Carbon nanomaterials and more

CHEM-E5120 INTERFACES AND NANOMATERIALS

MASTER PROGRAMME OF FUNCTIONAL MATERIALS

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Outline

PART I: CARBON NANOMATERIALS

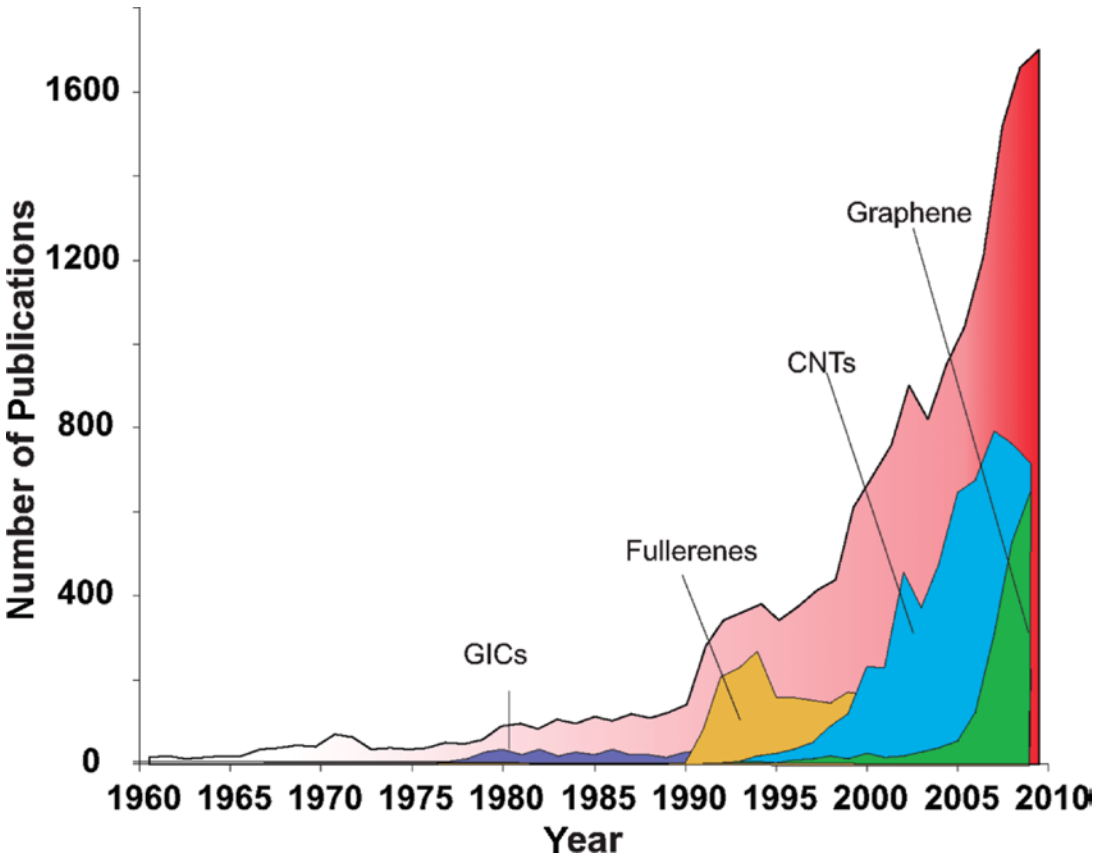
- Graphene
- Fullerenes
- Carbon nanotubes

PART II: OTHER SPECIAL NANOMATERIALS

- Mesoporous materials
- Hybrid materials
  - Core-shell structures
  - Organic –Inorganic hybrids
- Bio-induced nanomaterials

Carbon nanomaterials

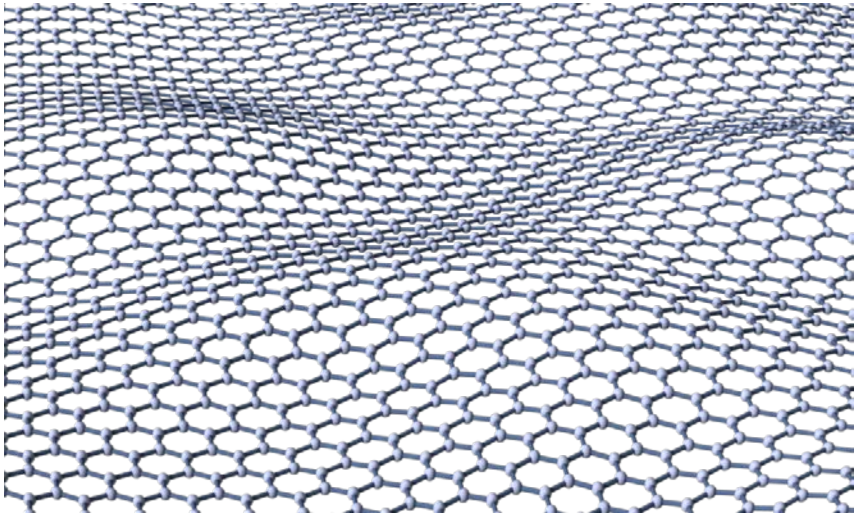
Interest in carbon nanomaterials



M.S. Dresselhaus and P. T. Araujo *ACS Nano* **2010**

Graphene

- Single two dimensional carbon sheet (“Mother of carbon nanomaterials)
- In graphite, multiple layers are stacked (and interact with each other)
- Name: Graph- from graphite, -ene from polycondensed aromatic hydrocarbon (naphtalene, anthracene etc.)
- All carbons are sp^2 hybridized ➔ cloud of π electrons
- 2 D crystal, very hydrophobic and inert



Andre Geim and Konstantin Novoselov obtained the Nobel Prize 2010 from the fundamental work and actual finding of graphene (Geim has also won the Ig Nobel prize)

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Synthesis of graphene 1/4

1) Peeling of graphite crystals (mechanical exfoliation)

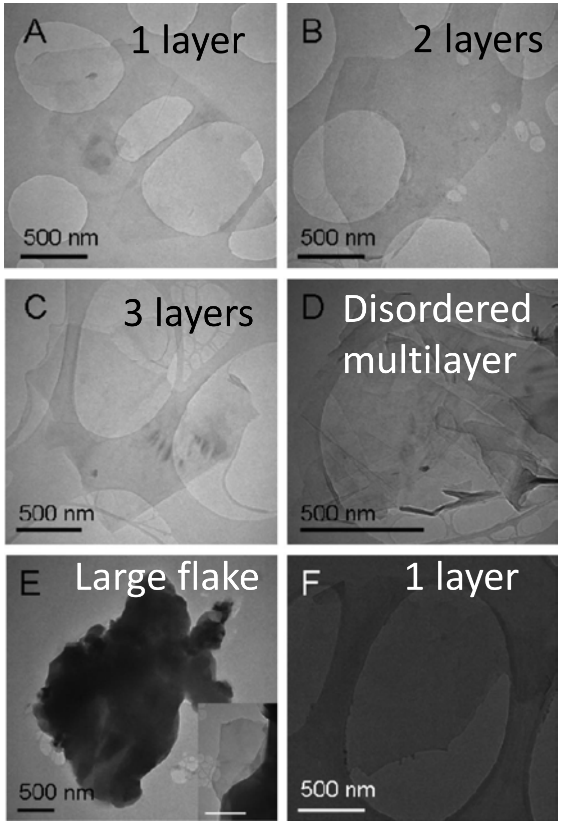
- The Scotch tape method
- Highly crystalline multi and single layer flakes, but low yield

http://www.mccormick.northwestern.edu/magazine/fall-2013/miracle-material.html

Synthesis of graphene 2/4

2) Exfoliation of graphite through its intercalation compounds

- Oxidation into graphene oxide (GO) ➔ reduction
- Thermal expansion ➔ intercalation compounds
- Solvent methods (problem of mismatch of surface energies)

