PHAS0058

Physics of Advanced Materials

Lecture 7: Nanomaterials

In this lecture...

- Fundamentals:
  - Quantum confinement in nanostructures
  - Surface and interface phenomena
  - Nanophotonics
  - Nanomagnetism and spintronics

- Types and structures of nanomaterials
- Synthesis techniques
- Applications
- Challenges and opportunities

Fundamentals and properties

Basic principles and unique properties that emerge at the nanoscale
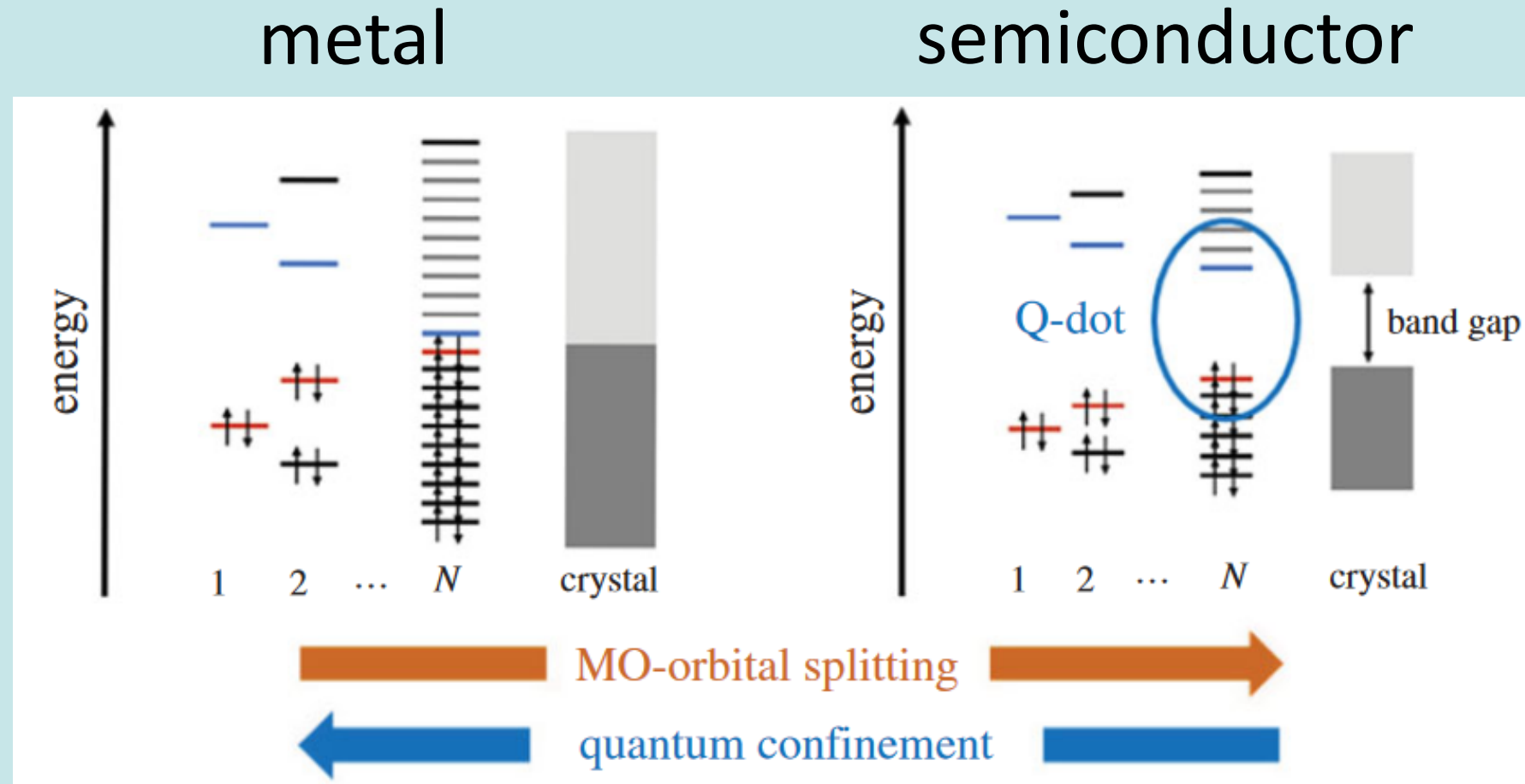
Physics of nanomaterials

Bottom-up approach: Splitting of orbital energies

- **start from:** atoms and molecules and build up to larger structures: clusters and bulk

- **focus**: how individual atomic orbitals combine to form molecular orbitals and then energy bands

- as you increase the number of atoms in a cluster, molecular orbitals split into more energy levels and into quasi-continuous bands

Top-down approach: Quantum confinement of bulk material
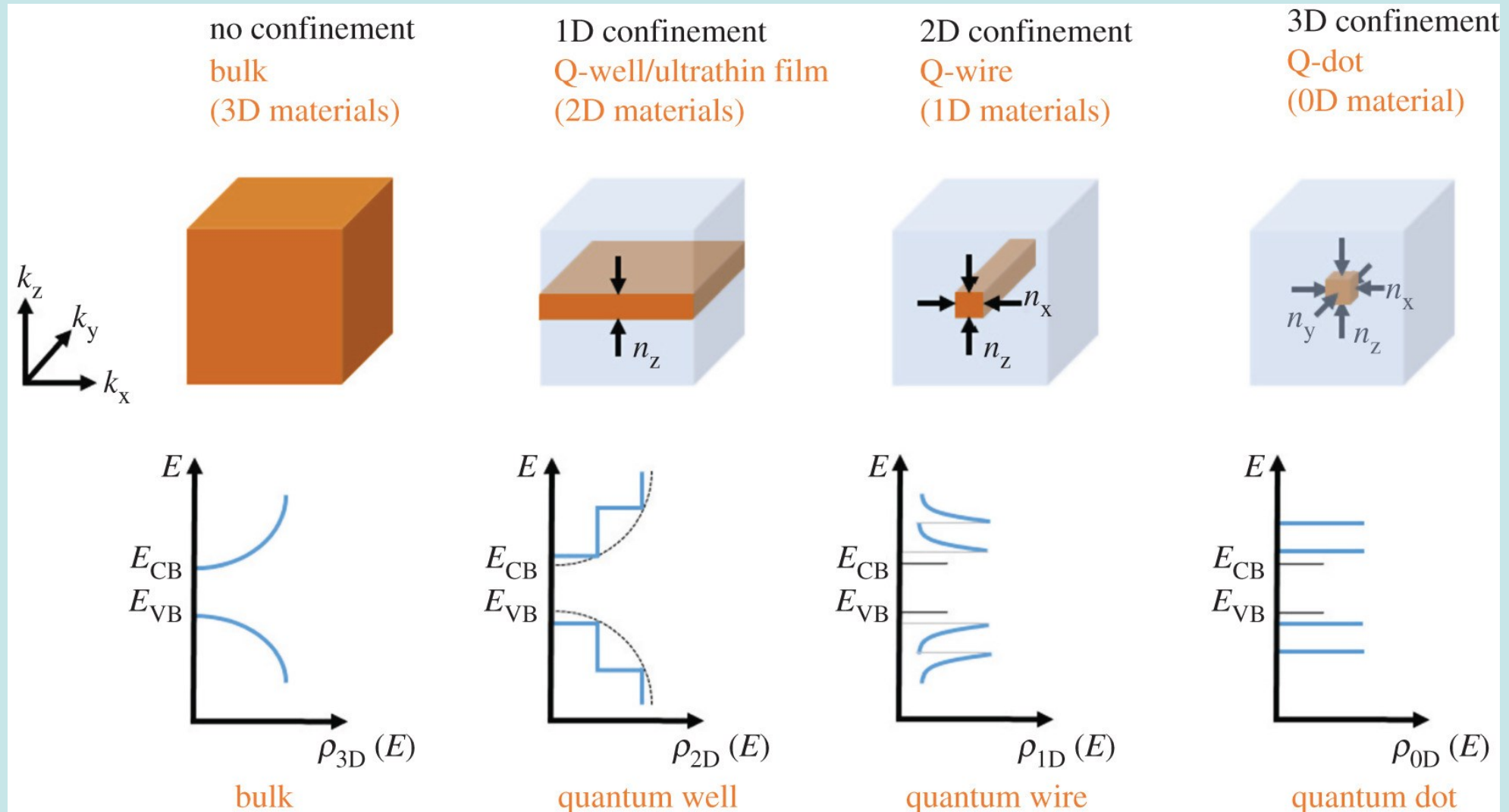
- **start from:** the bulk material and reduce size

