Nanomaterials Characterization Techniques

Chapter 1
Introduction of Materials at the Nanoscale

Academic Calendar 2nd Semester 1400-1401

What Will We Learn From This Chapter?

01. **Origin and Historical Development**

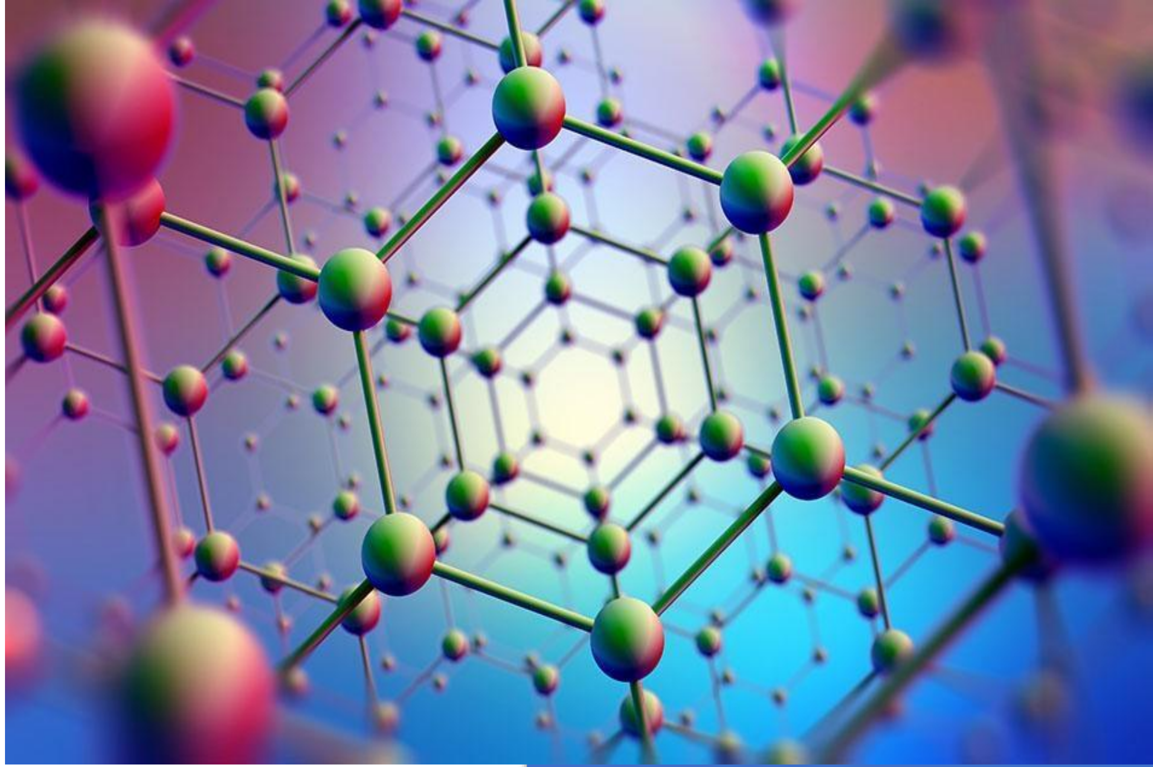
02. **Introduction to Nanomaterials**

03. **Quantum Confinement**

04. **Defects and Imperfections**

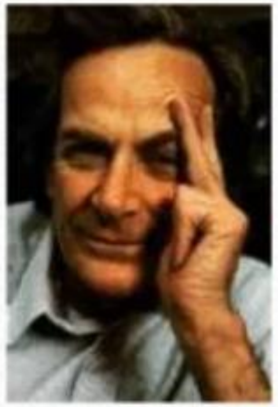
05. **Different Properties of Nanomaterials**

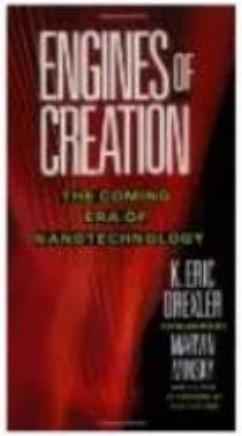
06. **Various Techniques of Nanomaterials Characterization**

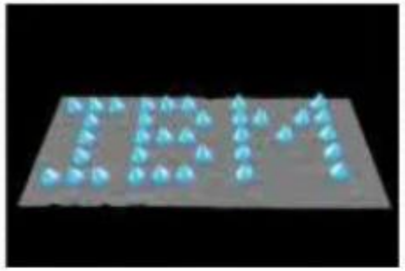


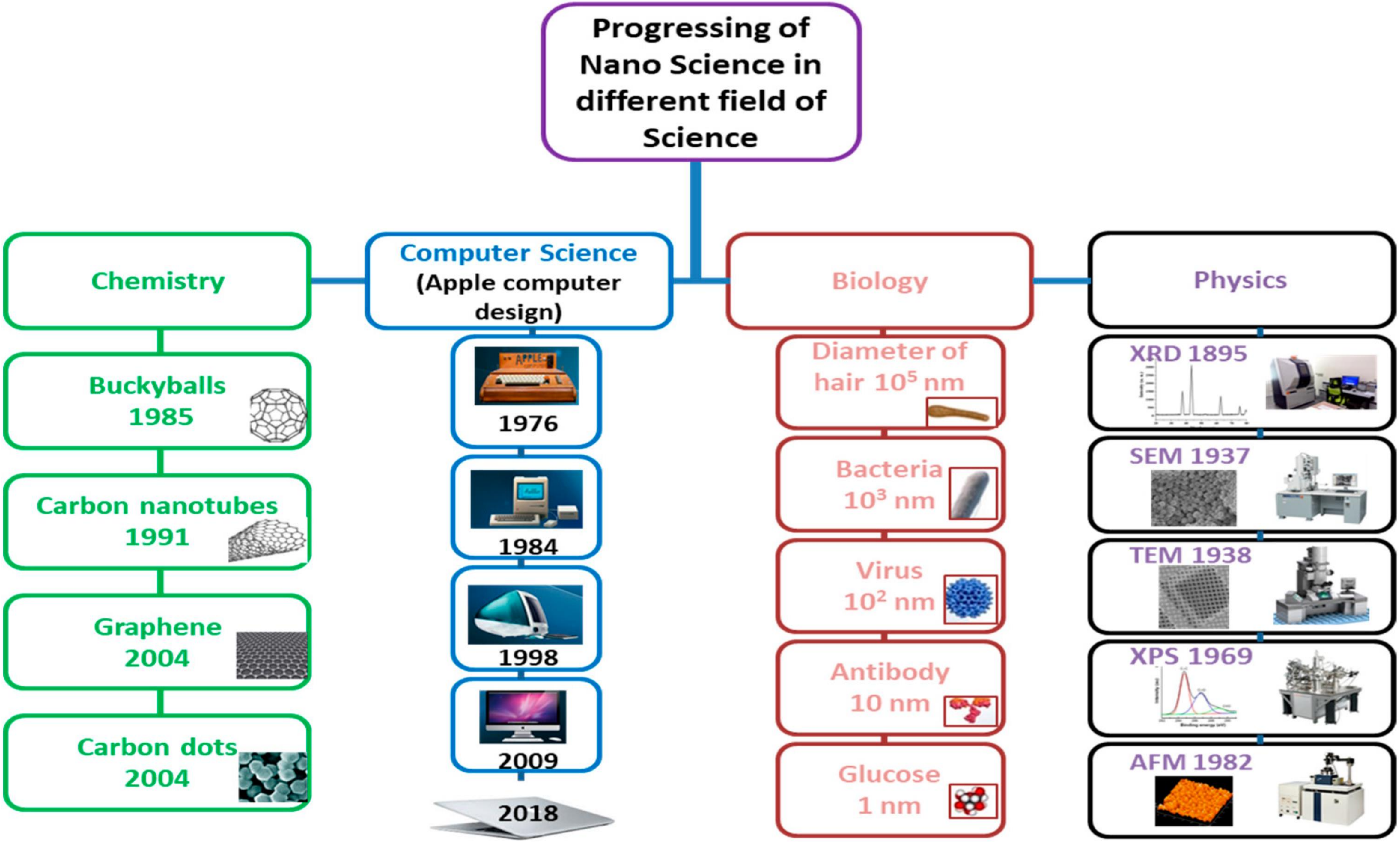
History of Nanotechnology

- **~ 2000 Years Ago** – Sulfide nanocrystals used by Greeks and Romans to dye hair
- **~ 1000 Years Ago (Middle Ages)** – Gold nanoparticles of different sizes used to produce different colors in stained glass windows
- **1959** – "There is plenty of room at the bottom" by R. Feynman
- **1974** – "Nanotechnology" - Norio Taniguchi uses the term nanotechnology for the first time
- **1981** – IBM develops Scanning Tunneling Microscope
- **1985** – "Buckyball" - Scientists at Rice University and University of Sussex discover C_{60}
- **1986** – "Engines of Creation" - First book on nanotechnology by K. Eric Drexler. Atomic Force Microscope invented by Binnig, Quate and Gerbe
- **1989** – IBM logo made with individual atoms
- **1991** – Carbon nanotube discovered by S. Iijima
- **1999** – "Nanomedicine" – 1st nanomedicine book by R. Freitas








Progressing of Nano Science in different field of Science
Chemistry
Buckyballs 1985
Carbon nanotubes 1991
Graphene 2004
Carbon dots 2004
Computer Science (Apple computer design)
1976
1984
1998
2009
2018
Biology
Diameter of hair 10⁵ nm
Bacteria 10³ nm
Virus 10² nm
Antibody 10 nm
Glucose 1 nm
Physics
XRD 1895
SEM 1937
TEM 1938
XPS 1969
AFM 1982