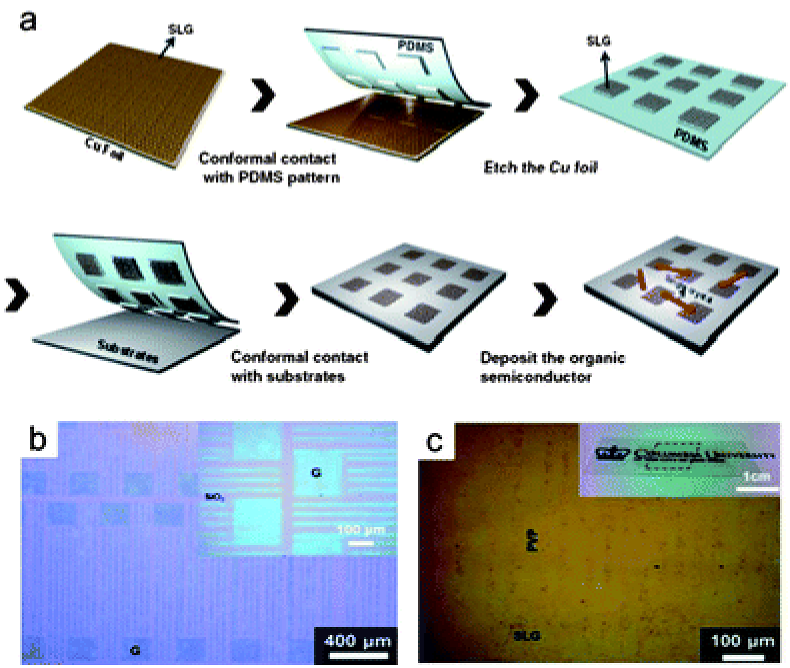


M. Lotya *et al. J. Am. Chem. Soc.*, 2009, 131, 3611-3620.

Synthesis of graphene 3/4

3) Chemical vapor deposition of a hydrocarbon gas

- Growth on substrates Ni, Cu
- Thermal decomposition of TiC (111)
- The surface structure affects the graphene structure (crystallinity, bond length)
- Typical reaction: methane, Copper foil, T = 1000 °C ➔ monolayer graphene with small amount of multilayer regions
- Roll-to-roll transfer by soft material ➔ stamping on the target substrate
- Applicable on large scale