- **focus**: how quantum confinement alters electronic structure when material dimensions approach de Broglie wavelength of electrons

- as dimensions decrease, electron motion is confined which leads to quantization of energy levels: the energy bands begin to split

Metals and seminconductors and nanoscale

Quantum Confinement in Nanostructures

Dr Monika Szumilo

DOS

T. Edvinsson, R. Soc. open sci. 5: 180387, https://doi.org/10.1098/rsos.180387

DoS vs. dimensionality

degrees of freedom	dispersion (kinetic energy)	density of states (close to the conduction band)	effective density of states (at the conduction band)
3D (bulk)	$E = \dfrac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2)$	$\rho_{3D} = \dfrac{1}{2\pi^2}\left(\dfrac{2m*}{\hbar^2}\right)^{\frac{3}{2}}(E - E_c)^{1/2}$	$N_c^{3D} = \dfrac{1}{\sqrt{2}}\left[\dfrac{m^*kT}{\pi\hbar^2}\right]^{3/2}$
2D (film)	$E = \dfrac{\hbar^2}{2m^*}(k_x^2 + k_y^2)$	$\rho_{2D} = \displaystyle\sum_{i=1}^{n}\dfrac{m^*}{\pi\hbar^2}H(E - E_c)$	$N_c^{2D} = \dfrac{m^*kT}{\pi\hbar^2}$
1D (wire)	$E = \dfrac{\hbar^2}{2m^*}(k_x^2)$	$\rho_{1D} = \dfrac{1}{m^*\pi\hbar}\left(\dfrac{m^*}{2(E - E_c)}\right)^{1/2}$	$N_c^{1D} = \sqrt{\dfrac{m^*kT}{2\pi\hbar^2}}$
0D (dot)	[a]	$\rho_{0D} = 2\delta(E - E_c)$	$N_c^{0D} = 2$

[a]The dispersion is formally not defined in a 0D (3D confined) system as there is no periodicity in any direction.

1D well – bandgap shift

solution to the Schrödinger equation for a particle confined in a one-dimensional potential well with infinite barriers:

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

2D shift in energy bandgap

$$\Delta E_e = \frac{\hbar^2 n^2 \pi^2}{2m_e^* d^2} \qquad \Delta E_h = \frac{\hbar^2 n^2 \pi^2}{2m_h^* d^2}$$

For the first energy state (n=1):

$$\Delta E = \Delta E_e + \Delta E_h$$

Use the particle-in-a-box model:

$$\Delta E = \frac{\hbar^2 \pi^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{1}{d^2}$$

T. Edvinsson, R. Soc. open sci. 5: 180387, https://doi.org/10.1098/rsos.180387

2D well – bandgap shift

Total energy for a particle in a 2D box:

$$E_{n_e, n_h} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{d_x^2} + \frac{n_y^2}{d_y^2} \right)$$

n_x and n_y – quantum numbers in the x- and y-directions
d_x and d_y – confinement dimensions in the x- and y-directions

For a symmetric well (d_x=d_y=d):

$$\Delta E_e = \frac{\hbar^2 \pi^2}{2m_e^*} \left(\frac{n_x^2}{d^2} + \frac{n_y^2}{d^2} \right) \qquad \Delta E_h = \frac{\hbar^2 \pi^2}{2m_h^*} \left(\frac{n_x^2}{d^2} + \frac{n_y^2}{d^2} \right)$$

For the lowest eergy state (n_x=n_y=1):

$$\Delta E_e = \frac{\hbar^2 \pi^2}{m_e^* d^2} \quad \Delta E_h = \frac{\hbar^2 \pi^2}{m_h^* d^2}$$

The total energy shift for the lowest quantum state in a 2D quantum well:

$$\Delta E = \Delta E_e + \Delta E_h = \frac{\hbar^2 \pi^2}{d^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

3D well – bandgap shift

Total energy for a particle in a spherical 3D box:

$$E_{n,l} = \frac{\hbar^2 k_{n,l}^2}{2m} = \frac{\hbar^2 x_{n,l}^2}{2mR^2}$$

n - quantum number
h – Planck's constant
m – effective mass of the particle
R – radius of the QD
x – root of the Bessel function

$$x_{1,0} = \pi \quad \rightarrow E_{0,1} = \frac{\hbar^2 \pi^2}{2m^* R^2}$$

Effective bandgap:

$$E_g^{eff} = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

Bandgap shifts

Effective bandgap:
$$E_g^{eff} = E_g^{bulk} + \Delta E_g$$

n - quantum number
h – Planck's constant
m – effective mass of the particle
R – radius of the QD
x – root of the Bessel function

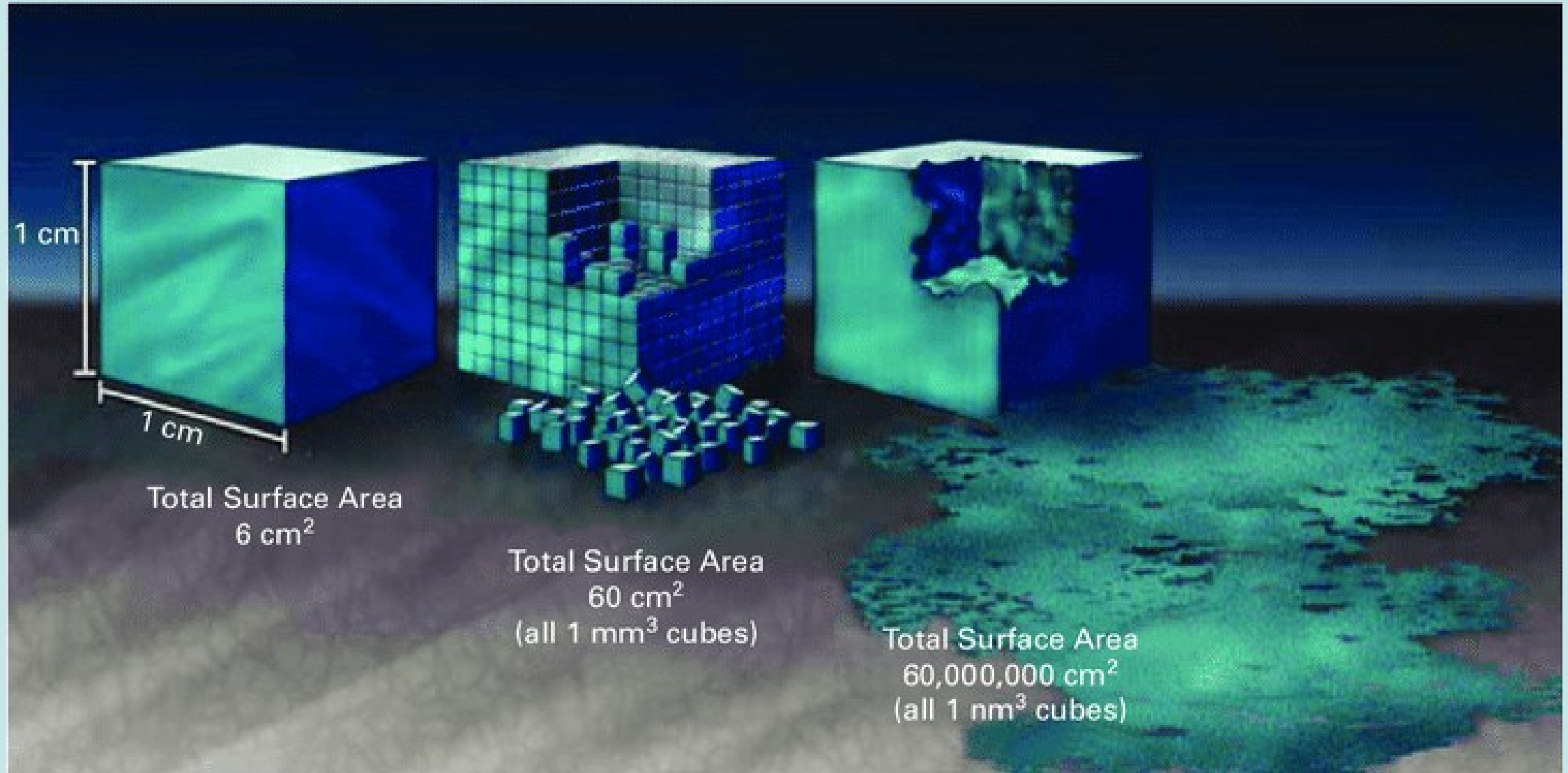$$\Delta E_g^{0D} = \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