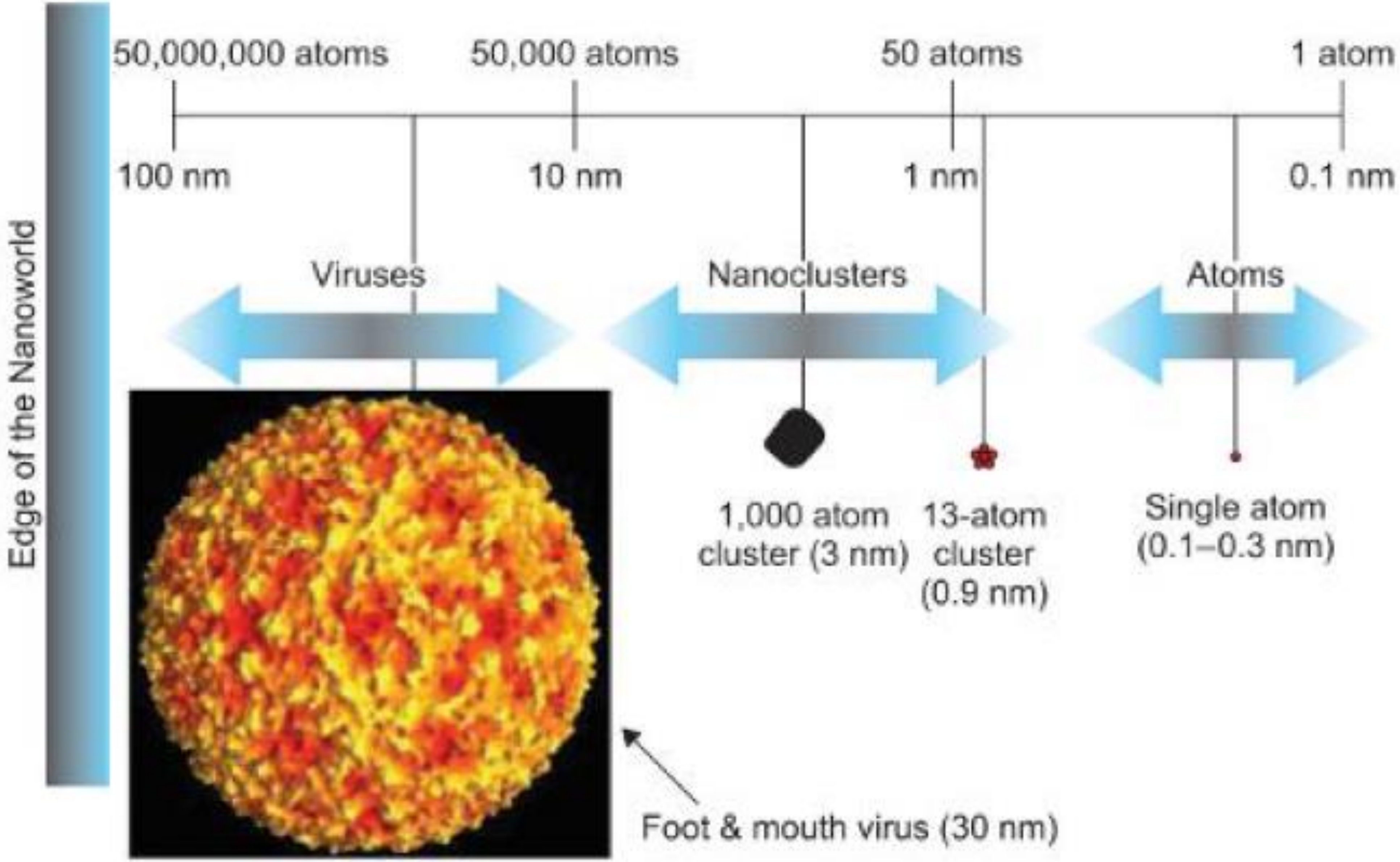
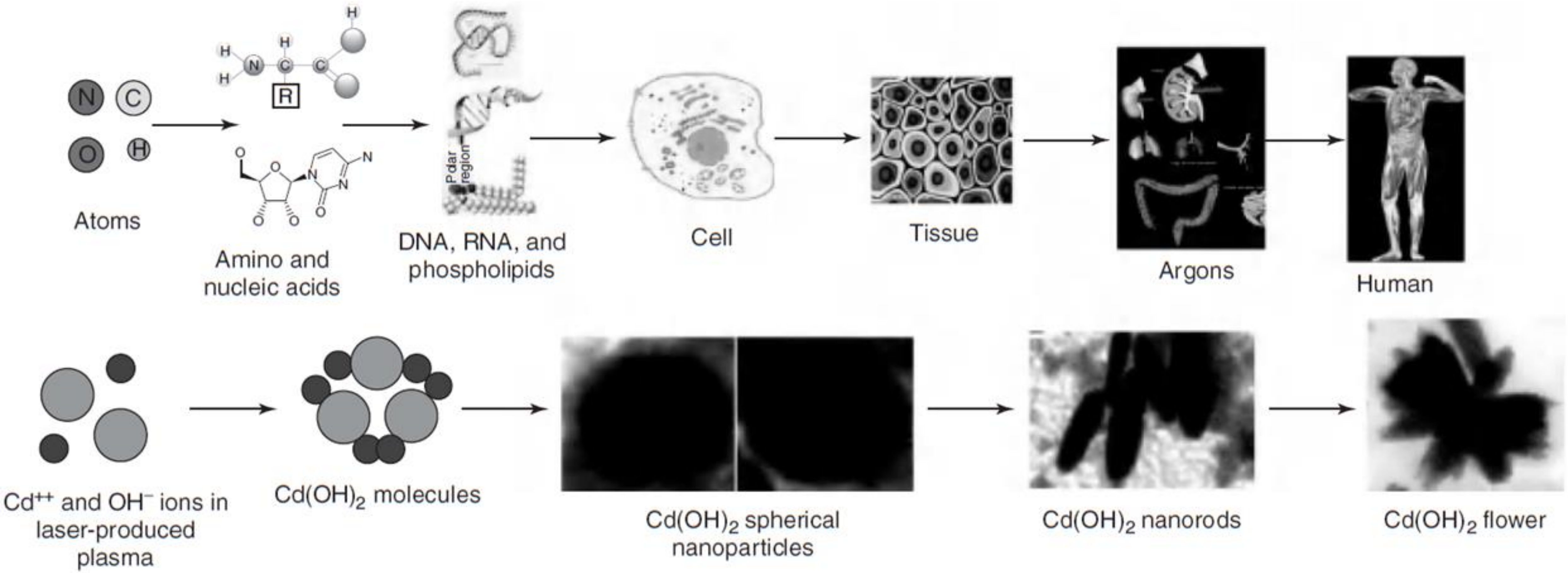


Fig. 0.1 The nanoworld. The size range of interest in nanotechnology and some representative objects.

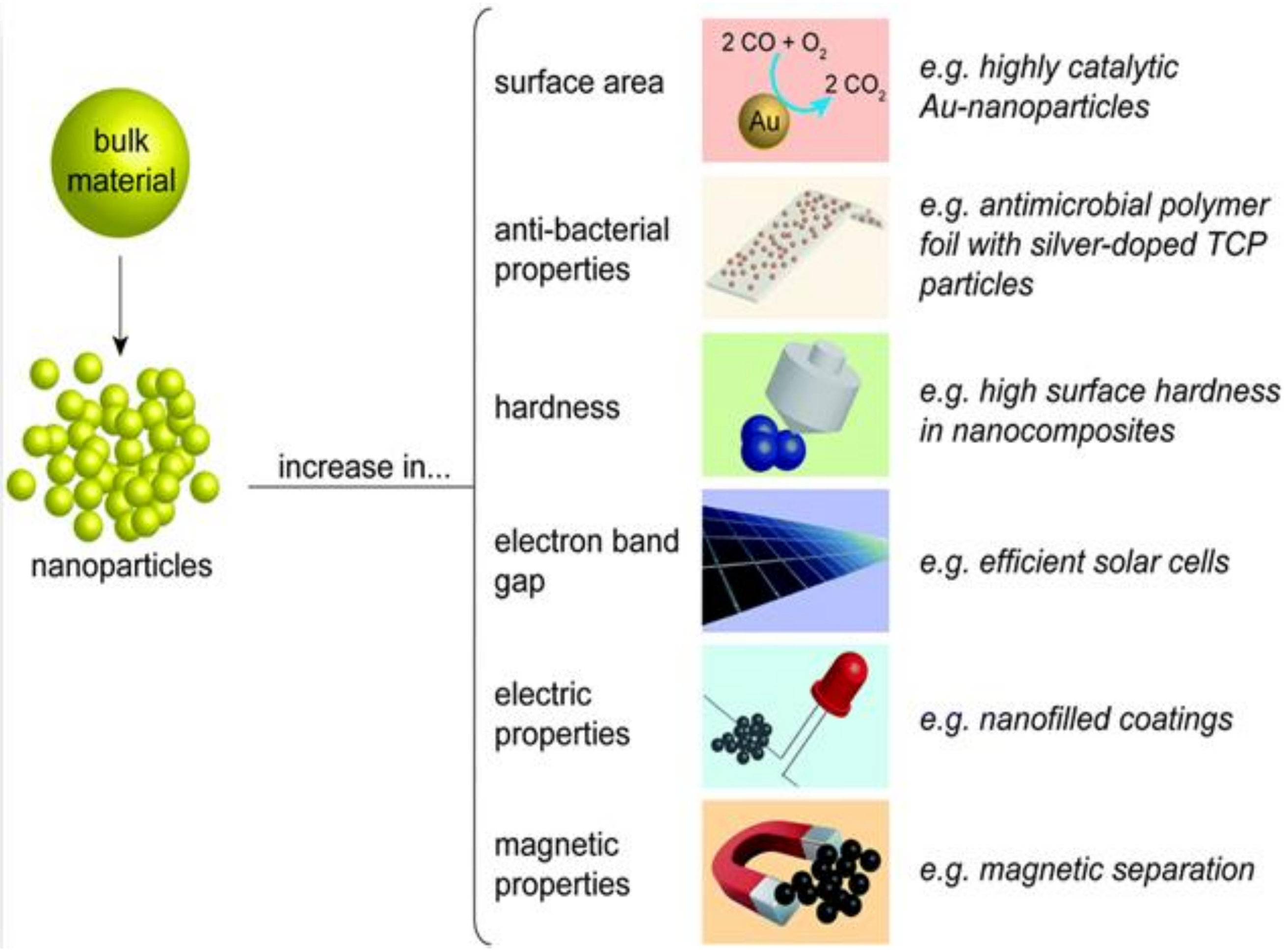


Nanoarchitectural evolution of cadmium oxide nanoflowers analogous to the evolution of human life from nonliving atoms.

Size- Dependent Properties

❖ **At the nanometer scale, properties become size-dependent; for example:**

1) Thermal Properties – melting temperature
2) Mechanical Properties – adhesion, capillary forces
3) Optical Properties – absorption and scattering of light
4) Electrical Properties – tunneling current
5) Magnetic Properties – superparamagnetic effect
6) Catalytic reactivity



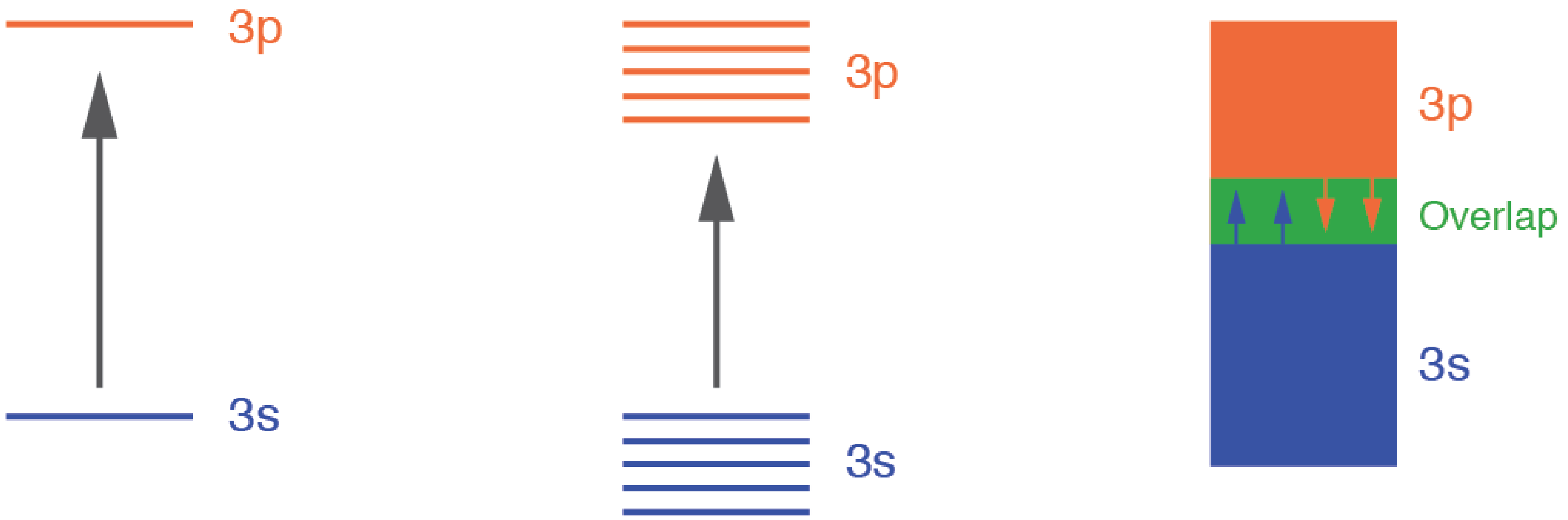
→ **New Properties Enable New Applications**