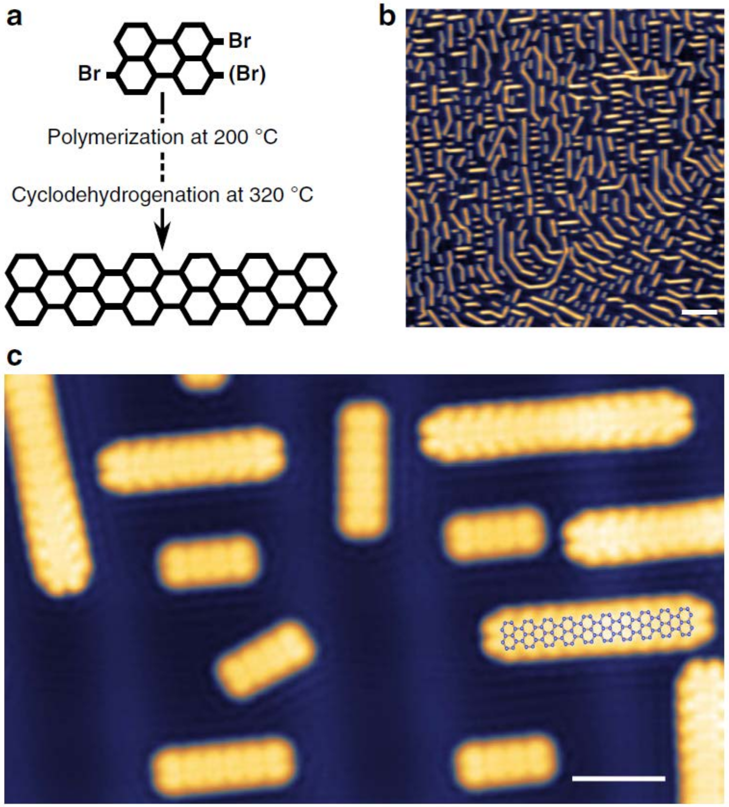


J. Kang *et al. Nanoscale*, 2012, 4, 5527-5537.

Synthesis of graphene 4/4

4) Processing via organic chemistry

- Not applicable for large entities
- Graphene nanoribbons

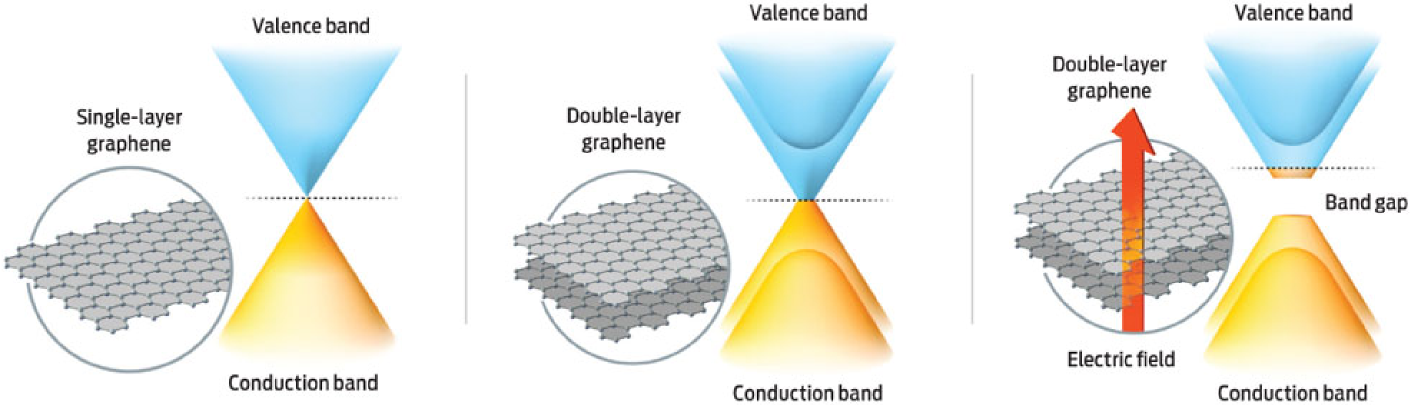


A. Kimouche, Nat. Commun., 2015, 6.

http://graphene-flagship.eu/material/graphene/Pages/What-is-graphene.aspx

Electrical conductivity of graphene

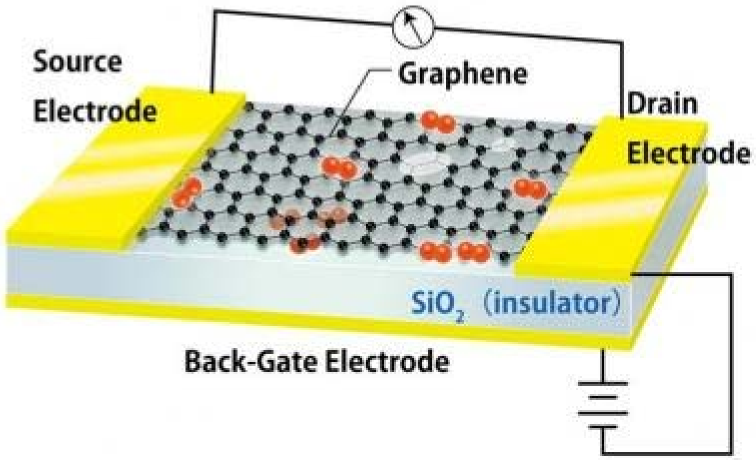
- Electrons can delocalize on the crystal and move with very low resistance
- Due to symmetry, the band gap of pristine single layer or double layer graphene is zero ➔ very conductive



http://spectrum.ieee.org/semiconductors/materials/graphene-makes-transistors-tunable

Electronic properties of graphene

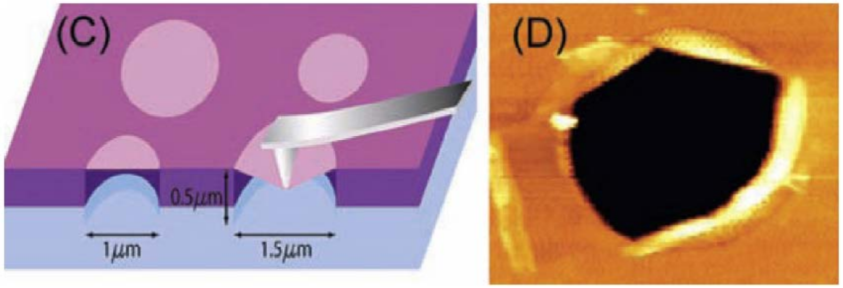
- Doping by electric field or other means opens up the gap ➔ enables transistors for sensing
- Electrical noise is very low, but sensitivity very high
- Mobility of the electrons is high ➔ behave as quantum particles in room temperature



https://www.graphene-info.com/oxygen-adsorption-graphene-can-be-controlled-using-field-effect-transistor

Mechanical properties of graphene

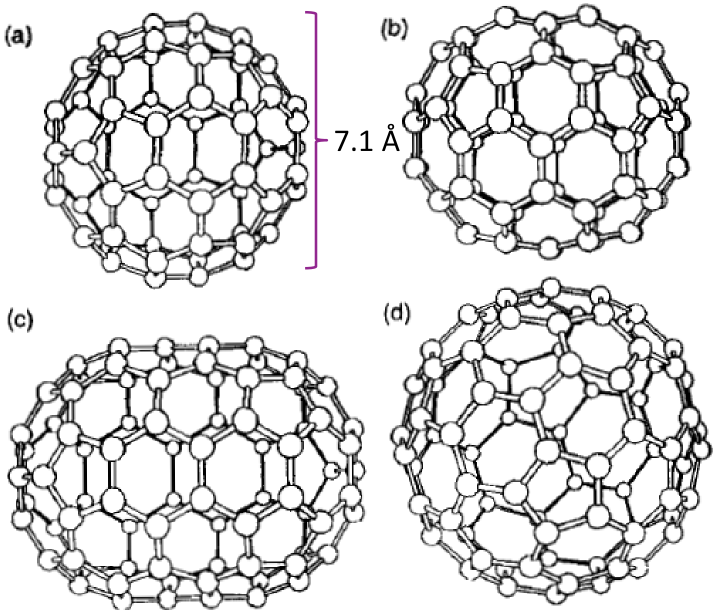
- Young's modulus 1 TPa
- Intrinsic strength 130 GPa, highest ever measured value
- Graphene bends easily
- Suits well for a strengthening component in composite structures



Lee *et al. Science.* **2008**

Carbon fullerenes

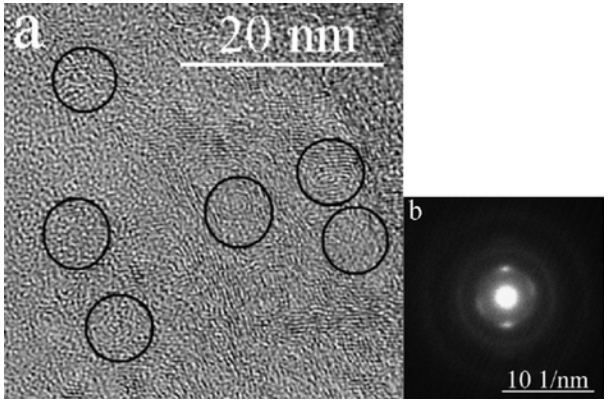
- Fullerene often refers to the C_{60} icosahedral structure = Buckminsterfullerene = Bucky ball
- Also larger molecular weights with different geometries
- In C_{60}, every carbon is equivalent, trigonally bonded, but the bonds are not equivalent
- 4 valence electrons, 3 bonds ➔ 2 single (1.46 Å) and 1 double bond (1.40 Å)
- Euler's theorem: a closed surface has 12 pentagons and arbitrary number of hexagons



1996 Nobel Prize in Chemistry to the founders of fullerene; Smalley, Curl, and Kroto

Synthesis of fullerenes and fullerites

- Arc discharge between graphite electrodes of He gas ➔ evaporation of carbon to form soot and fullerenes
- Contains typically less than 15 % of fullerenes ➔ separation by liquid chromatography
- Formation mechanism still unclear



- Fullerites are close packed crystals of fullerenes ➔ by crystallisation or sublimation
  - Hardness 150-300 GPa

M. Popov, V. Mordkovich, S. Perfilov, A. Kirichenko, B. Kulnitskiy, I. Perezhogin and V. Blank, Carbon, 2014, 76, 250-256.

