Nanoparticle Technology

Lecture 02: Introduction to Nanotechnology

CAU 중앙대학교
CHUNG-ANG UNIVERSITY

Lecture 02: table of contents

What is nanotechnology?

What is nano?

- Origin

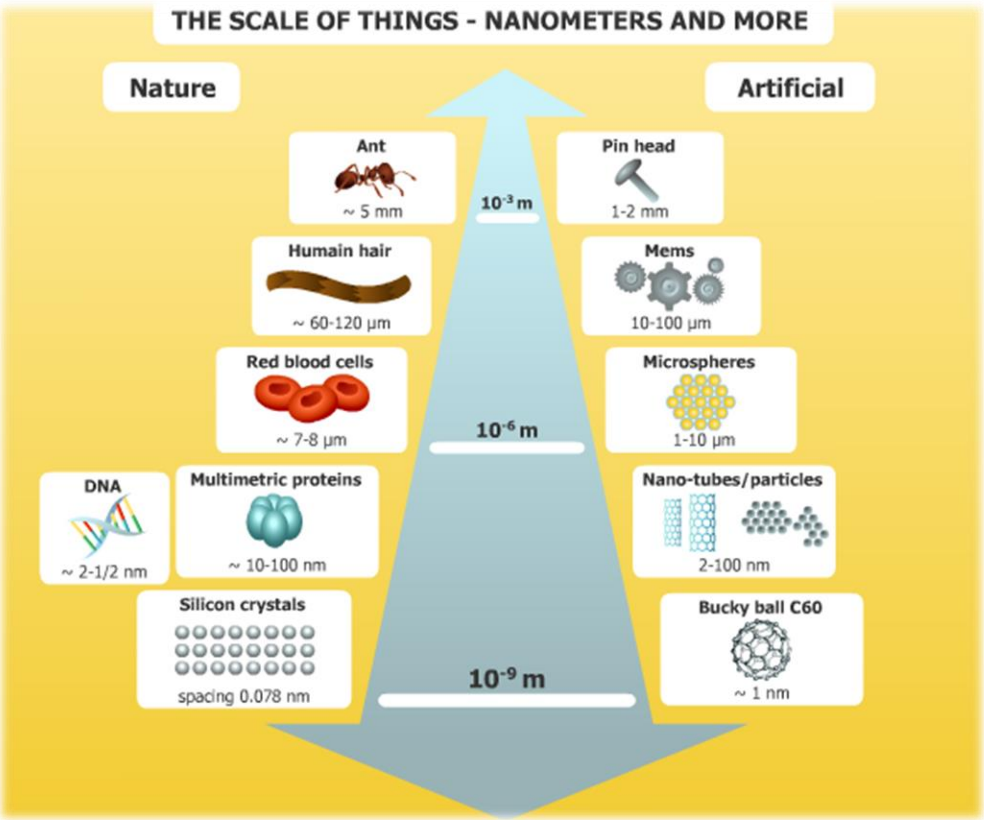
The word "nano" is originated from and the Greek "nanos" which means "dwarf" (i.e. an abnormally short person).

- Definition

1. Denoting 10^{-9} or one billionth (i.e. 1 nm = 10^{-9} m)
2. Indicating extreme smallness

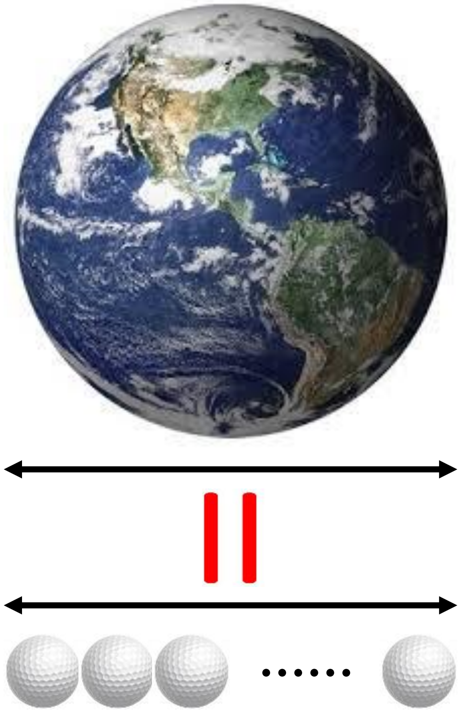
How small is nanoscale?