Band Theory in Solids

Significant leap required for an electron to move to the next higher level

Shorter leap required

Overlap permits electrons to freely drift between bands

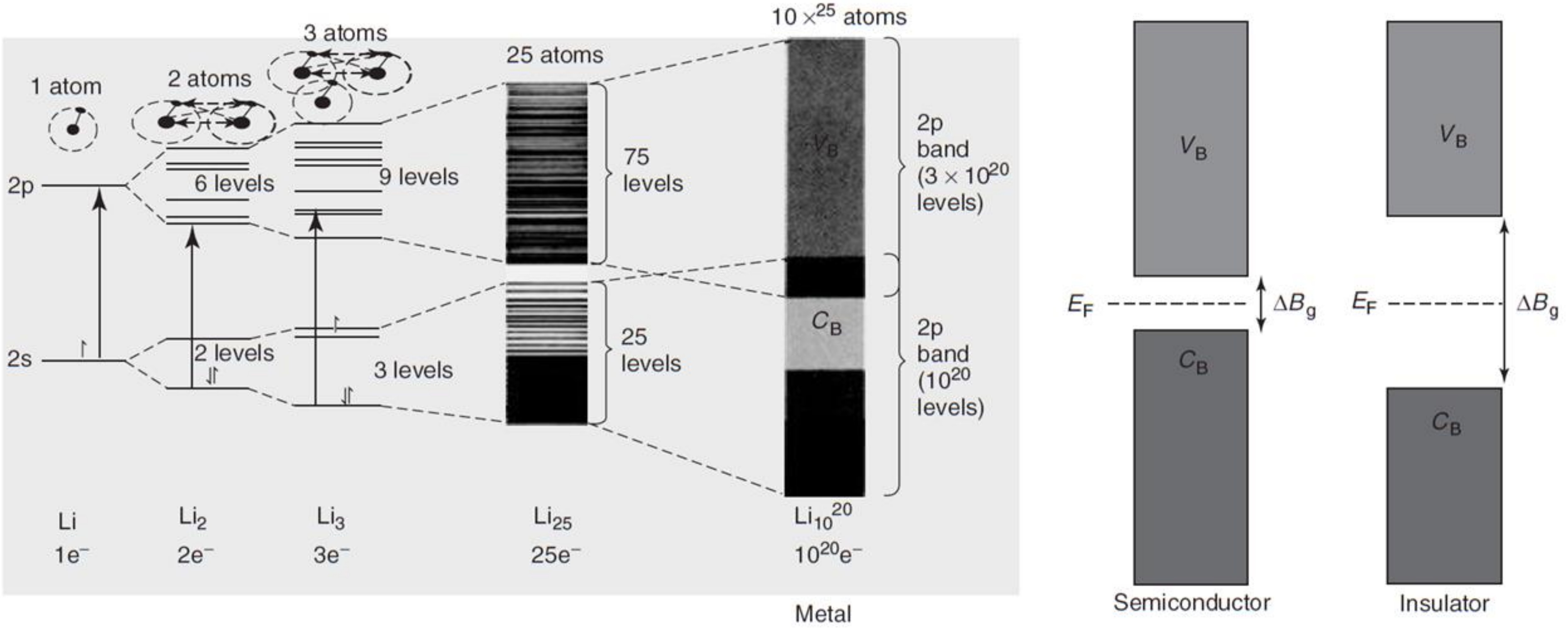


Single atom

Five atoms in close proximity

Multitudes of atoms in close proximity

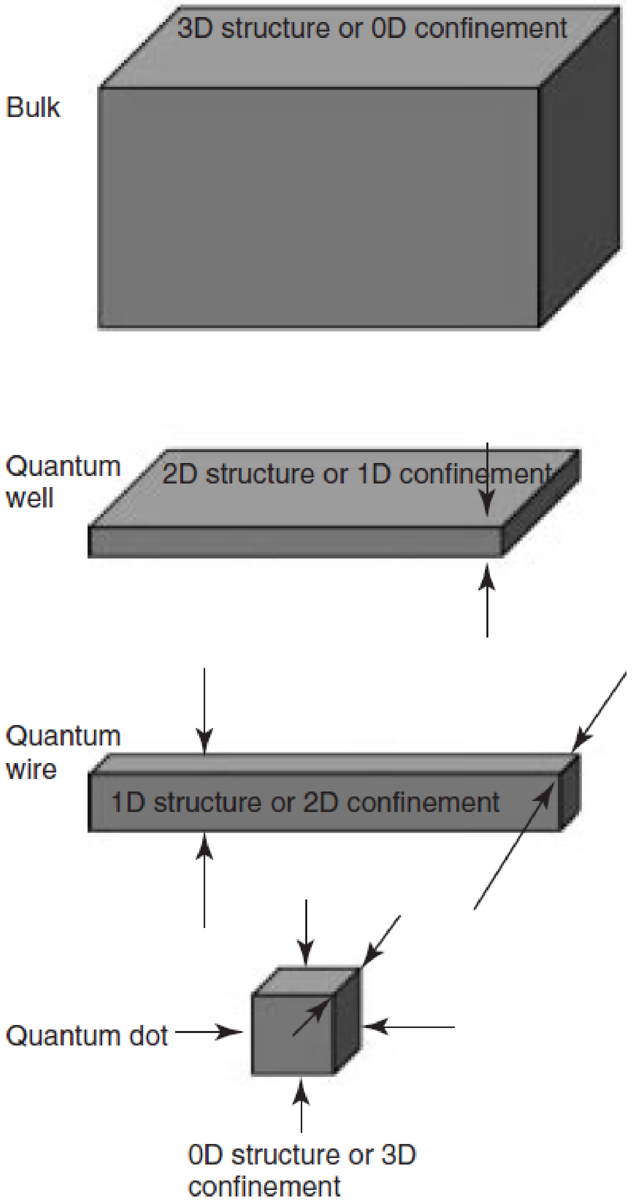
Band Theory in Solids



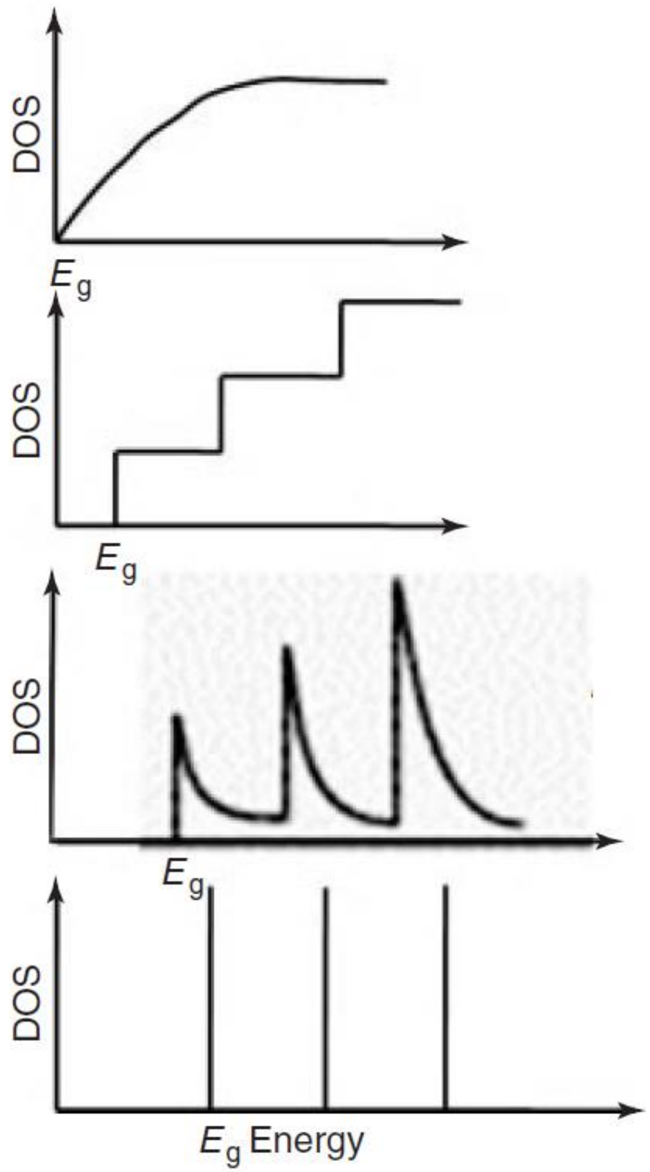
Evolution of bands of solids from discrete energy levels of individual atoms. Bands for metals, semiconductors, and insulators.