$$\Delta E_g^{1D} = \frac{\hbar^2 \pi^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\left(\frac{1}{L_x^2} + \frac{1}{L_y^2}\right)$$

Bandgap shift with confined dimensions:

- 0D (quantum dots): $\Delta E_g \propto \frac{1}{R^2}$

- 1D (nanowires): $\Delta E_g \propto \frac{1}{L_x^2} + \frac{1}{L_y^2}$

- 2D (quantum wells): $\Delta E_g \propto \frac{1}{L_z^2}$

$$\Delta E_g^{2D} = \frac{\hbar^2 \pi^2}{2L_z^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

Surface to volume ratio

Su, E. & J. et al.(2018, Bone & Joint Journal. 100-B. 9-16. 10.1302/0301-620X.100B1.BJJ-2017-0551.R1

Surface and interface phenomena

| origin	result	implications
surface atoms have fewer neighboring atoms compared to bulk atoms, leading to unsatisfied or dangling bonds.	higher surface energy (higher no. of active surface sites)	• enhanced chemical activity • altered thermodynamic stability (sintering, coalescence, etc.) • significantly lower melting T than bulk
	surface plasmon resonance (metals only)	• altered optical absorption and scattering
imbalance of forces at the surface (bonding vs. repulsive electron cloud interactions)	surface stress and reconstruction	- altered mechanical properties (hardness, elasticity, etc.) - lower surface energy facets exposed in adopted shapes of nanoparticles
lattice mismatch at interfaces	strain scattering of electrons and phonons at interfaces	- enhanced mechanical strength - reduced thermal and electrical conductivity
	higher surface free energy	- increased solubility and reactivity - altered phase diagrams
surface tension can lead to significant capillary forces	strong adhesion due to van der Waals forces and capillary condensation	- self-assembly of nanoparticles driven by capillary forces - stiction (static friction)

Nanophotonics

- **Diffraction Limit**: beyond the classical optics limits focusing light (approximately half the wavelength ($\lambda/2$)).
- **Near-Field Optics**: evanescent waves containing high spatial frequency information exist only within a distance d << λ from the surface. These non-propagating fields contain subwavelength information.
- **Light-Matter Coupling**: the strength of interaction between light and matter increases dramatically, enabling phenomena like:
  - Enhanced absorption and emission rates
  - Strong and ultrastrong coupling regimes
  - Purcell effect (enhanced spontaneous emission)
- **Dielectric Confinement**: Light can be confined in high-index dielectric nanostructures through total internal reflection, creating resonant modes with enhanced field strengths.
- **Local Density of Optical States** (LDOS): Describes available electromagnetic modes for photon emission at a specific position and frequency, directly affecting spontaneous emission rates.
- **Photonic Bandgaps**: Periodic nanostructures (photonic crystals) can create frequency ranges where light propagation is forbidden, analogous to electronic bandgaps in semiconductors.
- **Optical Nonlinearities**

Plasmonics – self study material

plasmons—collective oscillations of free electrons in metals (quasiparticles)

surface plasmon polariton (SPP) - a hybridized excitation arising from the coupling between photons and collective oscillations of free electron gas at metal-dielectric interfaces
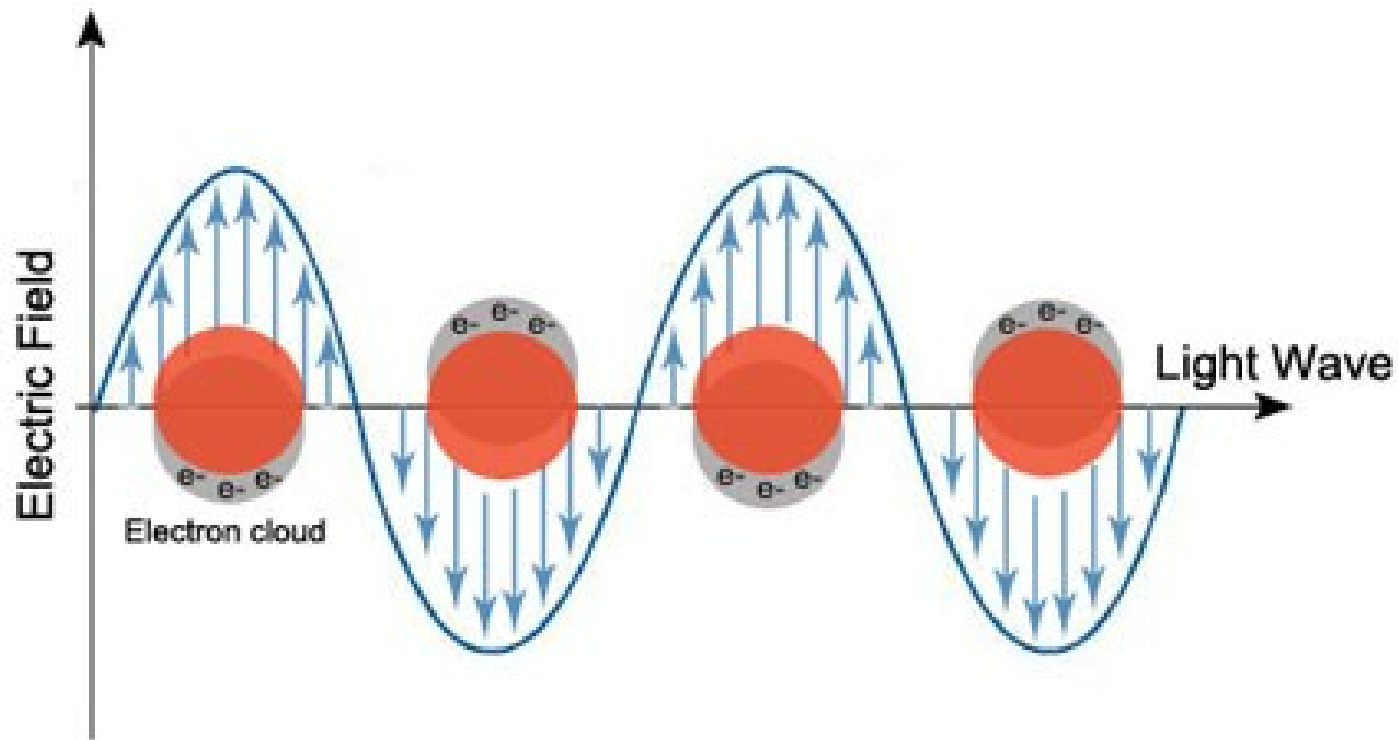
- subwavelength confinement
- support high frequencies
- typically metals or metal-like materials that exhibit negative real permittivity

Nanomagnetism

Critical single-domain radius:

A – exchange stiffness
K – anisotropy constant
μ_0 - vacuum permeability
M_s – saturation magnetisation

$$R_{sd} = \frac{36\sqrt{A|K_1|}}{\mu_0 M_s^2}$$

- Single-domain particles exhibit different magnetic reversal mechanisms (coherent rotation rather than domain wall motion), which directly impacts coercivity and switching behavior in spintronic devices.
- Just below the single-domain threshold, particles often display maximum coercivity (resistance to demagnetization)
- As particles approach and drop below this size, they become increasingly susceptible to thermal fluctuations, eventually leading to superparamagnetic behavior (where magnetization randomly flips direction due to thermal energy).
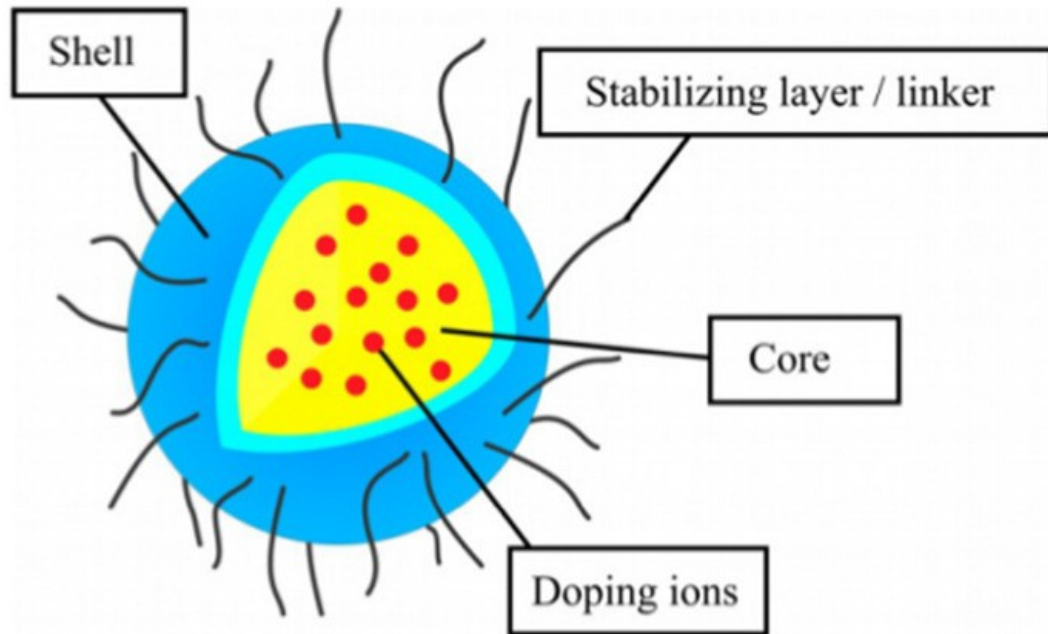
Types and structures