Electronic structure of fullerene

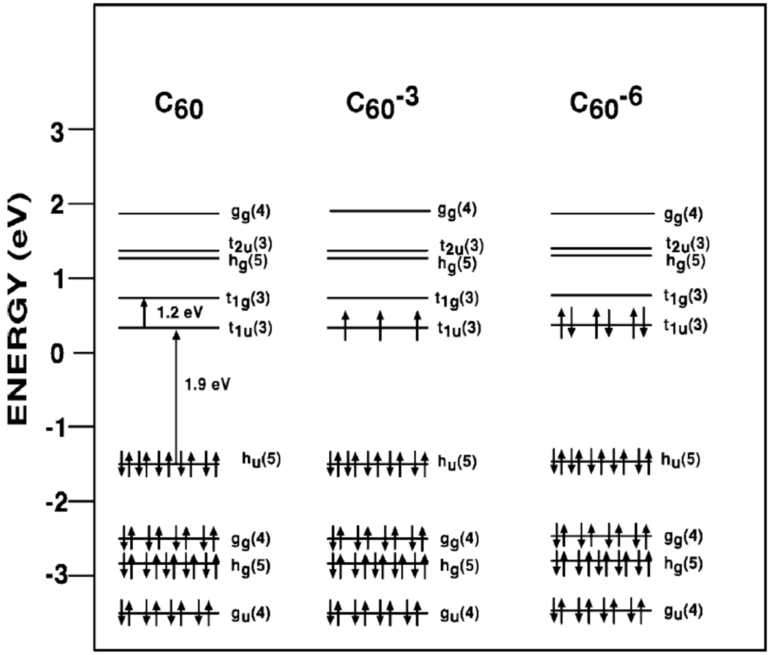
- The electronic structure of fullerene is molecule-like
- HOMO state is fully occupied by 10 electrons
- LUMO state is low and able to accept at least 6 electrons

➔ the HOMO-LUMO is gap rather small

➔ At least 6 single electron transfer may occur

LUMO

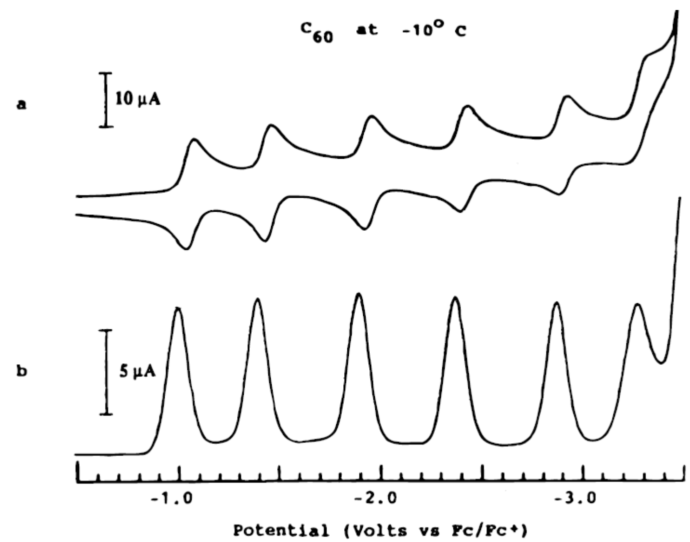
HOMO



Guha and Nakamoto *Coord. Chem. Rev.* 249 **2005**

Fullerene electrochemistry

- $C_{60}{}^{n-}$, where *n* = 1-6 have been detected
- Fullerene acts like a redox molecule with several redox states
- Efficient in charge transfer complexes, for example for light harvesting
  - Chromophore coupled with fullerene ➔ light induces charge separation➔ fullerene efficiently transfers the electrons



L. Echegoyen and L. E. Echegoyen, Acc. Chem. Res., 1998, 31, 593-601.

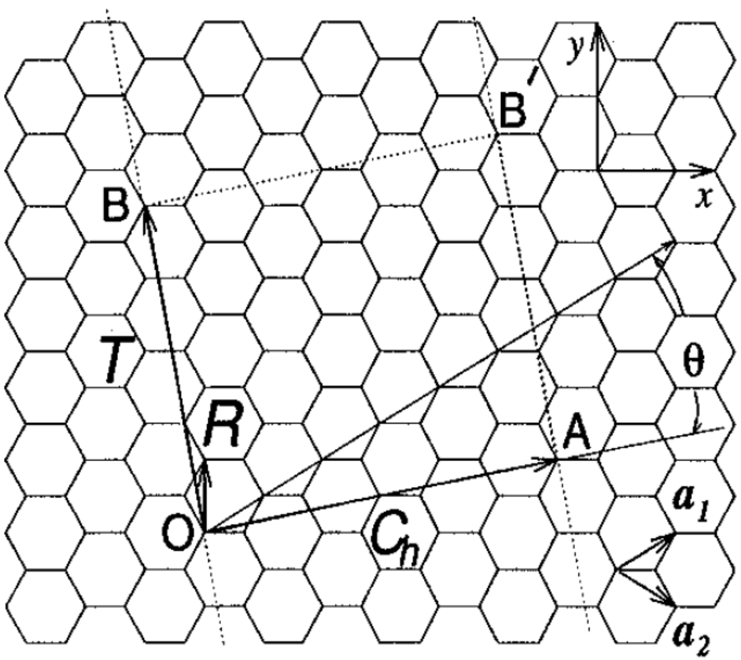
Carbon nanotubes

- The simplest structure is a single-walled carbon nanotube (SWCNT)
- The structure corresponds to a cylinder obtained by wrapping a graphene sheet
- Different structures with different diameter d_{t} and chiral angle θ

$$d_t = \frac{C_h}{\pi}, \qquad C_h = na_1 + ma_2$$

Where a_1 and a_2 are unit vectors in the graphene lattice

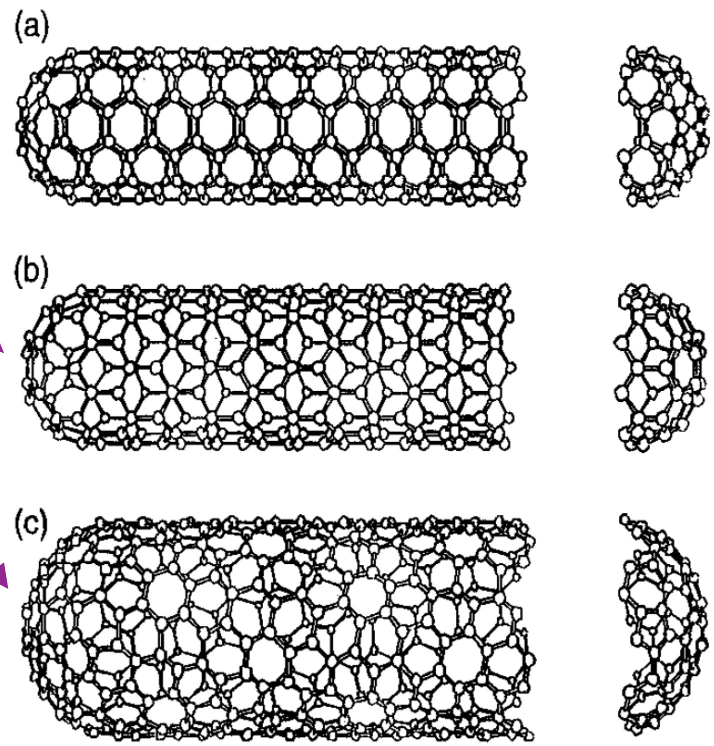
Thus, the integers *n* and *m* in the roll up vector define uniquely the geometry of SWCNTs



