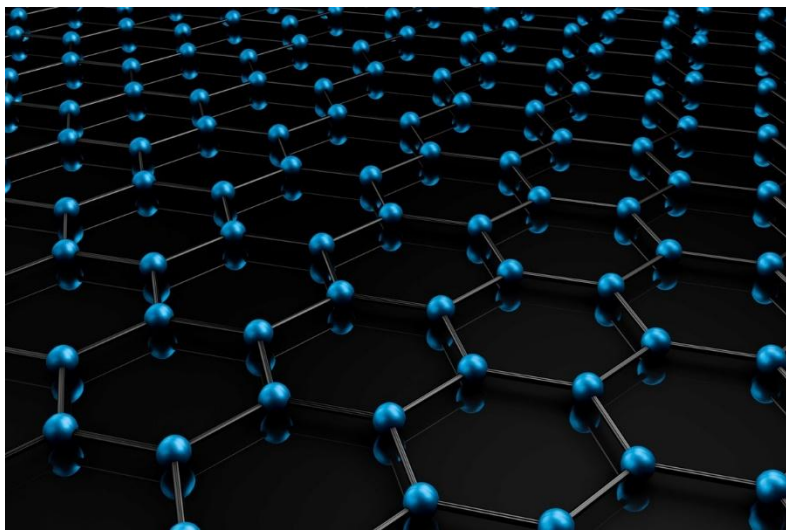
Slides courtesy of Prof.
Enzo Menna, DiSC

Source of figure: P. Wick et al. *Angew. Chem. Int. Ed.*, **2014**, 53, 7714.

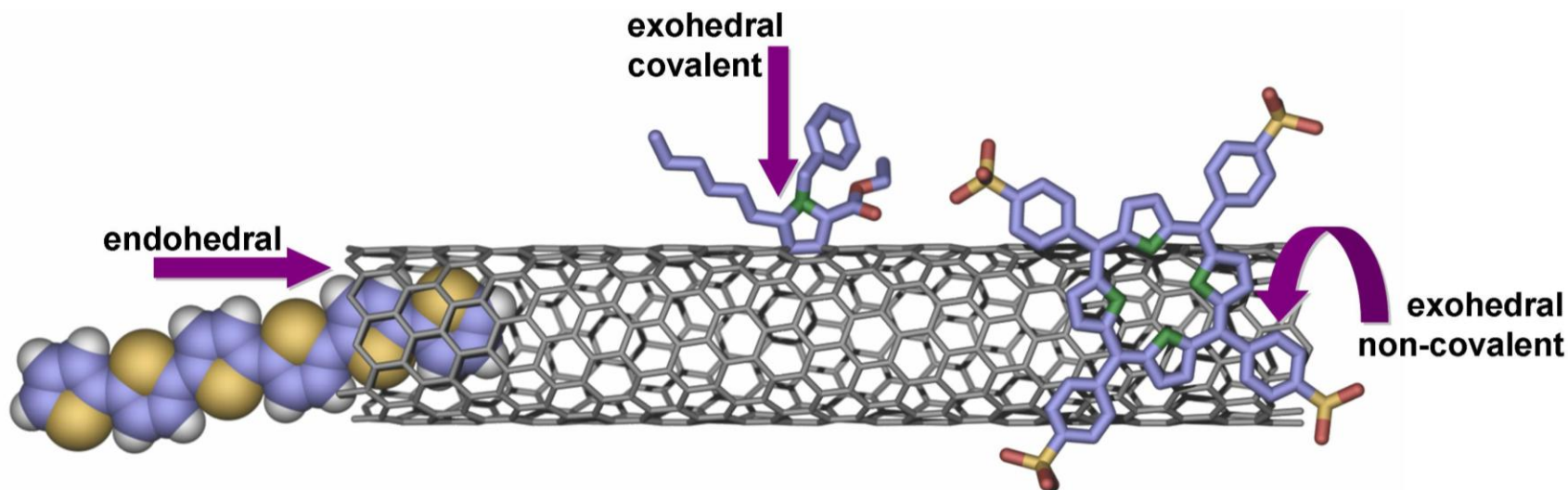
- zero-gap 2D semimetal with a tiny overlap between valence and conductance bands
- breaking strength is 42 N m^{-1} and the Young's modulus is 1.0 TPa, suggesting the **strongest material ever measured**
- external mechanical loads can change the electronic properties of graphene, such as field emission performance

GRAPHENE-BASED COMPOSITES

- graphene-filled polymer composites are commonly prepared by solution mixing, melt blending, and in situ polymerization
- electrical conductivity has shown significant improvement in graphene-filled polymers.