- Absolute value -



- Relative value -

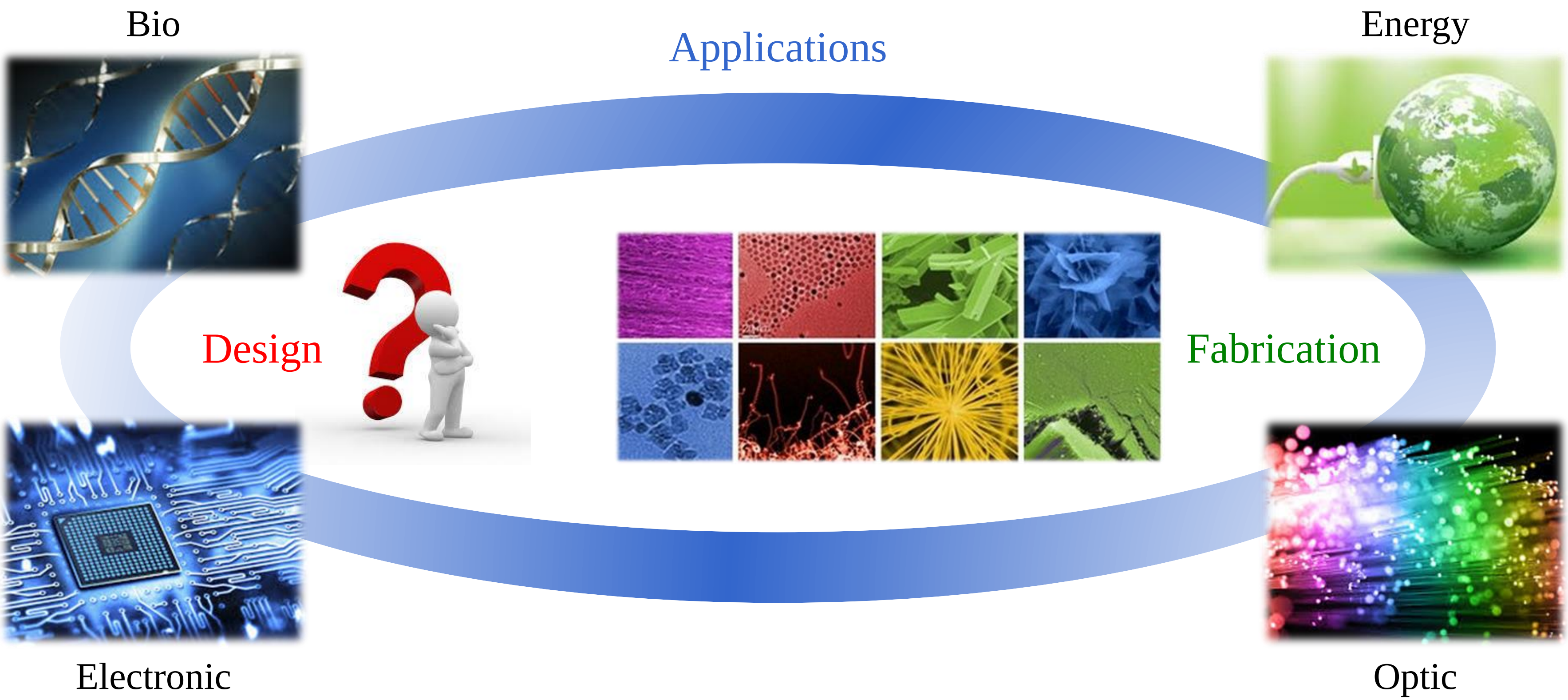
1 Earth



~ 10^{9} Golf balls

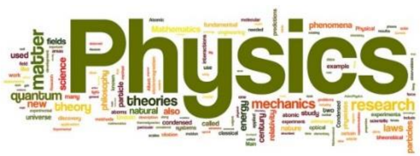
What is nanotechnology?

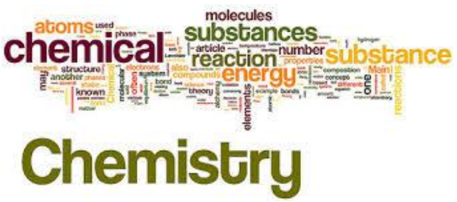
- In general, nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials.

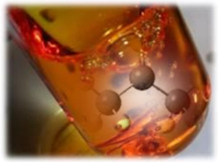


What is nanotechnology?

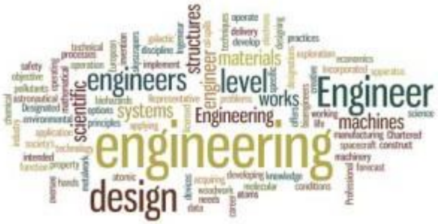
- Nanotechnology is an interdisciplinary which needs physics, chemistry, engineering, biology and etc..