Cao *et al.* Nanostructures and Nanomaterials - Synthesis, Properties and Applications

Chirality of carbon nanotubes

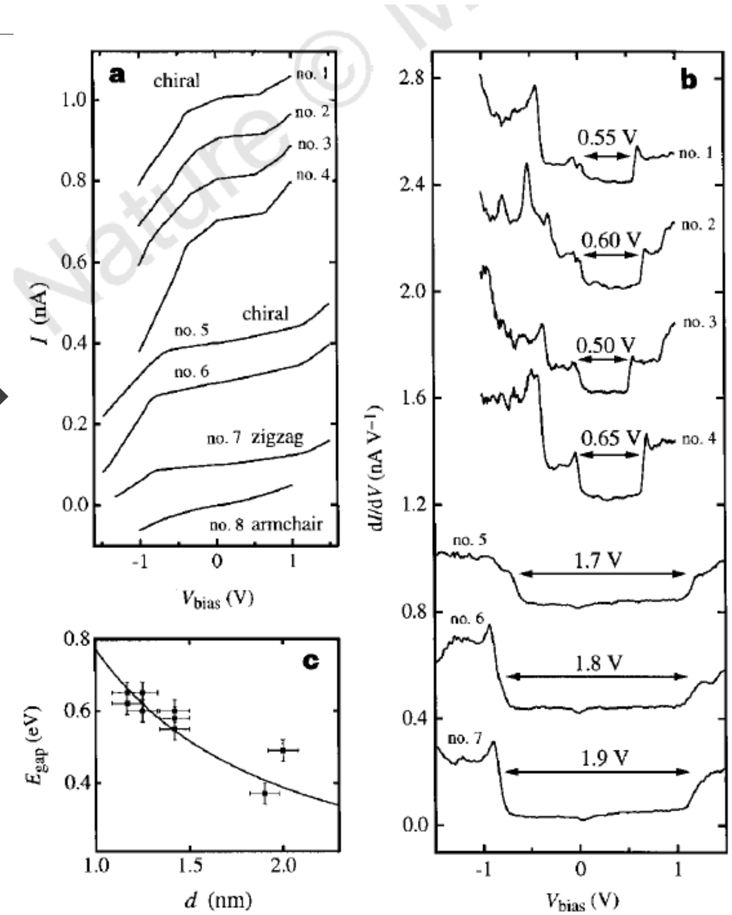
- The three basic geometries of carbon nanotubes:
  - armchair (*n*,*n*) θ = 30°
  - zigzag (*n*,0) θ = 0°
  - chiral (*n*,*m*) 0° < θ < 30°



Cao *et al.* Nanostructures and Nanomaterials - Synthesis, Properties and Applications

Structure vs. electronic structure

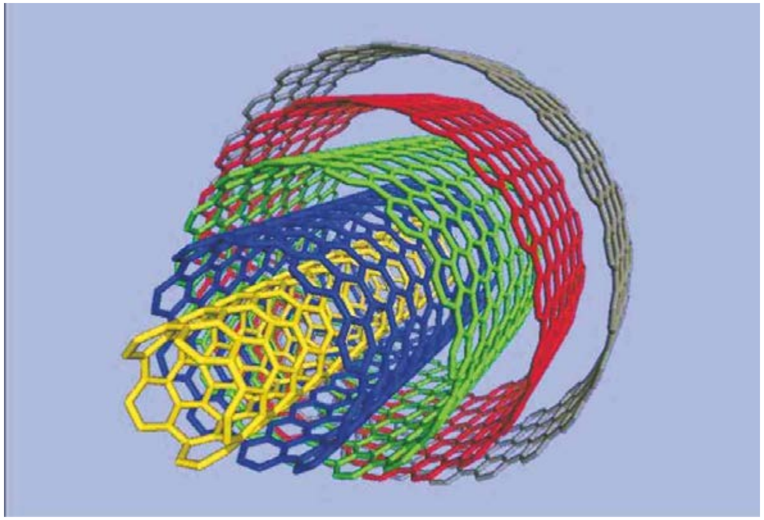
- Carbon nanotubes are either metallic or semiconducting
- Armchair: bands cross the Fermi level ➔ metallic
- For other tubes, if n-m = 3l (l is integer) ➔ tubes are metallic
- Otherwise they are semiconducting with band gap near 0.5 eV, depending on the diameter



Wildöer *Nature* 1998

Multiwalled carbon nanotubes (MWCNT)

- Several nested coaxial single wall nanotubes
- Typically a mixture of chiral and non-chiral tubes ➔ helicity (compare to turbostratic graphite)
- No typical ordering or alignment of the cylindrical planes
- Typical dimensions
  - Outer diameter 2-20 nm
  - Inner diameter 1-3 nm
  - Length 1-100 µm
  - Intertubular distance 0.340 nm

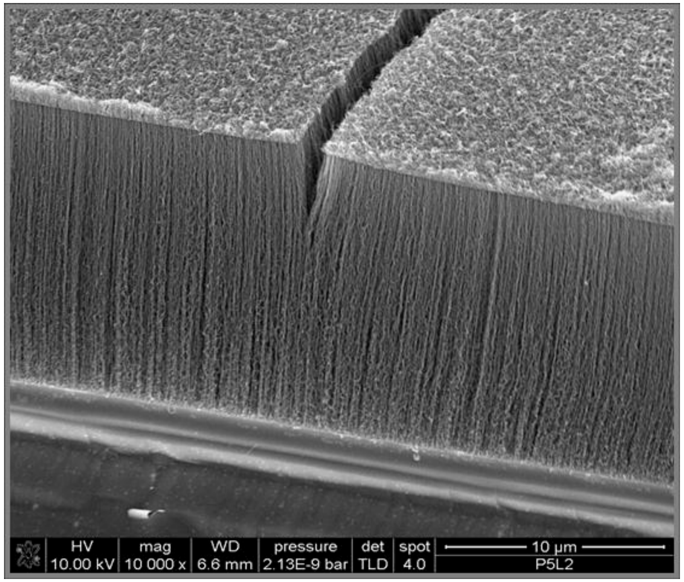


Thomas Swan and Co Ltd.

Synthesis of carbon nanotubes

- Arc evaporation (the first ones by Iijima in 1991)
- Laser ablation
- Pyrolysis
- PECVD (plasma enhanced chemical vapor deposition)
- Electrochemical methods

- Synthesis always results in side products, amorphous carbon, carbon nanoparticles etc.