Carbon nanotubes (SWCT, MWCT)

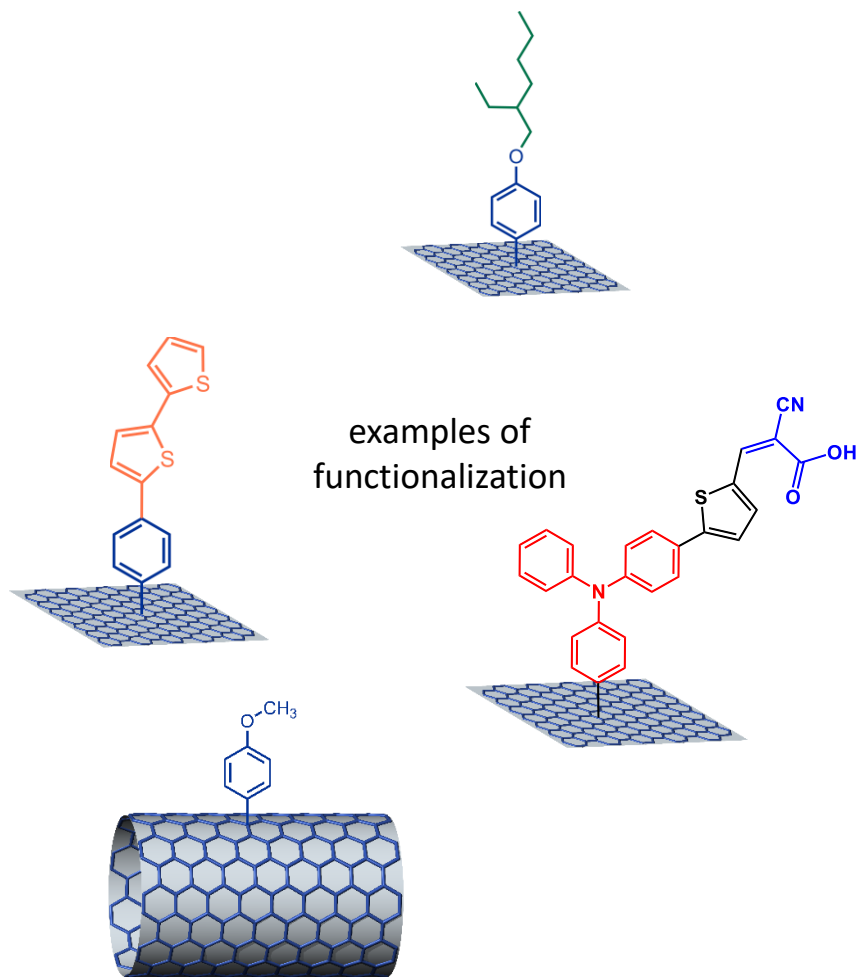


Slides courtesy of Prof.
Enzo Menna, DiSC

- Functional groups are designed to provide:
 - solubility
 - interaction with polymers
 - interaction with light
 - adsorption of molecules

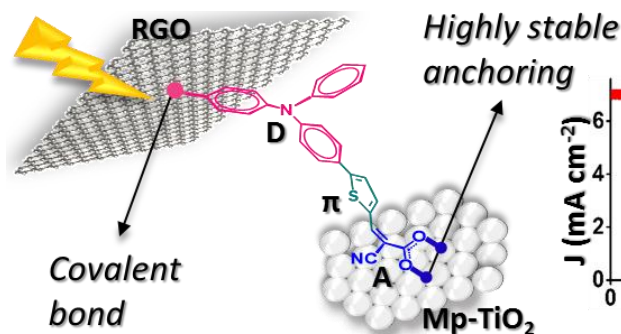
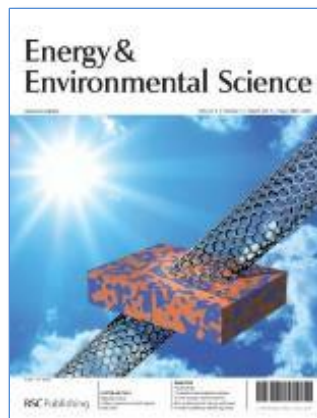
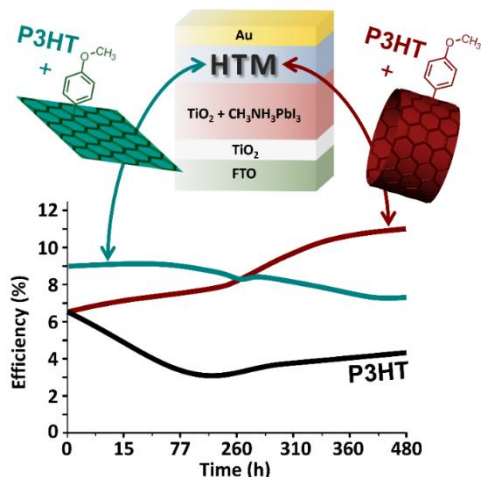
depending on the **APPLICATION**