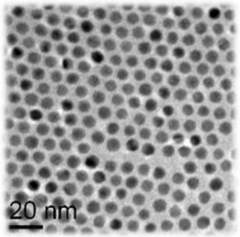


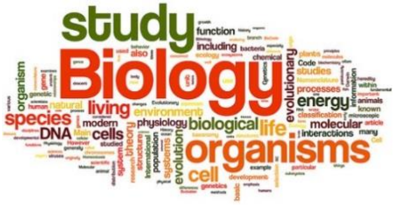


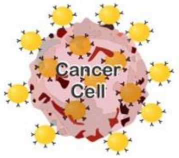


$$\Delta G_c = \frac{16\pi\gamma^3 V_m^2}{3\left(RT\ln S\right)^2}$$









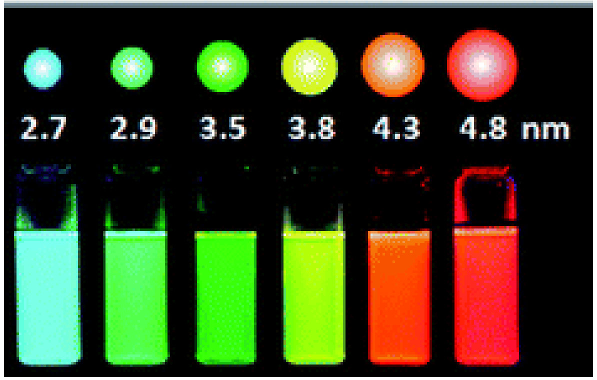
What happens in nanometer scale?

- Materials in **micro**meter scale mostly exhibit physical properties the same as that of bulk.
- Materials in **nano**meter scale may exhibit physical properties the different from that of bulk.

Optic property (color change of CdSe)

CdSe powder
Color: red

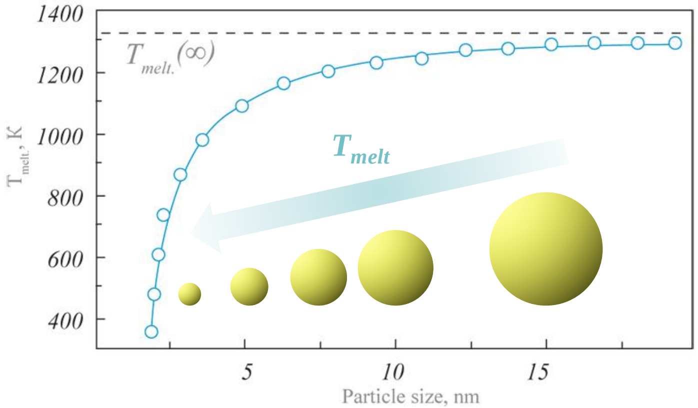
CdSe nanoparticle



Thermal property (melting point change of Au)

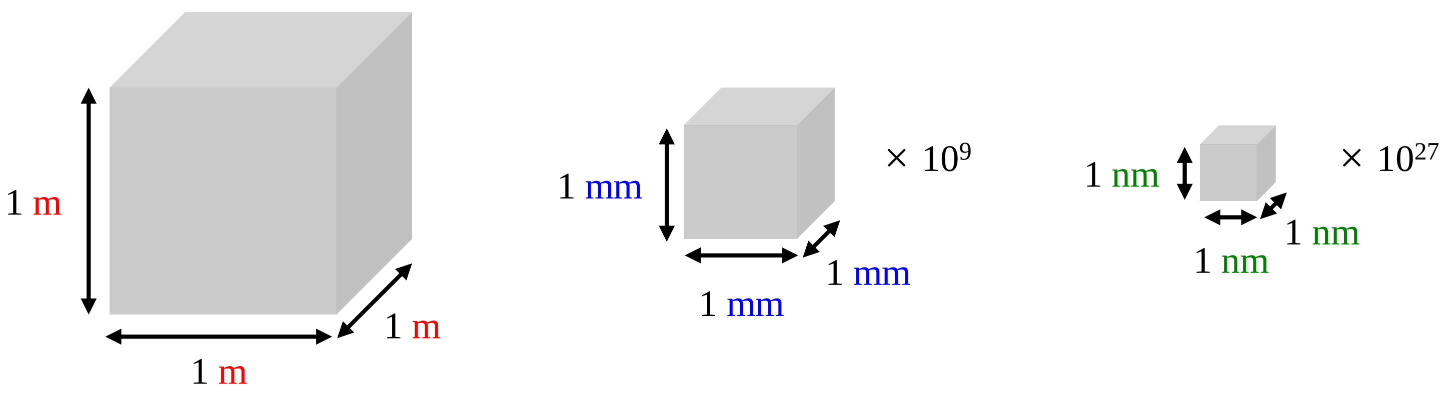
Au bar
Melting point: 1337.33 K

Au nanoparticle



Why the nanomaterial's property is changed?