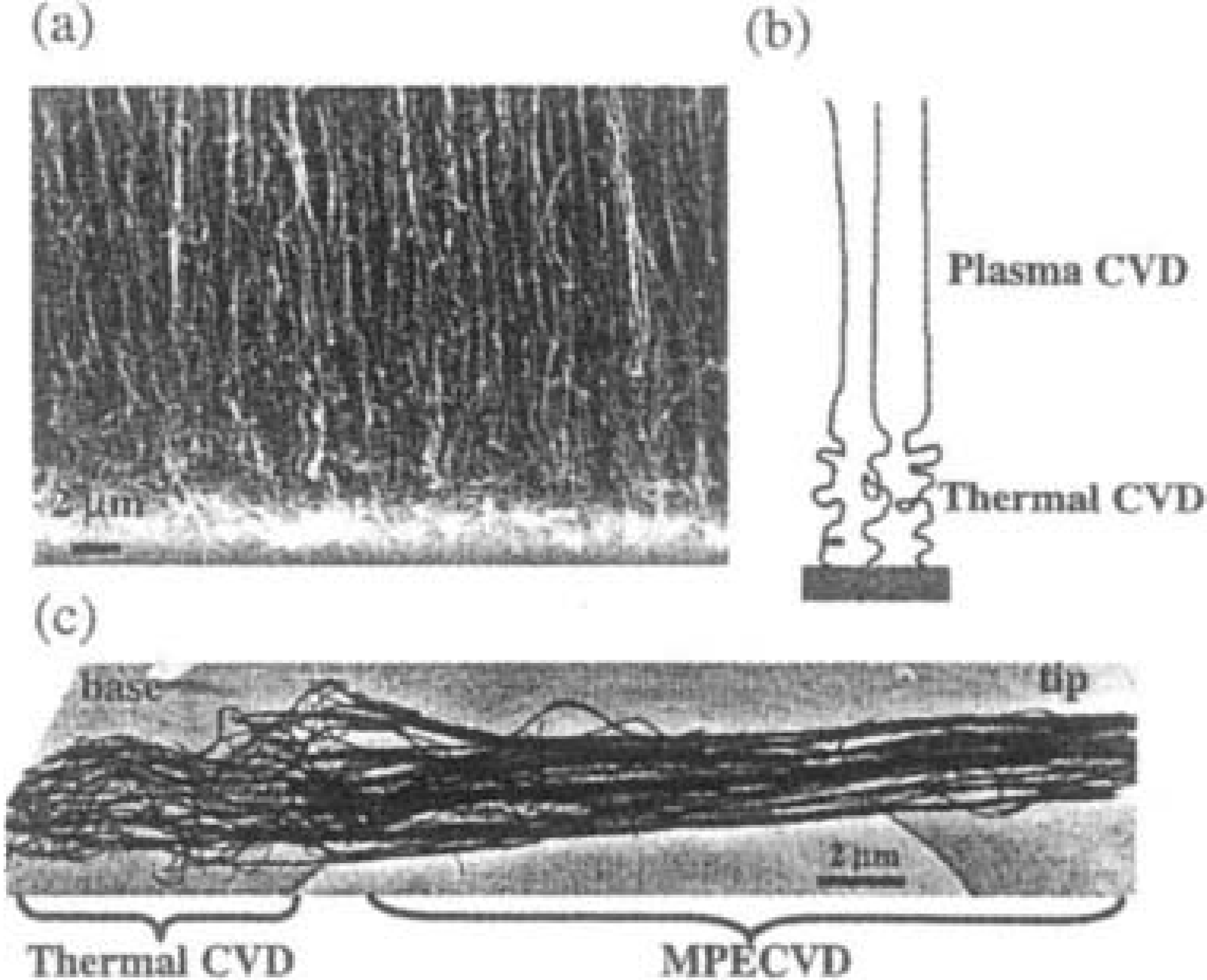


Prof. Dr. Mark H. Rümmeli, IFW Dresden

Growth mechanism of carbon nanotubes

- Formation happens through open end where carbon atoms arrive from the gas phase
  - Open end need to be maintained, either by high electric field (arc-discharge), entropy opposing the cap termination or by presence of metal cluster
  - High temperature of arc-discharge (2000-3000 °C) may cause sintering ➔ defects

- Metals such as Co, Ni and Fe catalyze the growth at lower temperatures (1000 °C)
- Plasma induced carbon nanotubes grow as forests on surfaces embedding the catalyst particles
  - Plasma induces growth of straight nanotubes, thermal treatment curly
- Catalyzed CVD method suitable for mass production



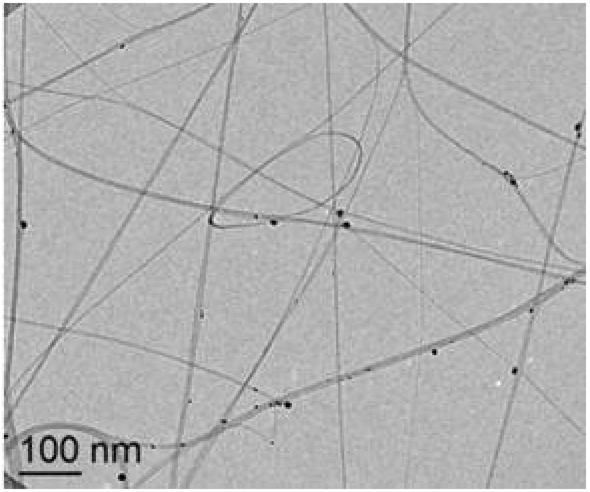
Cao *et al.* Nanostructures and Nanomaterials - Synthesis, Properties and Applications

Applications of carbon nanotubes

- Catalysis
- Storage of hydrogen and other gases
- Biological cell electrodes
- Quantum resistors
- Nanoscale electronic and mechanic devices (nanoelectromechanical systems = NEMS)
- Electron field emission tips
- Scanning probe tips
- Flow sensor (gas sensor)
- Nanocomposites

Nanobud

- Hybrid of carbon nanotube and fullerene
- The hybrid is formed in the synthesis
- Has beneficial optical, mechanical, chemical and electrical properties compared to carbon nanotubes
- No need to create defects to the nanotube ➔ conductivity remains high
- Fullerenes are much more reactive than nanotubes



http://www.canatu.com/nanobud/

Concept check: Carbon nanomaterials

True or false?