Quantum Confinement

Shape/size of nanostructures



Graphical representation of DOS



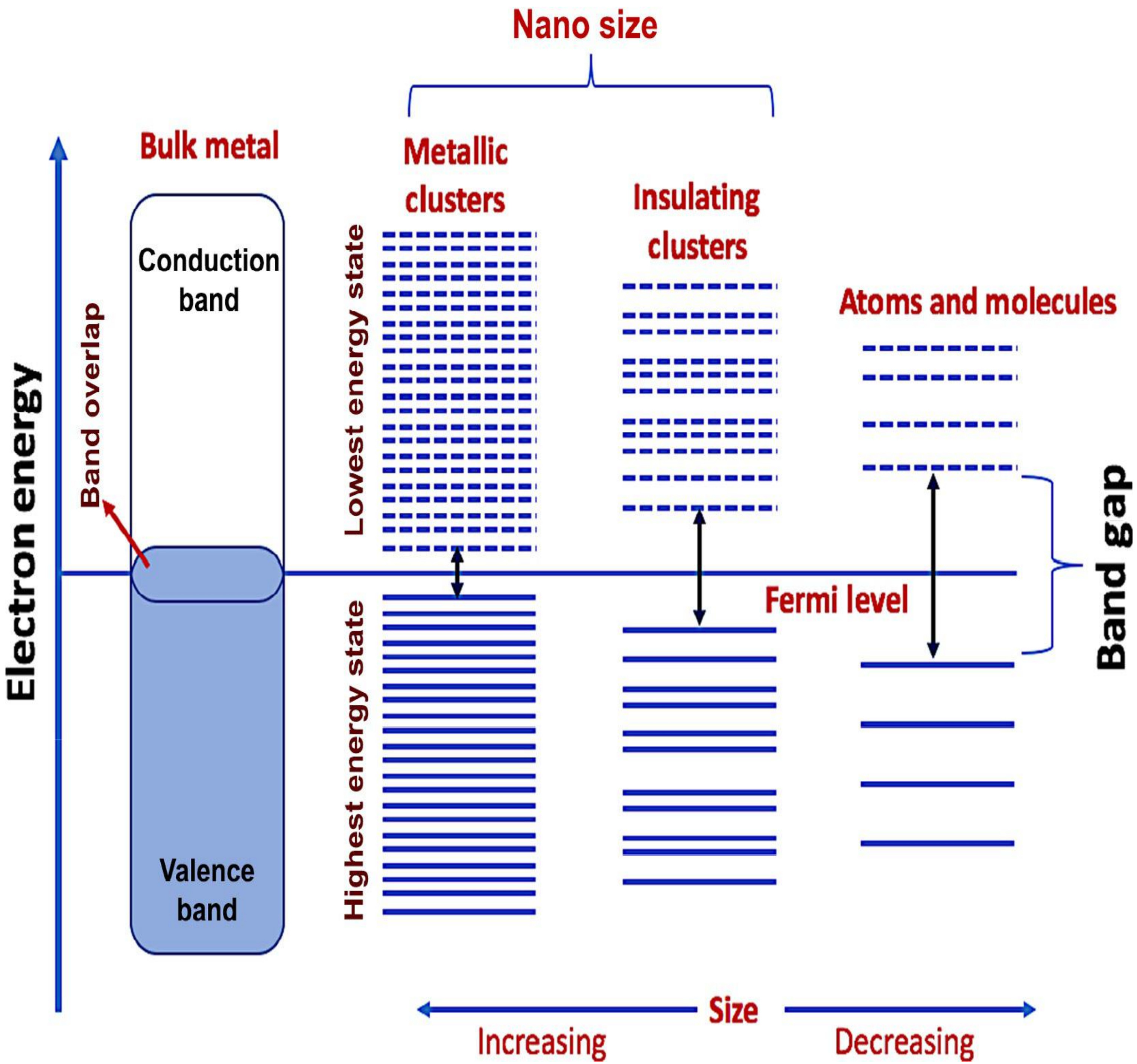
Expression for DOS

$$D\,(E)_{\text{bulk}} = \frac{8\pi\sqrt{2}}{h^3} m^{+3/2}\sqrt{E - E_C}$$

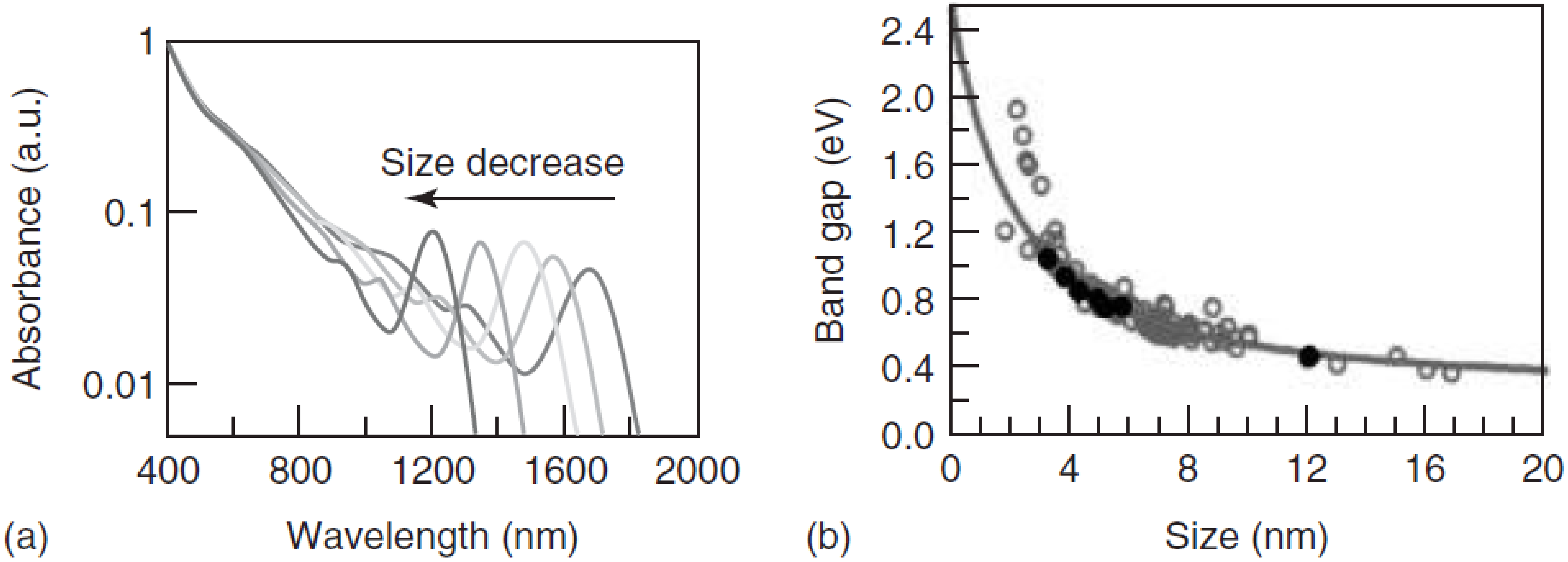
$$D\,(E)_{\text{2D}} = \frac{4\pi m^{+}}{h^2}$$

$$D\,(E)_{\text{bulk}} = \sqrt{\frac{2\pi m^{+}}{h^2}}\,\frac{1}{\sqrt{E - E_C}}$$

$$D\,(E)_{\text{0D}} = \sum_n 2\delta(E - E_n)$$

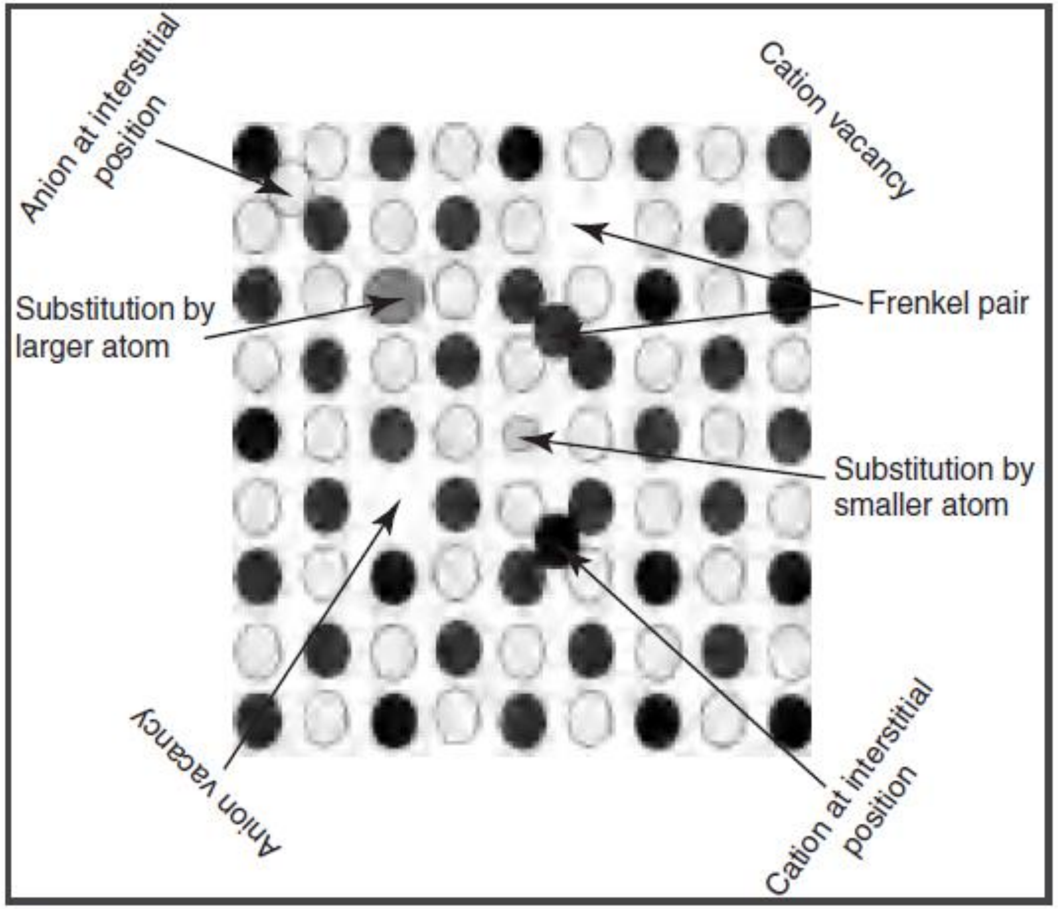

Nano size
Bulk metal
Metallic clusters
Insulating clusters
Atoms and molecules
Conduction band
Valence band
Band overlap
Electron energy
Lowest energy state
Highest energy state
Fermi level
Band gap
Size
Increasing
Decreasing

Quantum Confinement

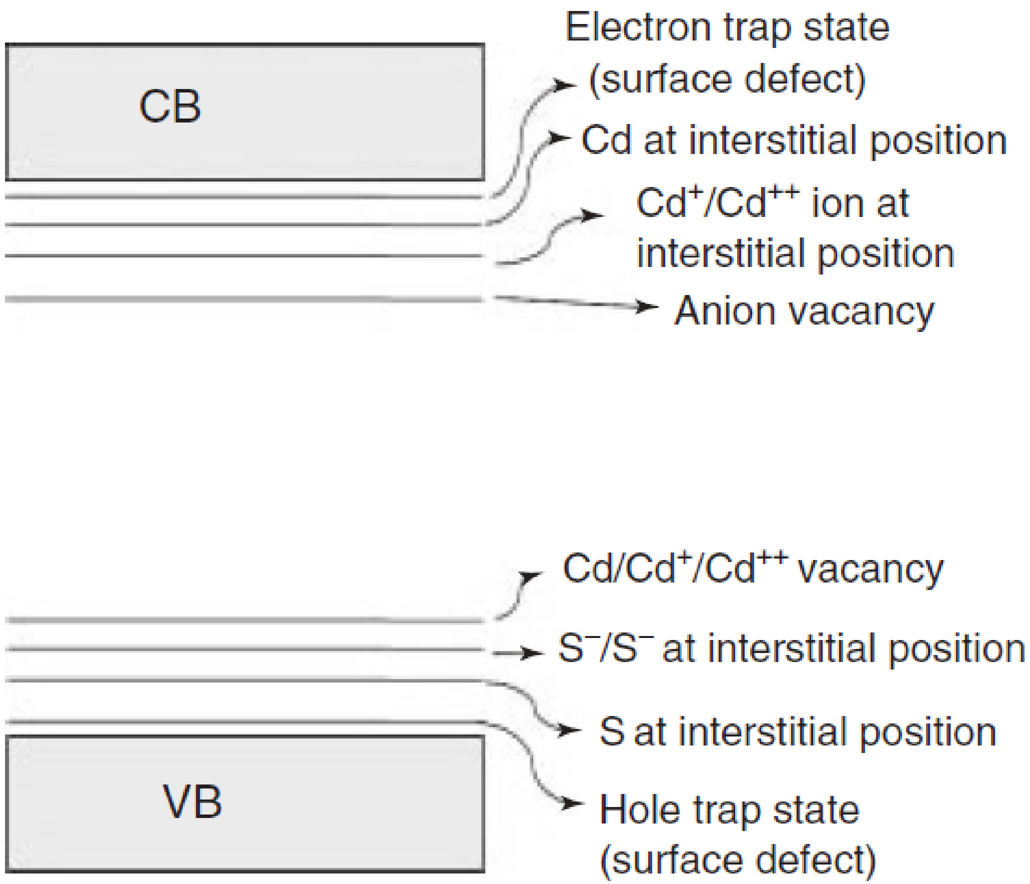


Variation in (a) SPR absorption peak position and (b) band gap energy of PbSe QDs with size.