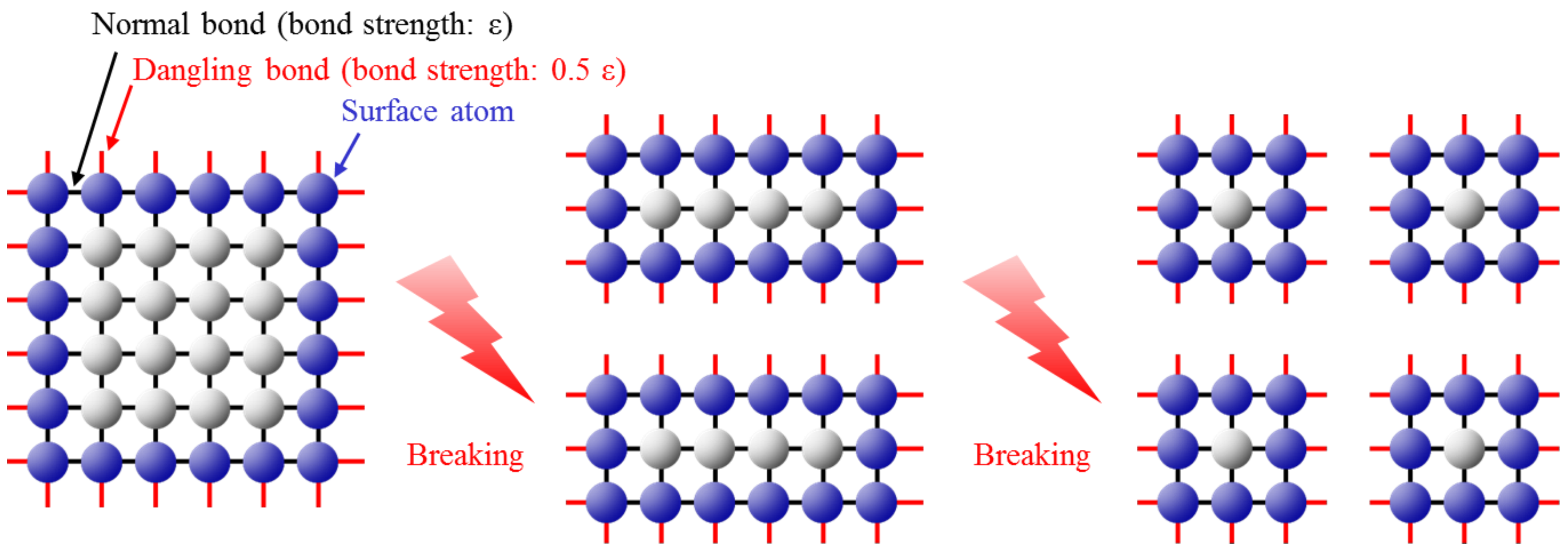
- Nanomaterials have a relatively larger surface area or surface area to volume ratio when compared to the same mass of material produced in a bulk form.



Volume (m^3)	**1**	**1**	**1**
Surface area (m^2)	**6**	**6,000**	**6,000,000,000**

What happens when surface/volume ratio increase?

- Increase of surface/volume ratio generates the unsatisfied valence (broken bond) at the surface atoms, indicating the increase of surface energy.



Surface energy: $\gamma = 0.5 N_b \varepsilon \rho_a$
(without surface relaxation)

N_b: number of broken bond
ε: bond strength
ρ_a: number density of atoms at surface

History of nanotechnology

Nanoparticle Technology

History

“Lycurgus” Cup (Rome, 4th Century)

Colloidal gold and silver in the glass allow it to look different color depending on light position.

Light outside

Light inside

History

Window from Chartres Cathedral (France, 13th Century)

Various metal oxide with different size were used in the glass allowing it to look different color.