Graphene and its derivatives

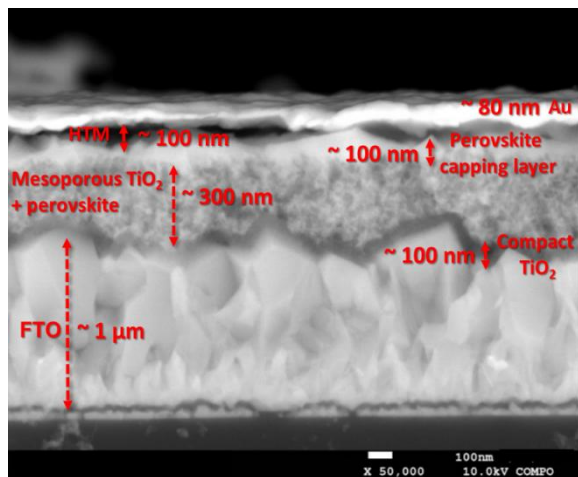


Slides courtesy of Prof.
Enzo Menna, DiSC

Solar energy conversion



- dye sensitized solar cells
- photocatalytic HYDROGEN generation

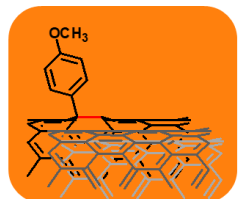


Based on electronic and thermal properties of CNSs:

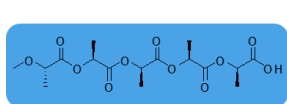
enhanced electrical conductivity
semiconducting properties
thermal conductivity
thermal stability

Slides courtesy of Prof.
Enzo Menna, DiSC

■ Nanocomposite polymers

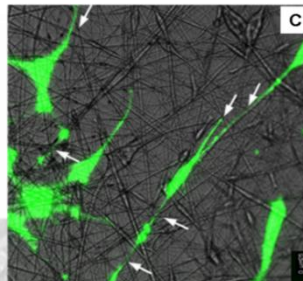
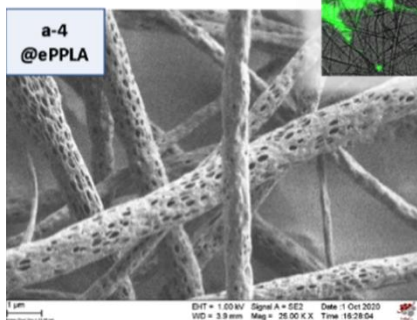


MWCNT-PhOMe

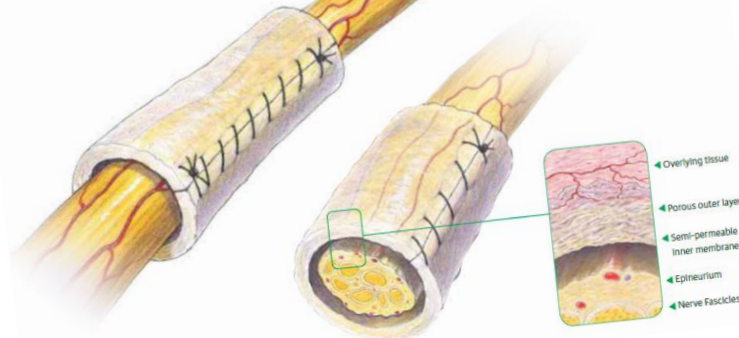


PLLA

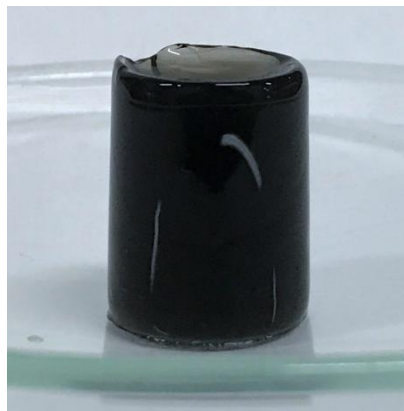
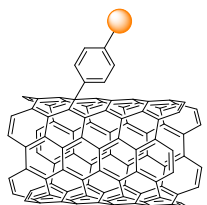
growth of
neurons



NeuraWrap™ Nerve Protector
The novel approach for treatment of nerve injury



■ Nanocarbon hydrogels



Based on electrical, mechanical and morphological properties of CNSs:

- electrical communication between cells
- tunable stiffness of composites
- surface nanotopology

Soft and conductive scaffolds