Defects and Imperfections

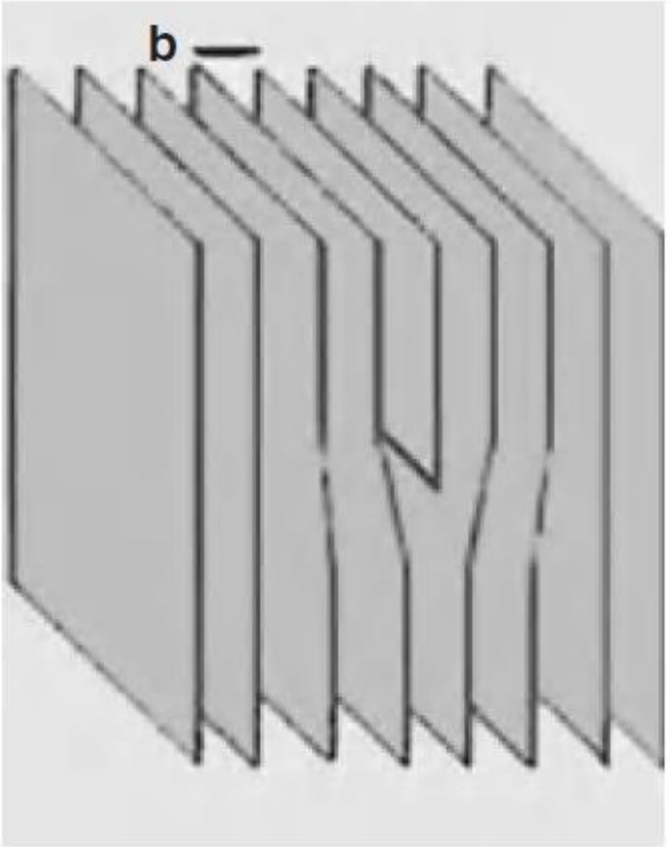


(a)

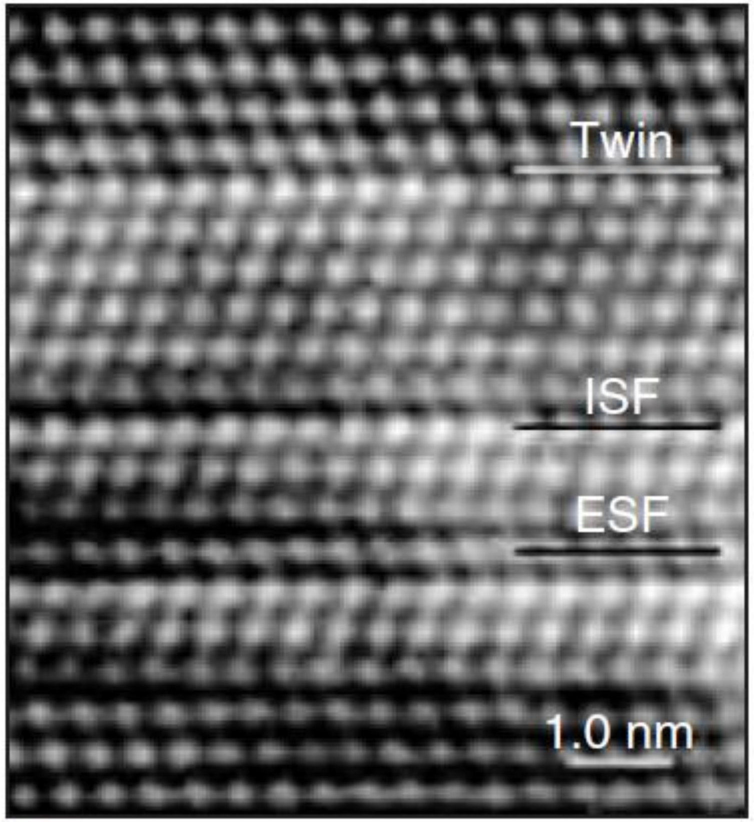


(b)

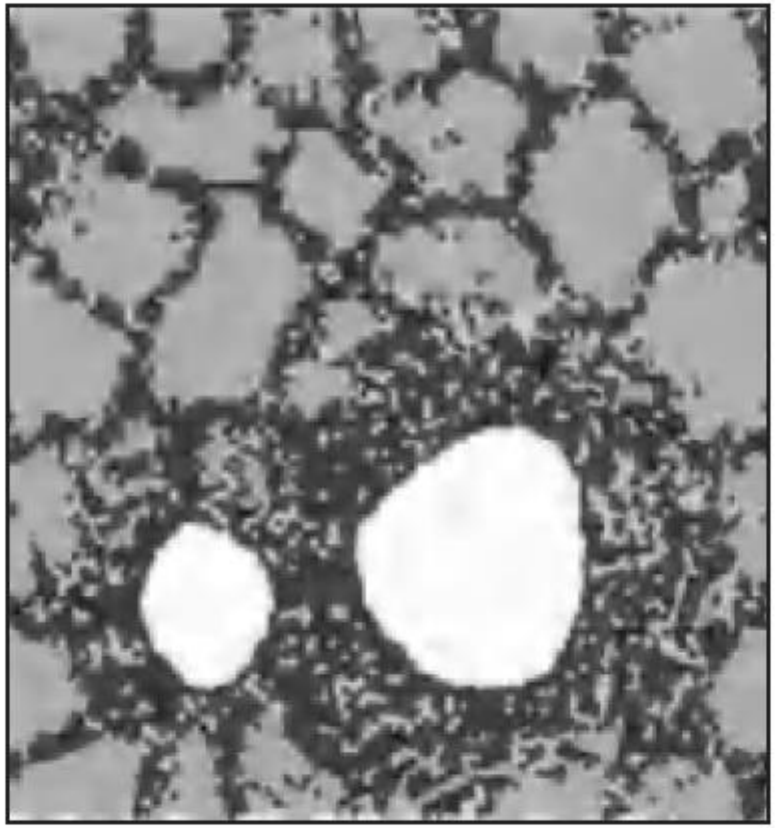
Defects and Imperfections



(c)

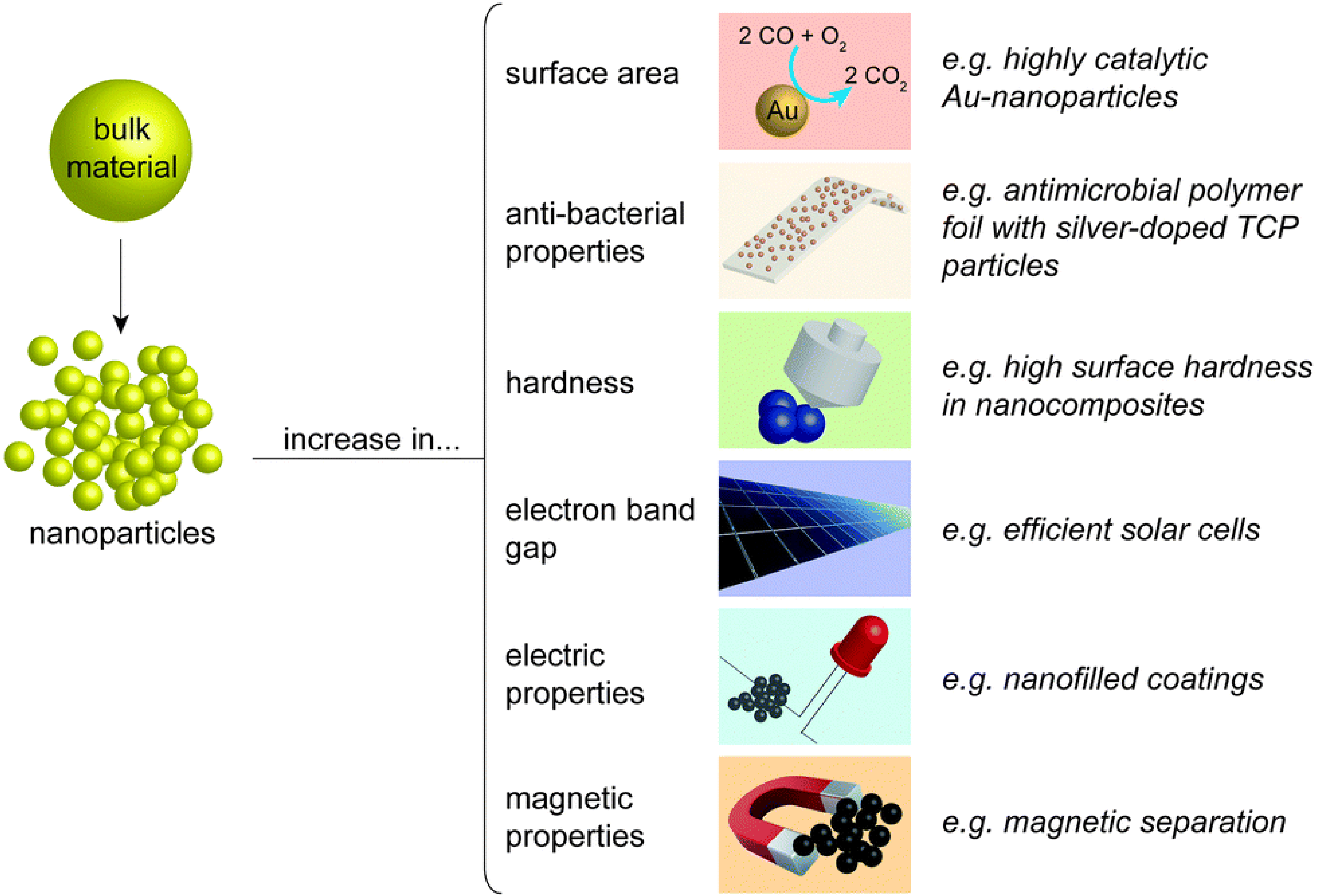


(d)



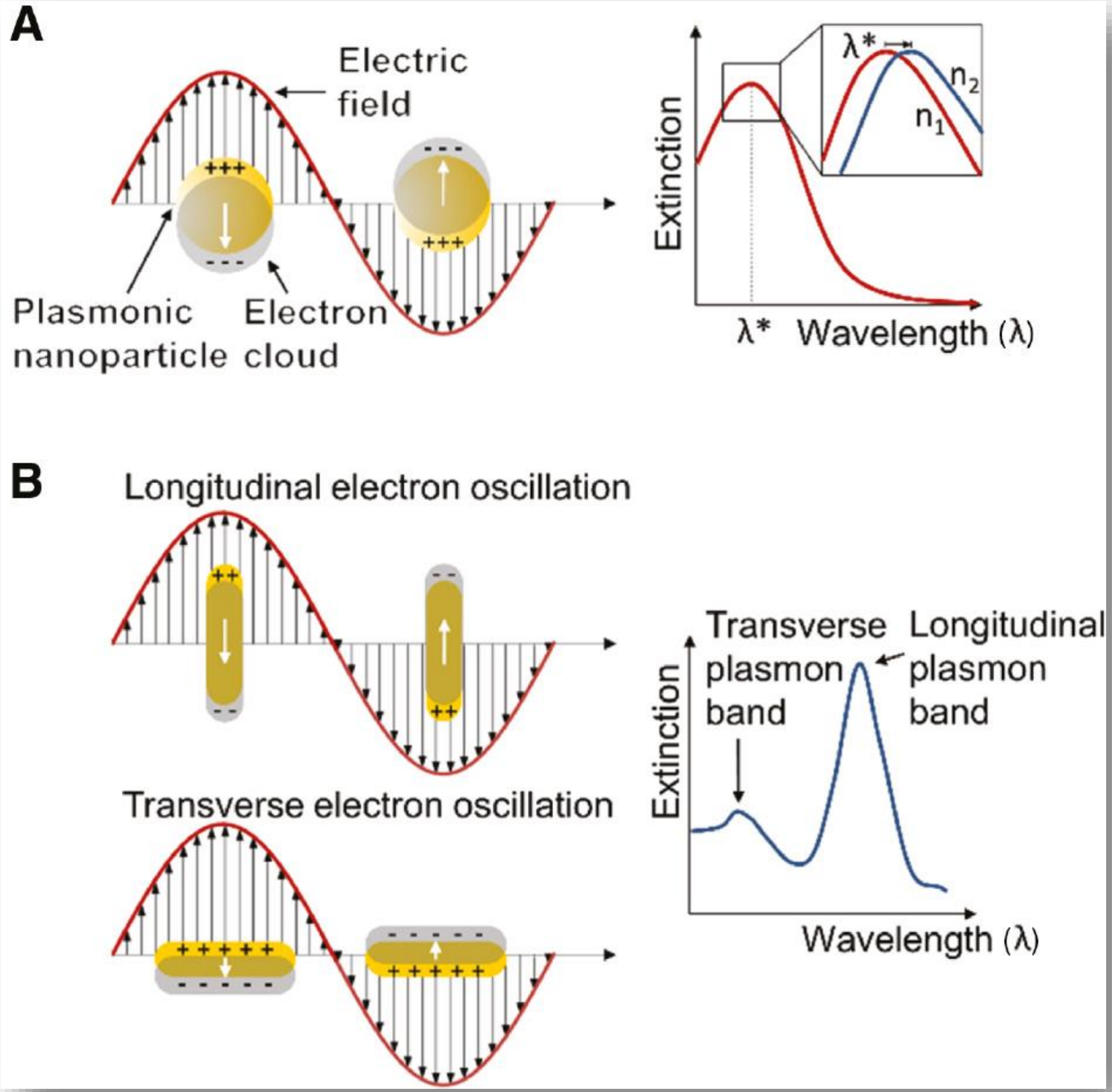
(e)