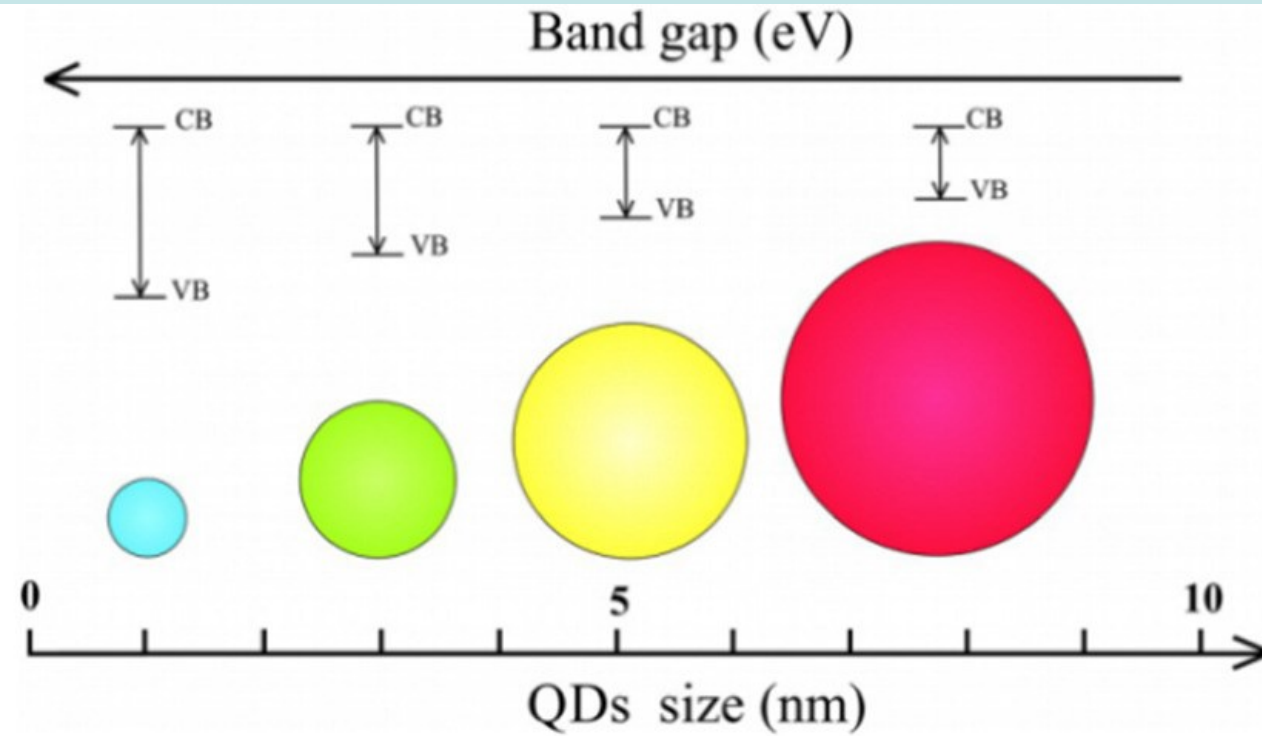Various forms of nanomaterials

# Nanowires and nanorods
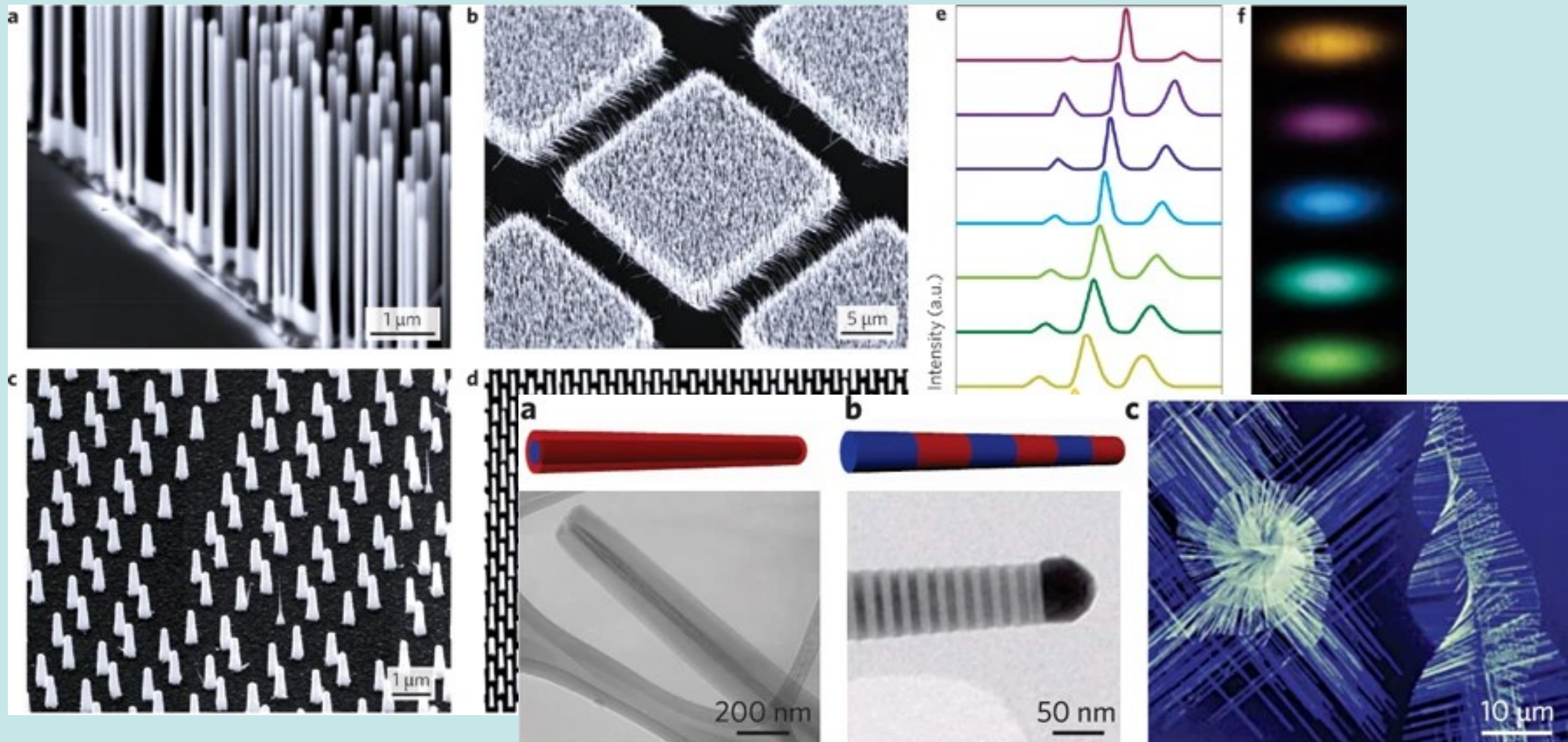
Core/shell structure

Carbon-based nanomaterials
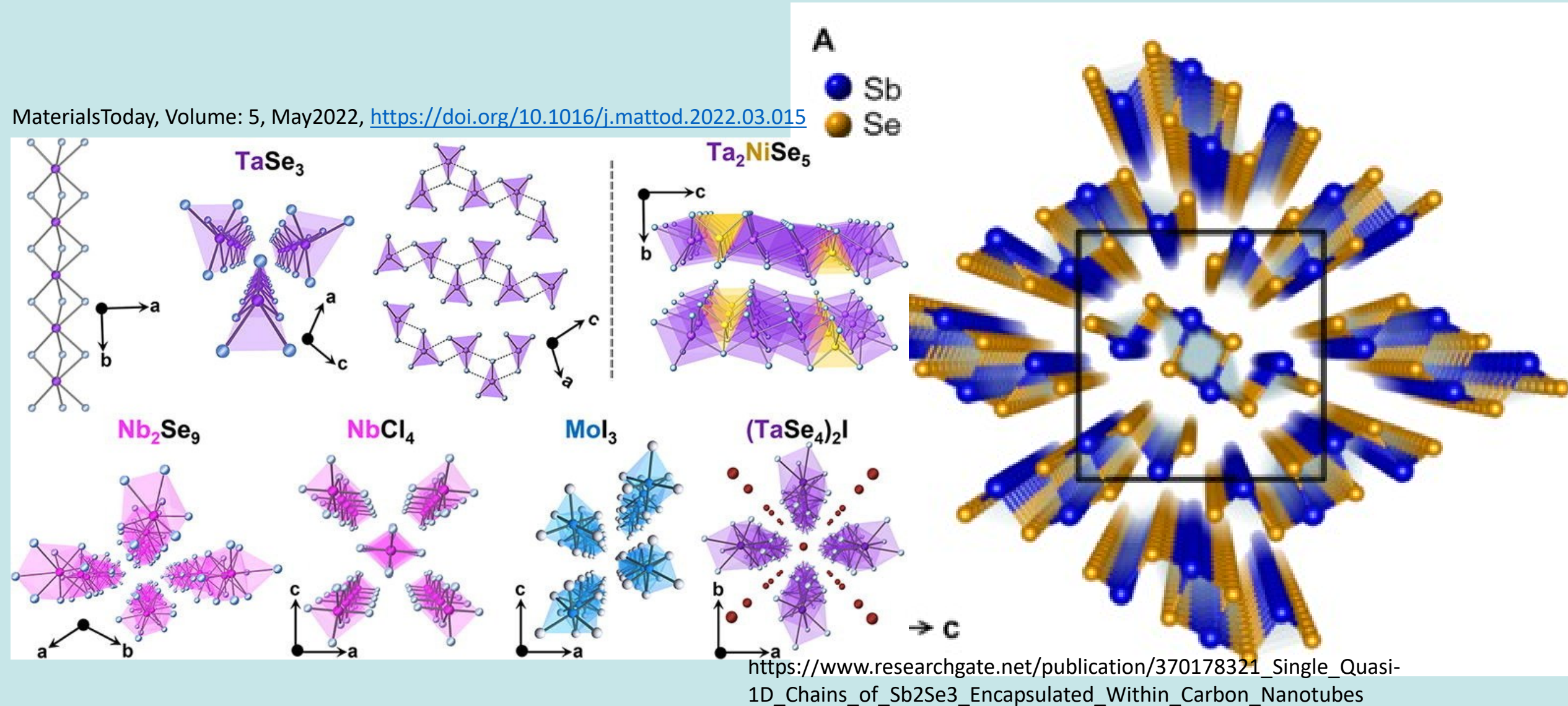
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CARBON:

- uniquely forms stable nanomaterials in all dimensionalities

- can be functionalized with a wide range of chemical groups

- shows good compatibility with biological systems

- abundant and potentially more sustainable

- dramatically different properties from the same element
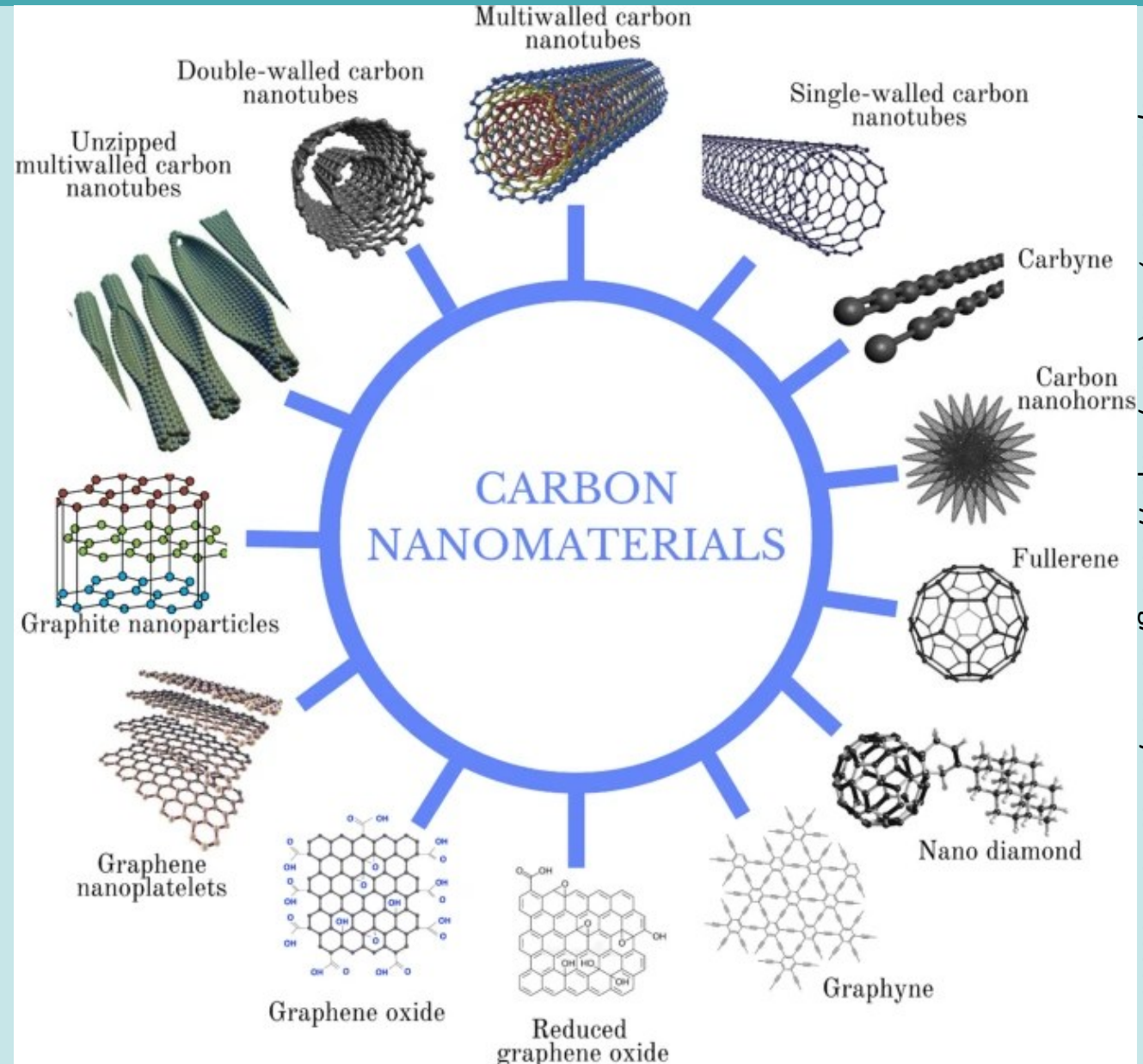
Quasi 1D van der Waals structures