A) Carbon nanomaterials only consist of carbon

B) All the C-C bonds are identical in carbon nanomaterials

C) Chirality greatly affects the mechanical properties of carbon nanotubes

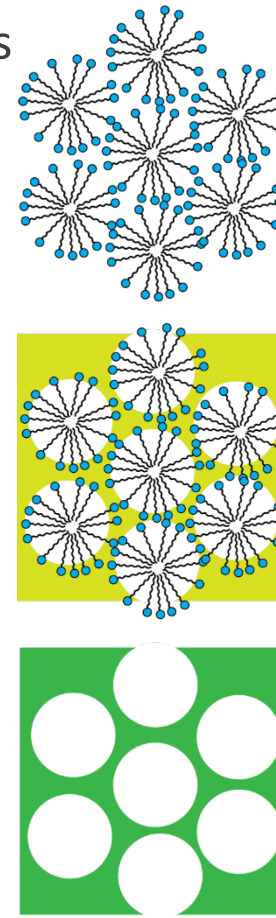
Other special nanomaterials

Micro and mesoporous materials

	Pore size d (nm)	Examples
Microporous	< 2	Zeolites and their derivatives
Mesoporous	**2 < d < 50**	**Surfactant templated mesoporous materials, xerogels, aerogels**
Macroporous	> 50	

Ordered mesoporous structures

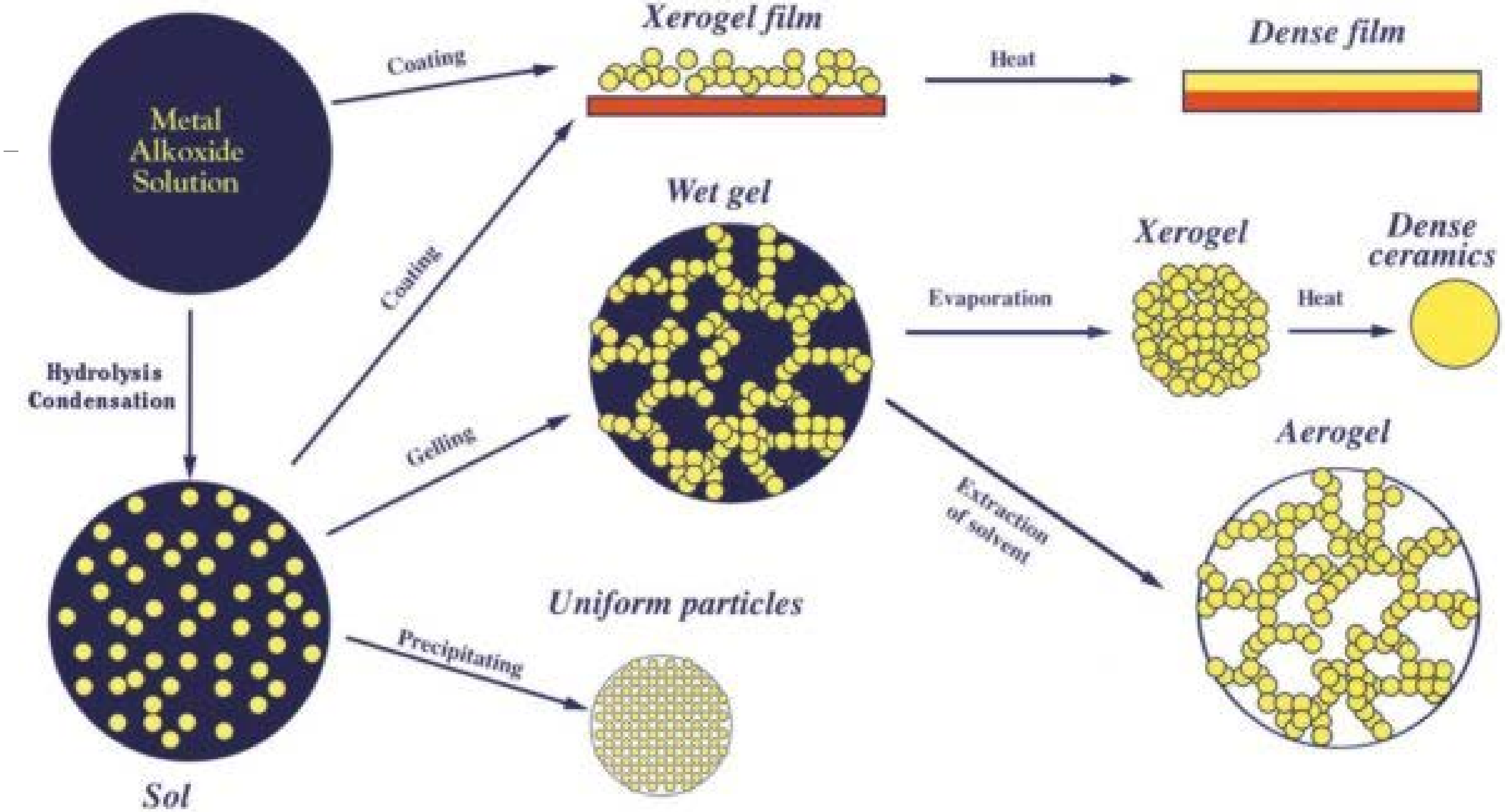
- Synthesized by using self-assembled surfactants as template ➔ simultaneous sol-gel condensation around the template
- Very large pore volume (70 %) and surface area (> 700 m^2/g)
- Applications:
  - Supports
  - Adsorbents
  - Sieves
  - Nanoscale chemical reactors



Ordered micelles

Sol-gel templated in ordered micelles

Solid mesoporous material



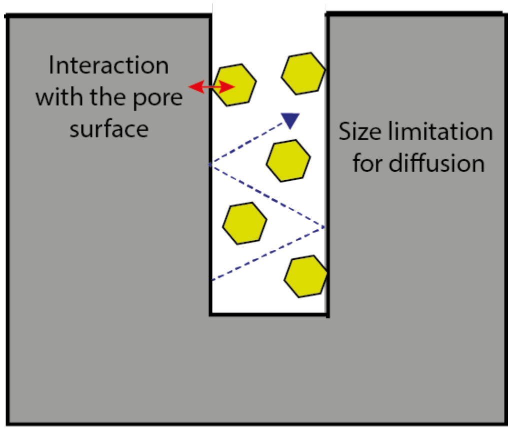
https://www.gelest.com/applications/sol-gel-applications/

Diffusion through mesoporous structures

- Powders, bulk and films
- Bulk: macroscopic grains with crystallographic order are randomly packed ➔ hinders diffusion through the bulk
- Mesoporous films have typically parallel rather than perpendicular alignment
- The best alignment and hierarchical structures achieved only on small scale

Confinement of liquids in mesoporous materials

- On mesoscopic systems viscous forces are very strong
- At micro and nanoscale turbulence is not reached because high enough flow speed cannot be obtained ➔ difficulty in mixing
  - compare water vs. honey
- Capillary forces very important (wetting of the pore)
- Due to size limitation, diffusion changes inside the pores (for both solvent and a solute)
- Due to the large surface area and its close proximity, the organisation and interactions between the molecules also change ➔ Catalysis and other chemical reactions



Xerogels

- Solvent of the sol-gel material is removed by evaporation in ambient conditions (*T* may be elevated) (condensing through sintering)
- The material shrinks upon drying
- Random porous structure, typical porosity 50 %
- Porous structures of several oxides (Al_2O_3, TiO_2 etc.) ➔ porous glasses
- The xerogel formation is a balance between capillary forces collapsing the structure and the condensation of the material