Nanomaterials Properties and Applications



Physical Properties	Chemical Properties
• Size and size distribution • Shape and specific surface area • Agglomeration/ aggregation • Surface modifications and topography • Crystalline structure • Solubility	• Chemical composition and concentration • Surface chemistry • Zeta potential/surface charge • Reactivity (photocatalytic activity, radical formation potential, redox potential) • Hydrophilicity/hydrophobicity

Nanomaterials Properties



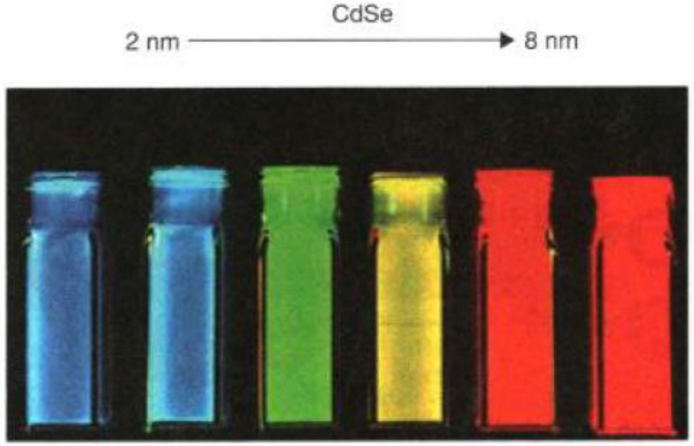


Fig. 5.7 Fluorescence from CdSe quantum dots of different sizes. Change in wavelength of fluorescence as a function of size from CdSe quantum dots excited with UV light. Note how the wavelength is reduced (bluer emission) as the size of the quantum dot is reduced. Reproduced with permission from Prof. Bawendi, Department of Chemistry, MIT.

Nanomaterials Properties

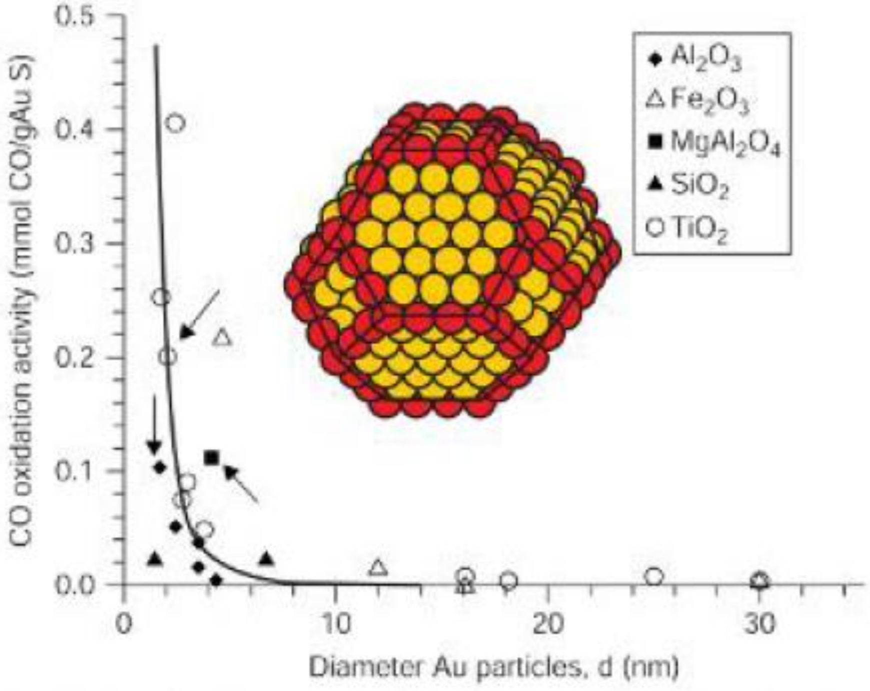
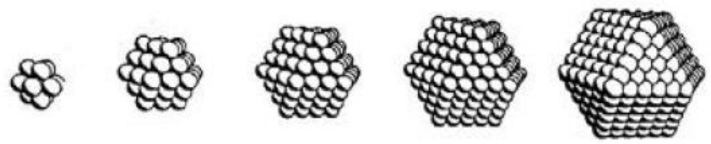


Fig. 1.13 Reactivity of gold nanoparticles. Measured activities of gold nanoparticles on various supports (box) for carbon monoxide oxidation as a function of particle size. The black line is a fit using a $1/d^3$ law and is seen to broadly represent the variation indicating that the dominant effect size effect is the proportion of gold atoms that are at a corner between facets at the surface (see text). Such atoms are highlighted in red on the nanoparticle shown. Reproduced with the permission of Elsevier Science from N. Lopez et al. [16].