-- quasi-one-dimensional chains or fibrous units held together by van der Waals forces in the perpendicular directions
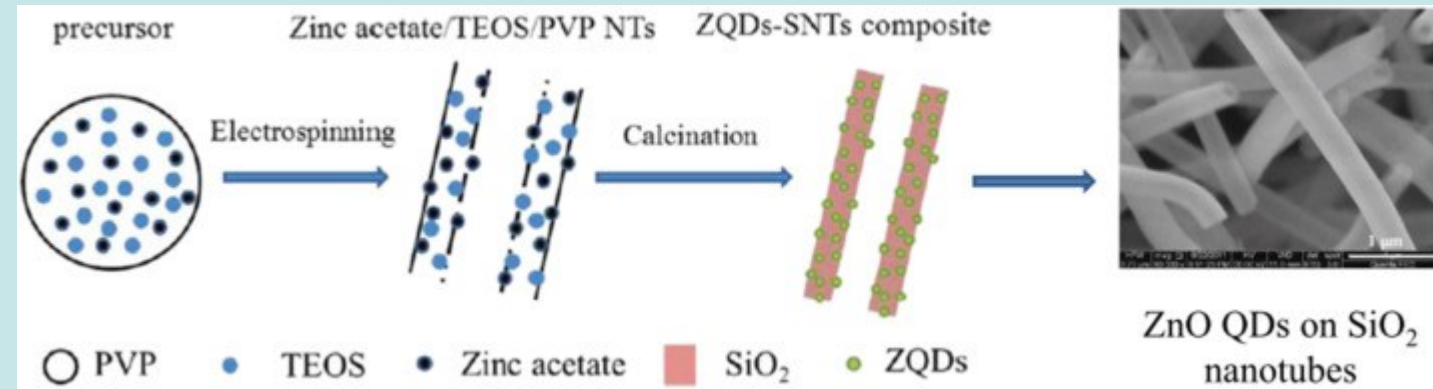
MaterialsToday, Volume: 5, May2022, https://doi.org/10.1016/j.mattod.2022.03.015

https://www.researchgate.net/publication/370178321_Single_Quasi-1D_Chains_of_Sb2Se3_Encapsulated_Within_Carbon_Nanotubes

Photonic crystals

- **photonic crystals** - a material that has a nanostructure that affects the motion of electromagnetic energy

- **quantum dots/**nanometer-sized devices that can efficiently control and manipulate light (slow down, enhance, produce, etc.)