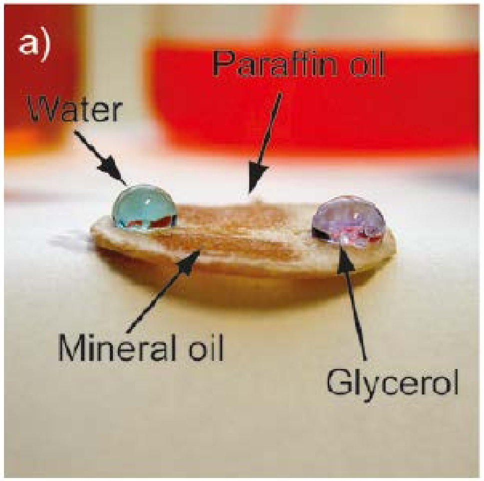
➔ Porosity and pore size depend on T and the composition

Aerogels

- Removal of solvent from a gel by supercritical drying
  - ➔ No shrinkage of the structure, very high porosity (75-99%)
- At supercritical conditions, capillary forces do not play a role because there is no surface tension
- Applicable to all sol-gel materials
- Also for hydrogels of nanofibrillar structures

http://pubs.acs.org/doi/suppl/10.1021/am200475b

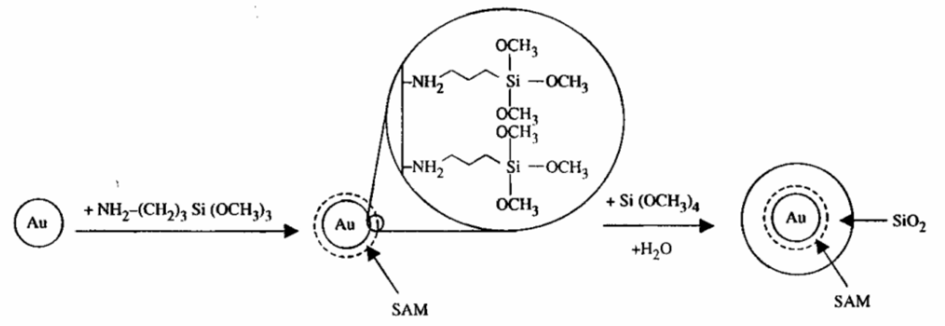
Hydrophobised nanocellulose aerogel

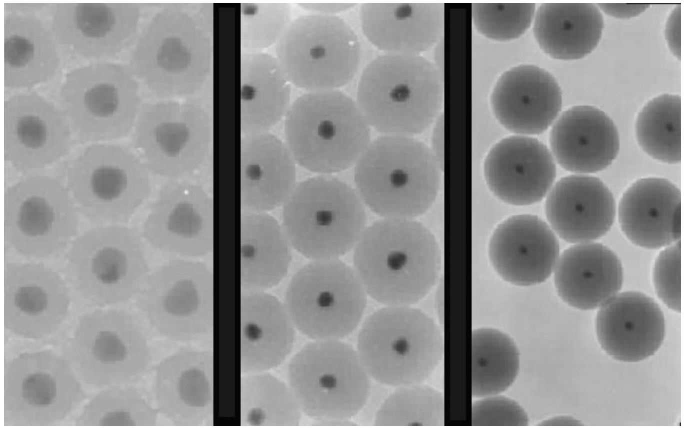


Korhonen et al. ACS Appl Mat & Int. 2011

Core-shell structures

- Metal-oxide structures: Au nanoparticle embedded in silica core
  - Au is vitreophobic ➔ strong interface between Au and silica has to be formed
  - Monolayer of silane coupling agent is adsorbed on the Au surface and turns the surface vitreophilic➔ deposition of silica shell
  - Silica shell prevents aggregation of the nanoparticles but does not disturb the optical properties





Metal-polymer and oxide-polymer core-shell structures

- Metal/oxide core with uniform and well-defined polymer shell
- Ag-polystyrene/metachrylate through emulsion polymerization in oleic acid
- Polymer-coated oxide through polymerization
  - Adsorption of monomers on the particle ➔ polymerization
  - Emulsion polymerization
- Polymer-coated oxide through adsorption
  - Based on self-assembly of the polymer or polyelectrolyte layers

Organic-inorganic hybrids

- Materials in which organic and inorganic components interpenetrate on nanoscale
- Both form percolated networks

Class I hybrids:

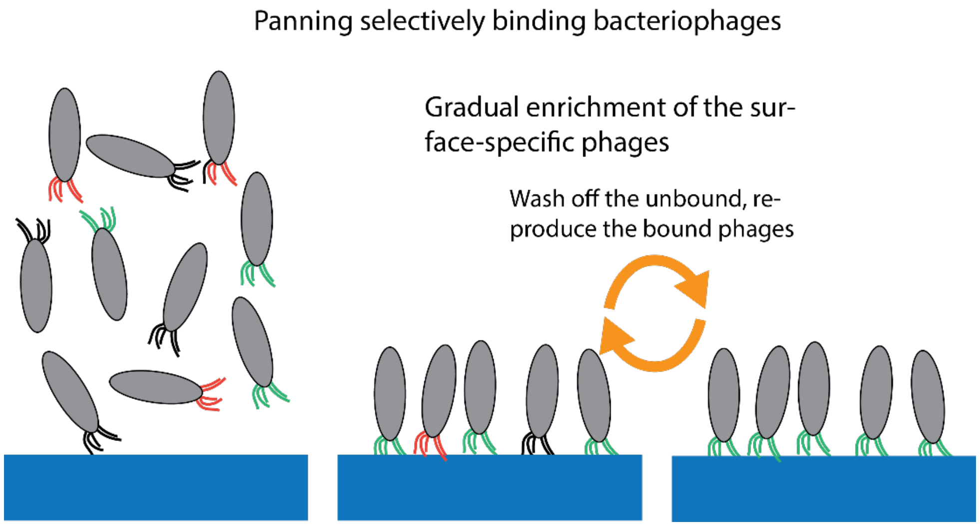
- Organic (with rather low molecular weight) compounds in inorganic matrix

Class II hybrids:

- Organic and inorganic compounds chemically bonded with each other

Bio-induced (biohybrid) materials

- Some biomolecules have high affinity to inorganic materials
- Strong interaction to biomolecules controls mineralization of inorganic materials (bone, enamel, nacre)
- There are efficient biological combinatorial methods for choosing the best binders
- Phage display



Concept check

Which have higher porosity?

A) Xerogels

B) Aerogels

True or false?

A) Mesopores allow regular diffusion of molecules

B) Chemical interactions play a significant role in formation of hybrid nanomaterials

Related Literature

Fullerenes, nanotubes, mesoporous materials, core-shell structures, bio-induced materials:

- Cao *et al.* Nanostructures and Nanomaterials - Synthesis, Properties and Applications, Chapter 6: Special Nanomaterials

Graphene:

- Inagaki *et al.* Materials Science and Engineering of Carbon: Fundamentals (2nd Edition), Chapter 3.5.3 Graphene and its derivatives