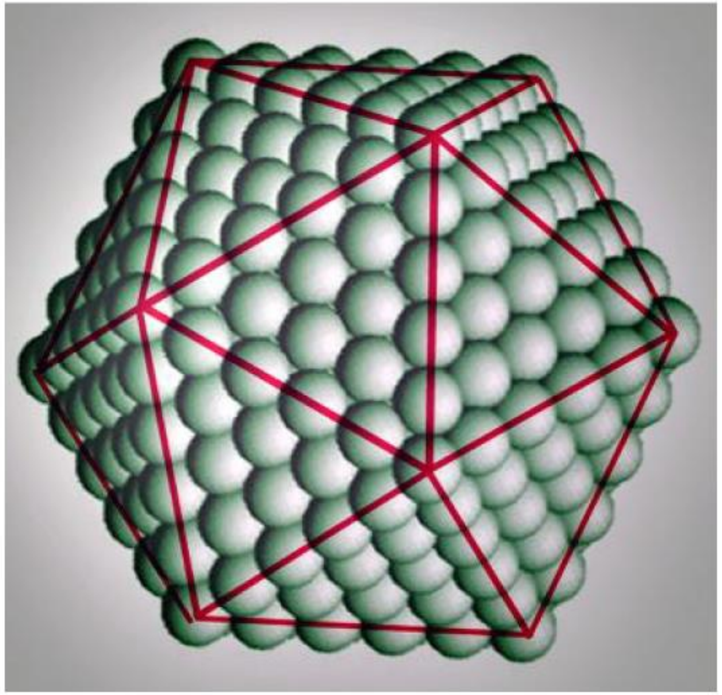
(Number of atoms in shell n)=$10n^2+2$

3.3nm

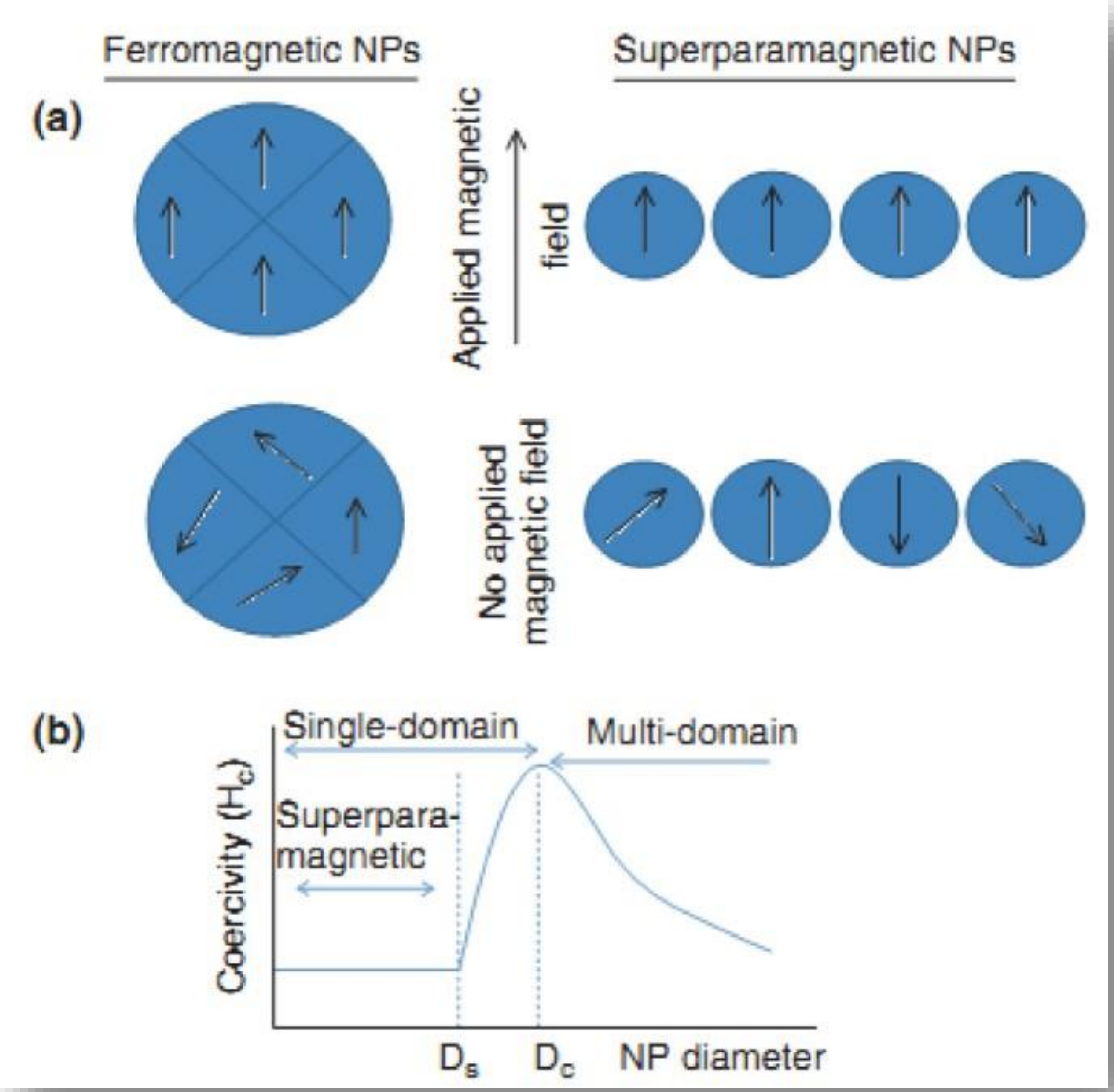
Full-Shell "Magic Number" Clusters

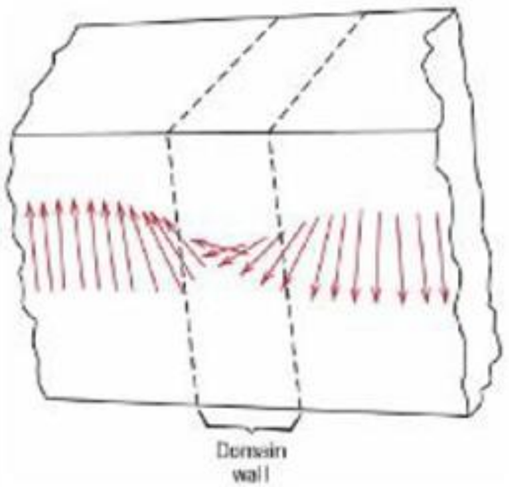


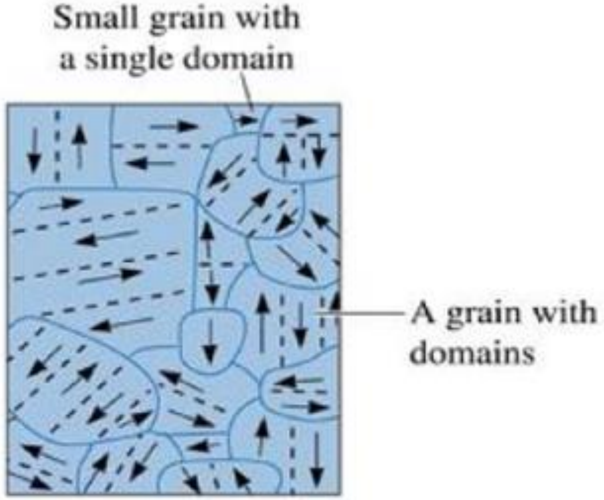
Number of shells	1	2	3	4	5
Number of atoms in cluster	M_{13}	M_{55}	M_{147}	M_{309}	M_{561}
Percentage surface atoms	92%	76%	63%	52%	45%



Nanomaterials Properties







The gradual change in magnetic dipole orientation across a domain wall

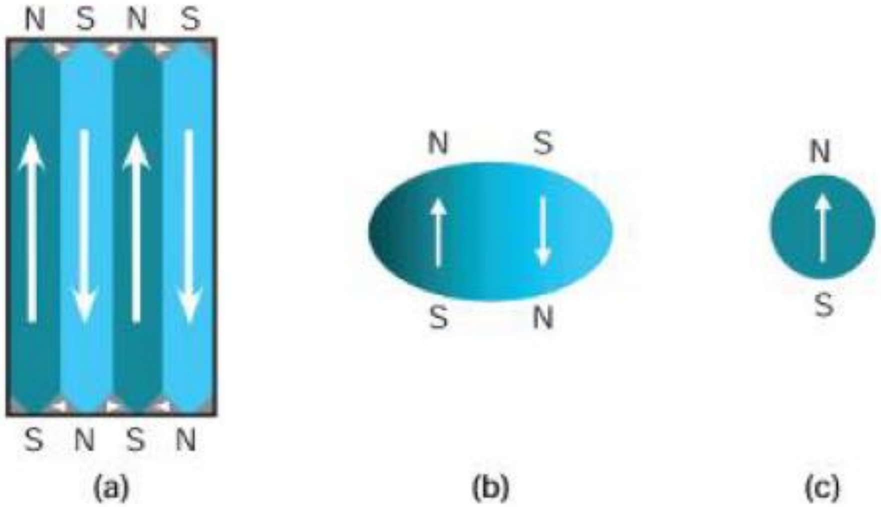
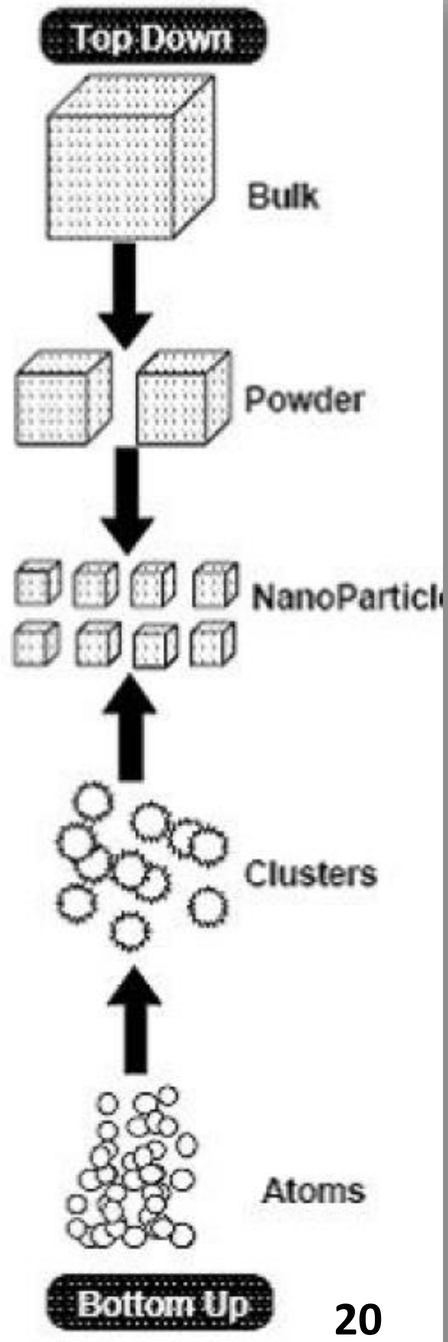


Fig. 1.4 Single-domain particles. Domain formation in iron to minimize energy. Below a critical size (approx. 100 nm), the energy balance favors just a single domain and the piece of iron stays permanently and fully magnetized.

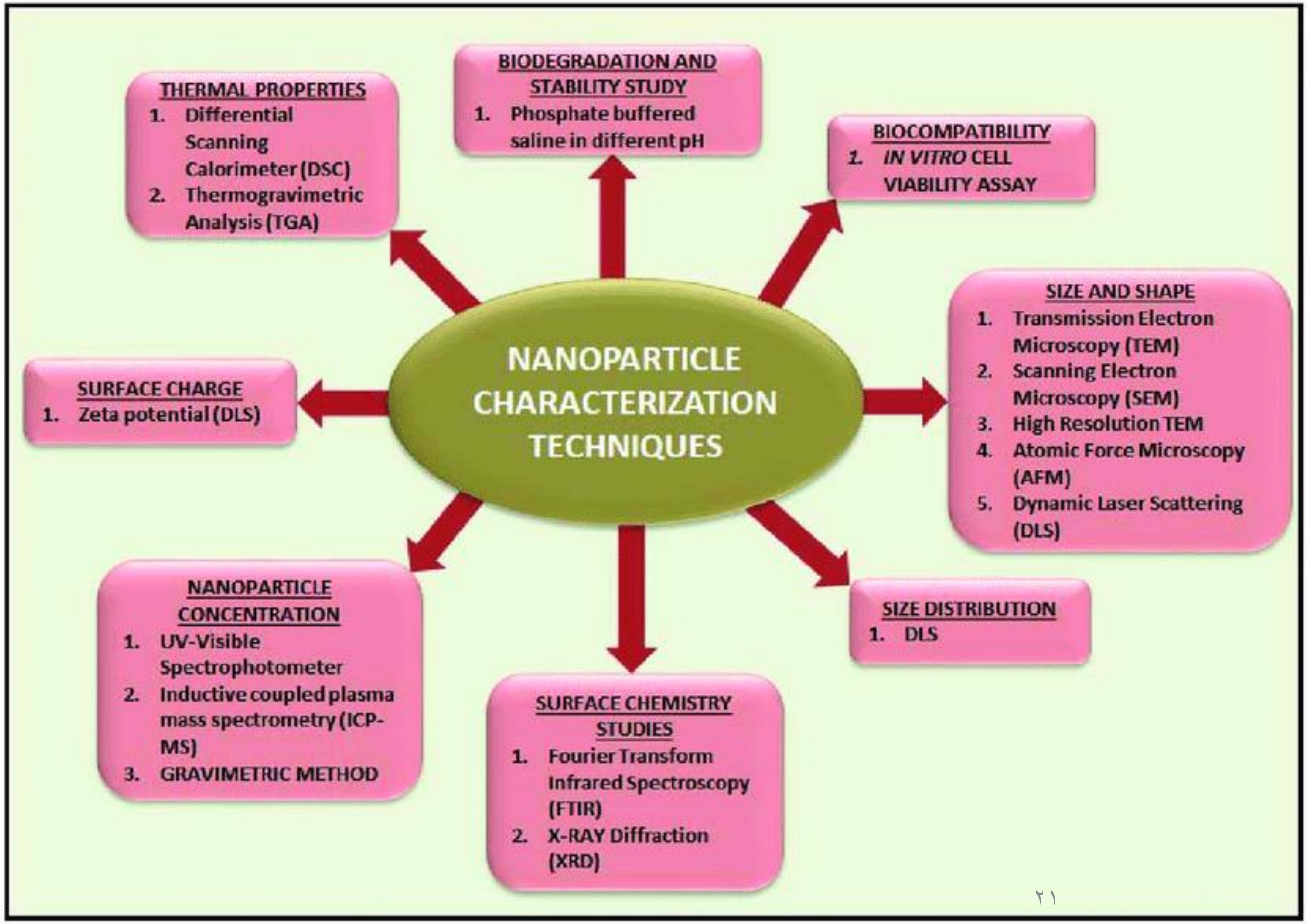
Various Synthesis Methods of Nanoscale Materials