- **metamaterials** - engineered nanostructures with optical properties not found in nature, including negative refractive index
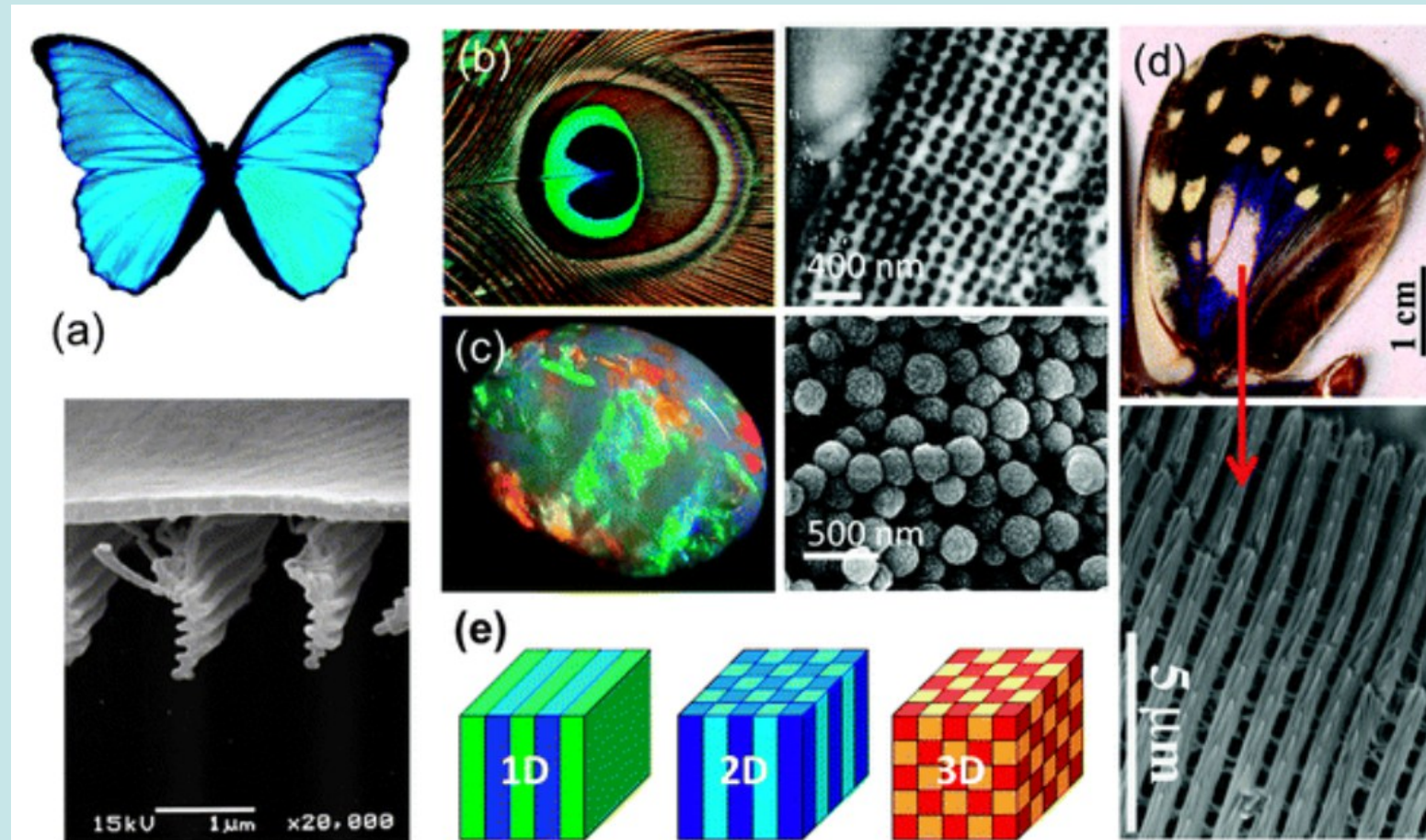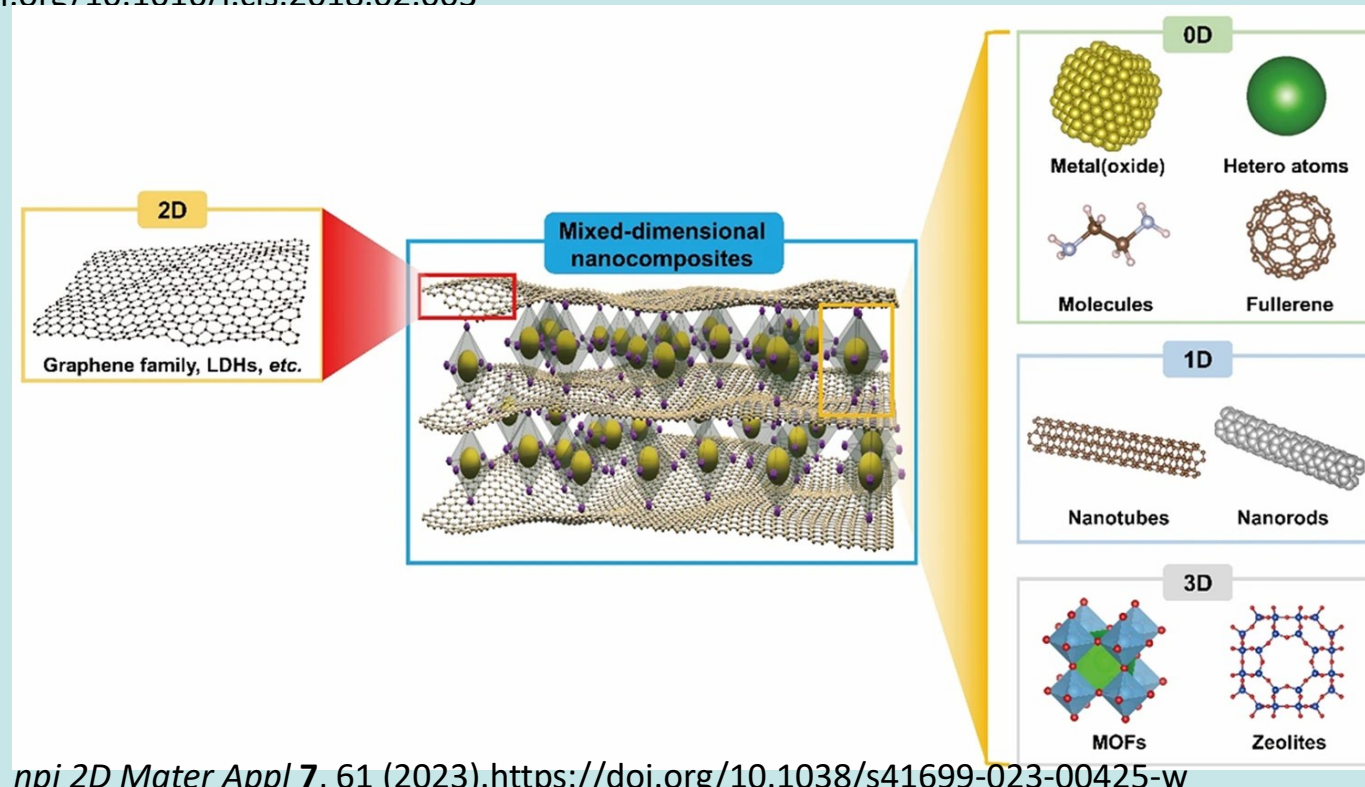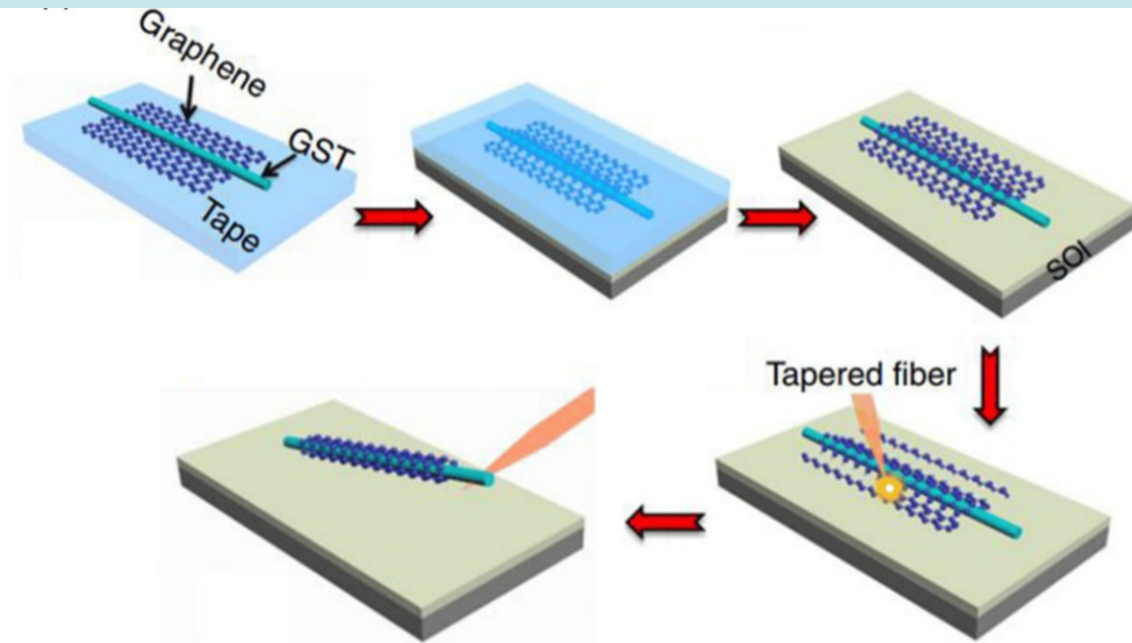

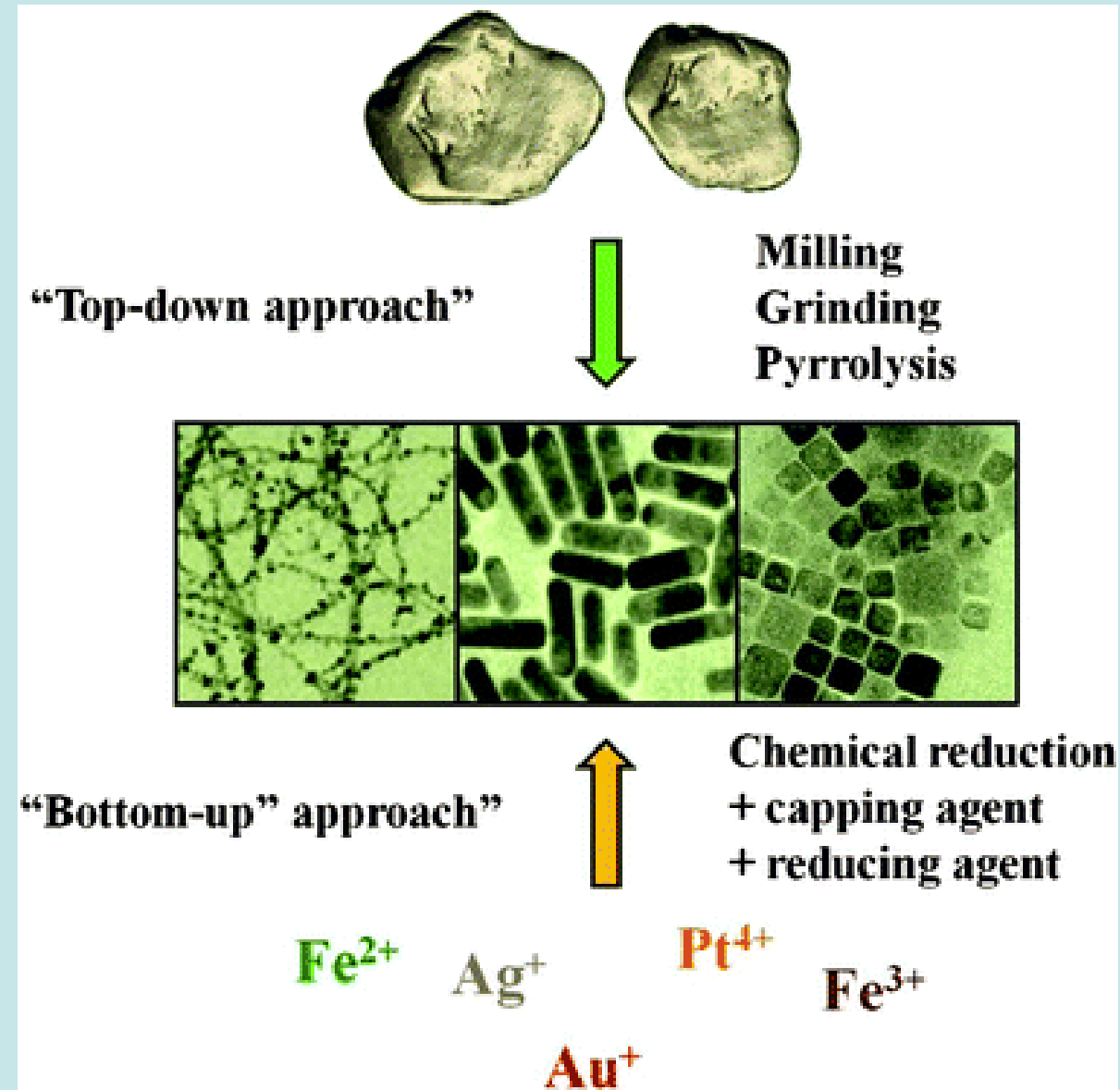J. Mater. Chem. C, 2015, **3**, 6109-6143