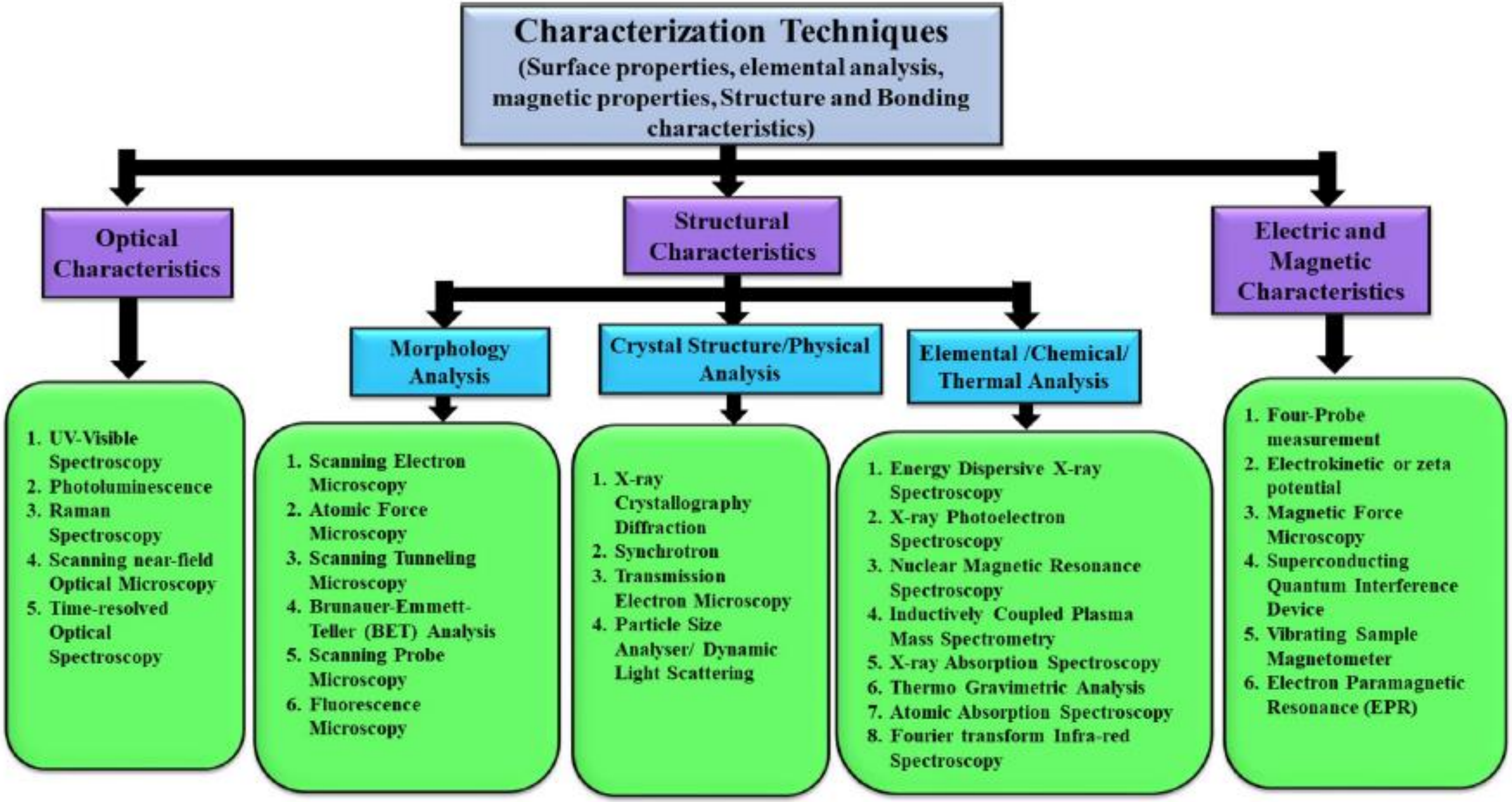
Nano Material Synthesis Methods

- **Top-Down Method**
  - **Physical Methods**
    1. Mechanical Method – Attrition Ball Milling
    2. Physical Vapour Deposition
    3. Lithography
    4. Pyrolysis – Thermal Evaporation
- **Bottom-Up Method**
  - **Chemical Methods**
    1. Sol-Gel
    2. Chemical Vapour Deposition
    3. Co-Precipitation
    4. Micro Emulsions
    5. Hydrothermal
    6. Sonochemical
    7. Microwave
  - **Biological Methods**
    1. Using Plant Extracts
    2. Using Enzymes
    3. Using Agricultural Wastes
    4. Using Algae, Bacterial, Fungus, Yeasts &Actinomycetes



Various Techniques of Nanomaterials Characterization




Characterization Techniques
(Surface properties, elemental analysis, magnetic properties, Structure and Bonding characteristics)
Optical Characteristics
Structural Characteristics
Electric and Magnetic Characteristics
Morphology Analysis
Crystal Structure/Physical Analysis
Elemental /Chemical/ Thermal Analysis
1. UV-Visible Spectroscopy
2. Photoluminescence
3. Raman Spectroscopy
4. Scanning near-field Optical Microscopy
5. Time-resolved Optical Spectroscopy
1. Scanning Electron Microscopy
2. Atomic Force Microscopy
3. Scanning Tunneling Microscopy
4. Brunauer-Emmett-Teller (BET) Analysis
5. Scanning Probe Microscopy
6. Fluorescence Microscopy
1. X-ray Crystallography Diffraction
2. Synchrotron
3. Transmission Electron Microscopy
4. Particle Size Analyser/ Dynamic Light Scattering
1. Energy Dispersive X-ray Spectroscopy
2. X-ray Photoelectron Spectroscopy
3. Nuclear Magnetic Resonance Spectroscopy
4. Inductively Coupled Plasma Mass Spectrometry
5. X-ray Absorption Spectroscopy
6. Thermo Gravimetric Analysis
7. Atomic Absorption Spectroscopy
8. Fourier transform Infra-red Spectroscopy
1. Four-Probe measurement
2. Electrokinetic or zeta potential
3. Magnetic Force Microscopy
4. Superconducting Quantum Interference Device
5. Vibrating Sample Magnetometer
6. Electron Paramagnetic Resonance (EPR)

Experimental Techniques for Nanoparticle Characterization

Technique	Main information derived	Section
XRD (group: X-ray based techniques)	Crystal structure, composition, crystalline grain size	1
XAS (EXAFS, XANES)	X-ray absorption coefficient (element-specific) – chemical state of species, interatomic distances, Debye–Waller factors, also for non-crystalline NPs	1
SAXS	Particle size, size distribution, growth kinetics	1
XPS	Electronic structure, elemental composition, oxidation states, ligand binding (surface-sensitive)	1

Technique	Main information derived	Section
FTIR (group: further techniques for structure/composition/main properties)	Surface composition, ligand binding	2
NMR (all types)	Ligand density and arrangement, electronic core structure, atomic composition, influence of ligands on NP shape, NP size	2
BET	Surface area	2
TGA	Mass and composition of stabilizers	2
LEIS	Thickness and chemical composition of self-assembled monolayers of NPs	2
UV-Vis	Optical properties, size, concentration, agglomeration state, hints on NP shape	2

Technique	Main information derived	Section
PL spectroscopy	Optical properties – relation to structure features such as defects, size, composition	2
DLS	Hydrodynamic size, detection of agglomerates	2
NTA	NP size and size distribution	2
DCS	NP size and size distribution	2
ICP-MS	Elemental composition, size, size distribution, NP concentration	2
SIMS, ToF-SIMS, MALDI	Chemical information (surface-sensitive) on functional group, molecular orientation and conformation, surface topography, MALDI for NP size	2
RMM-MEMS, ζ-potential, pH, EPM, GPC, DSC, etc.	Please check the relevant parts of the manuscript	2

Technique	Main information derived	Section
SQUID-nanoSQUID (group: magnetic nanomaterials)	Magnetization saturation, magnetization remanence, blocking temperature	**3**
VSM	Similar to SQUID through M–H plots and ZFC-FC curves	3
Mössbauer	Oxidation state, symmetry, surface spins, magnetic ordering of Fe atoms, magnetic anisotropy energy, thermal unblocking, distinguish between iron oxides	3
FMR	NP size, size distribution, shape, crystallographic imperfection, surface composition, M values, magnetic anisotropic constant, demagnetization field	3

Technique	Main information derived	Section
XMCD	Site symmetry and magnetic moments of transition metal ions in ferro- and ferri-magnetic materials, element specific	3
Magnetic susceptibility, magnetophoretic mobility	Please check the relevant parts of the manuscript	3
Superparamagnetic relaxometry	Core properties, hydrodynamic size distribution, detect and localize superparamagnetic NPs	3

Technique	Main information derived	Section
TEM (group: microscopy techniques)	NP size, size monodispersity, shape, aggregation state, detect and localize/quantify NPs in matrices, study growth kinetics	**4**
HRTEM	All information by conventional TEM but also on the crystal structure of single particles. Distinguish monocrystalline, polycrystalline and amorphous NPs. Study defects	4
Liquid TEM	Depict NP growth in real time, study growth mechanism, single particle motion, superlattice formation	4
Cryo-TEM	Study complex growth mechanisms, aggregation pathways, good for molecular biology and colloid chemistry to avoid the presence of artefacts or destroyed samples	4

Technique	Main information derived	Section
Electron diffraction	Crystal structure, lattice parameters, study order–disorder transformation, long-range order parameters	**4**
STEM	Combined with HAADF, EDX for morphology study, crystal structure, elemental composition. Study the atomic structure of hetero-interfaces	4
Aberration-corrected (STEM, TEM)	Atomic structure of NP clusters, especially bimetallic ones, as a function of composition, alloy homogeneity, phase segregation	4
EELS (EELS-STEM)	Type and quantity of atoms present, chemical state of atoms, collective interactions of atoms with neighbors, bulk plasmon resonance	4
Electron tomography	Realistic 3D particle visualization, snapshots, video, quantitative information down to the atomic scale	4

Technique	Main information derived	Section
SEM-HRSEM, T-SEM-EDX	Morphology, dispersion of NPs in cells and other matrices/supports, precision in lateral dimensions of NPs, quick examination–elemental composition	**4**
EBSD	Structure, crystal orientation and phase of materials in SEM. Examine microstructures, reveal texture, defects, grain morphology, deformation	4
AFM	NP size and shape in 3D mode, evaluate degree of covering of a surface with NP morphology, dispersion of NPs in cells and other matrices/supports, precision in lateral dimensions of NPs, quick examination–elemental composition	4
MFM	Standard AFM imaging together with the information of magnetic moments of single NPs. Study magnetic NPs in the interior of cells. Discriminate from non-magnetic NPs	4

Parameters needed to be determined and the corresponding characterization techniques

Entity characterized	Characterization techniques suitable
Size (structural properties)	TEM, XRD, DLS, NTA, SAXS, HRTEM, SEM, AFM, EXAFS, FMR, DCS, ICP-MS, UV-Vis, MALDI, NMR, TRPS, EPLS, magnetic susceptibility
Shape	TEM, HRTEM, AFM, EPLS, FMR, 3D-tomography
Elemental-chemical composition	XRD, XPS, ICP-MS, ICP-OES, SEM-EDX, NMR, MFM, LEIS
Crystal structure	XRD, EXAFS, HRTEM, electron diffraction, STEM

Entity characterized	Characterization techniques suitable
Size distribution	DCS, DLS, SAXS, NTA, ICP-MS, FMR, superparamagnetic relaxometry, DTA, TRPS, SEM
Chemical state–oxidation state	XAS, EELS, XPS, Mössbauer
Growth kinetics	SAXS, NMR, TEM, cryo-TEM, liquid-TEM
Ligand binding/composition/density/arrangement/mass, surface composition	XPS, FTIR, NMR, SIMS, FMR, TGA, SANS

Entity characterized	Characterization techniques suitable
Surface area, specific surface area	BET, liquid NMR
Surface charge	Zeta potential, EPM
Concentration	ICP-MS, UV-Vis, RMM-MEMS, PTA, DCS, TRPS
Agglomeration state	Zeta potential, DLS, DCS, UV-Vis, SEM, Cryo-TEM, TEM
Density	DCS, RMM-MEMS
Single particle properties	Sp-ICP-MS, MFM, HRTEM, liquid TEM
3D visualization	3D-tomography, AFM, SEM

Entity characterized	Characterization techniques suitable
Dispersion of NP in matrices/supports	SEM, AFM, TEM
Structural defects	HRTEM, EBSD
Detection of NPs	TEM, SEM, STEM, EBSD, magnetic susceptibility
Optical properties	UV-Vis-NIR, PL, EELS-STEM
Magnetic properties	SQUID, VSM, Mössbauer, MFM, FMR, XMCD, magnetic susceptibility