Interfaces

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Advances in Colloid and Interface Science, 256 (2018), 352-372, https://doi.org/10.1016/j.cis.2018.02.003

Cao, T. et al. Microsyst. Nanoeng. **2018**, 4, 7

npj 2D Mater Appl **7**, 61 (2023).https://doi.org/10.1038/s41699-023-00425-w

Synthesis

How to make a nanomaterial?

Two approaches

Top-Down Methods
1.Mechanical Milling/Ball Milling
2.Lithographic Techniques
3.Etching Processes

Bottom-Up Methods
1.Chemical Synthesis
2.Vapor Phase Methods
3.Biological and Biomimetic Approaches
4.Self-Assembly
5.Template-Directed Synthesis

Applications and challenges

Where are they used?

Practical uses of nanomaterials

Quantum Dots (QDs)	• Display technology • Biomedical imaging • Photovoltaics • Quantum computing • Single-photon sources
Nanowires	• Nanoelectronics • Sensors • Energy harvesting • Optoelectronics • Thermoelectrics
Nanoparticles	• Catalysis• Drug delivery • Antibacterial applications • Magnetic storage • Water purification
2D Materials	• Flexible electronics • Optoelectronics • Barrier materials • Energy storage • Sensing
Carbon Nanotubes	• Structural composites • Conductive additives • Field emission displays • Sensors • Hydrogen storage
Core-Shell Structures	• Catalysis • Controlled drug release • Multimodal imaging • Magnetic separation
Plasmonic Nanostructures	• Sensing • Photothermal therapy • Enhanced spectroscopy • Photocatalysis • Metamaterials

Environmental and health impacts
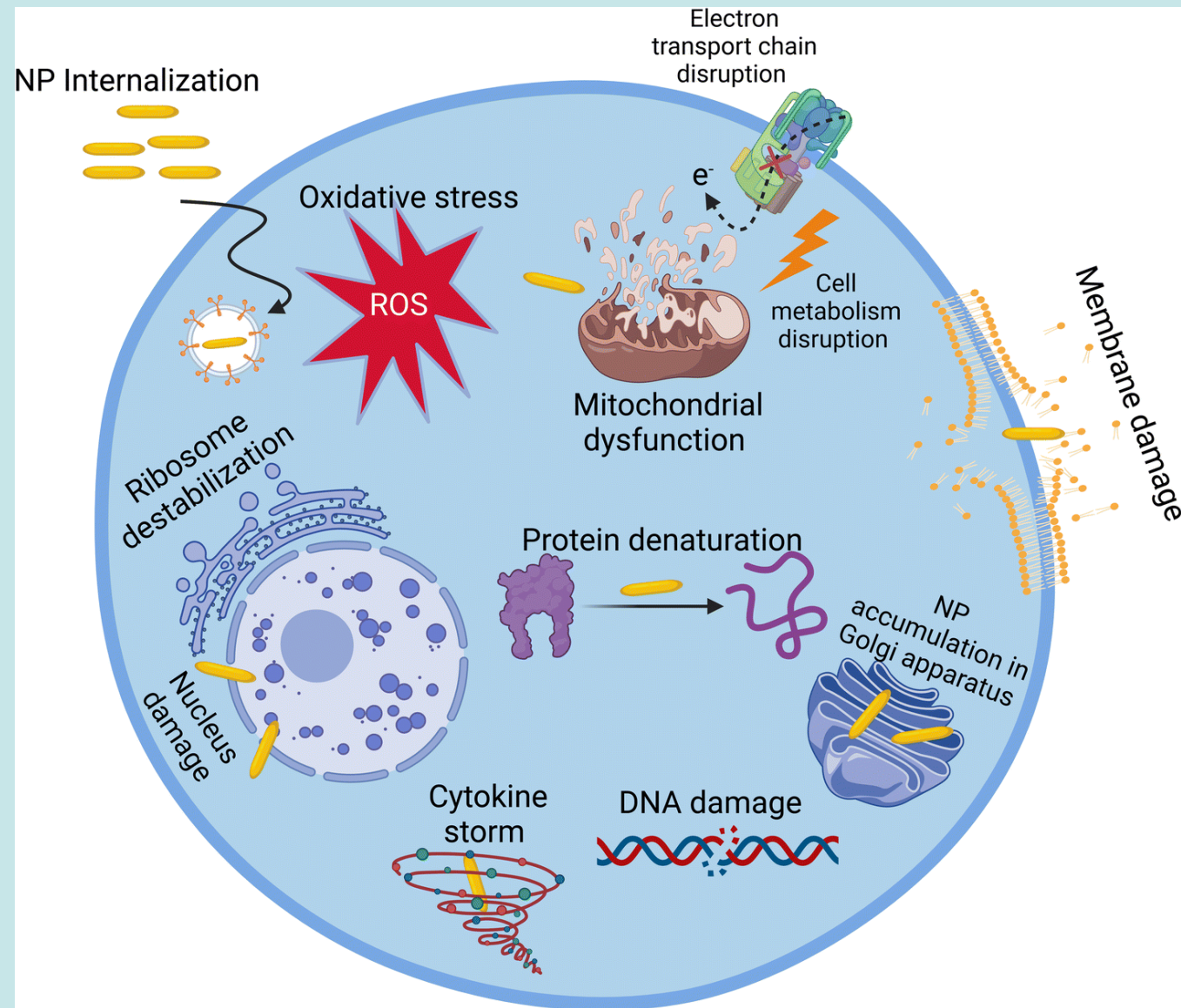
A serious threat:
- unique hazard profile
- potential bioaccumulation in food chains
- multiple exposure routes

Safe-by-Design approaches:
Surface functionalization to reduce toxicity
- Biodegradable nanomaterials
- Encapsulation strategies
- Life cycle assessment implementation

Future directions of research

- Sustainable and Green Nanomaterials

- Quantum Nanomaterials

- Biologically Interfaced Nanomaterials

- Energy Conversion and Storage

- Hierarchical Nanomaterials

- Extreme Environment Nanomaterials

Summary

- Quantum confinement in nanomaterials causes size-dependent properties

- Bandgaps increase as dimensions decrease

- Surface phenomena dominate at nanoscale due to high surface-to-volume ratio

- Environmental concerns arise from nanomaterials' unique hazard profiles

Next:

2D materials