History

Colloidal gold dispersion: firstly intended synthesis

Michael Faraday (1791 ~ 1867)

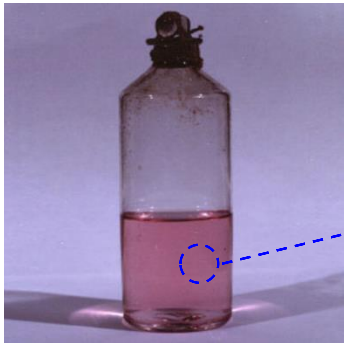
Royal medal winner (1846)

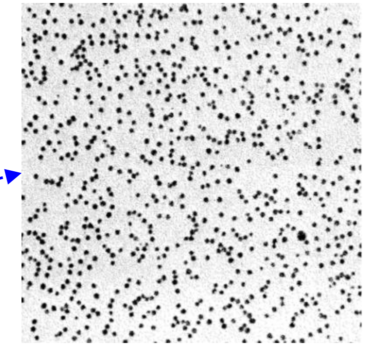
Lecture entitled as “Experimental relations of gold to light”
- Royal Society in London (1857)

Faraday’s colloidal ruby gold (1857)
: Stable until 1945

Electron micrograph (1985)
: 2 ~ 6 nm

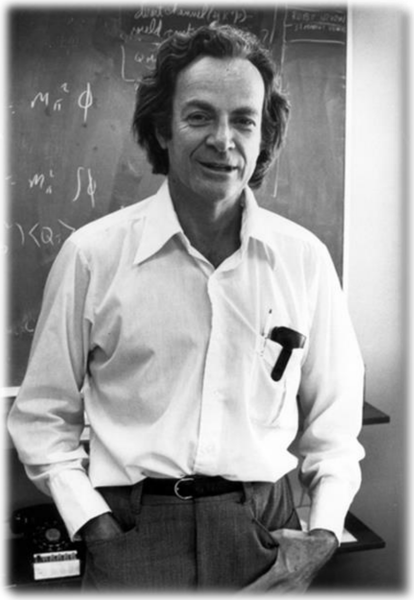
Bulk gold





History

Inspiration for nanotechnology



Richard P. Feynman (1918 ~ 1988)

Nobel prize winner in physics (1965)

Lecture entitled as "There is plenty of room at the bottom"
- American Physical Society in California (1959)

APS physics American Physical Society

"What I want to talk about is the problem of manipulating and controlling things on a small scale."

History

Electron microscope

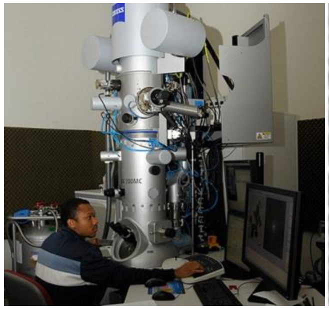
Ernst Ruska (1906 ~ 1988)

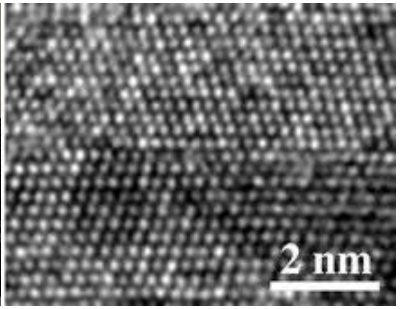
Nobel prize winner in physics (1986)

Paper entitled as “The magnetic concentrating coil for fast electron beam”
- *Z. Tech. Phys.*, 12 (1931) 389-448.

Electron microscope (1933)

Electron microscope (present)





History

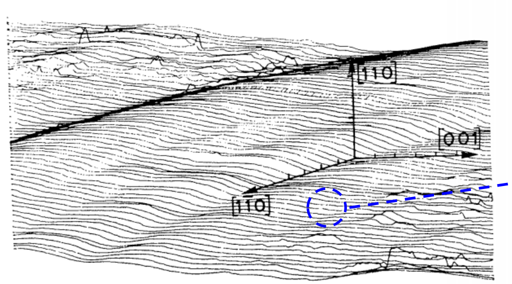
Scanning tunneling microscope (STM)

Gerd Binnig (1947 ~)
Heinrich Rohrer (1933 ~ 2013)

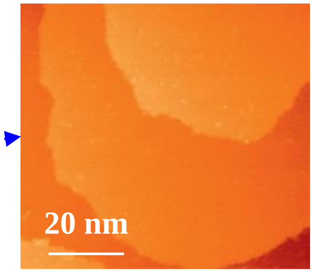
Nobel prize winner in physics (1986)

Paper entitled as "Surface studies by scanning tunneling microscopy"
- *Phys. Rev. Lett.*, 49 (1982) 57-61.

STM image of Au (110) surface (1982)



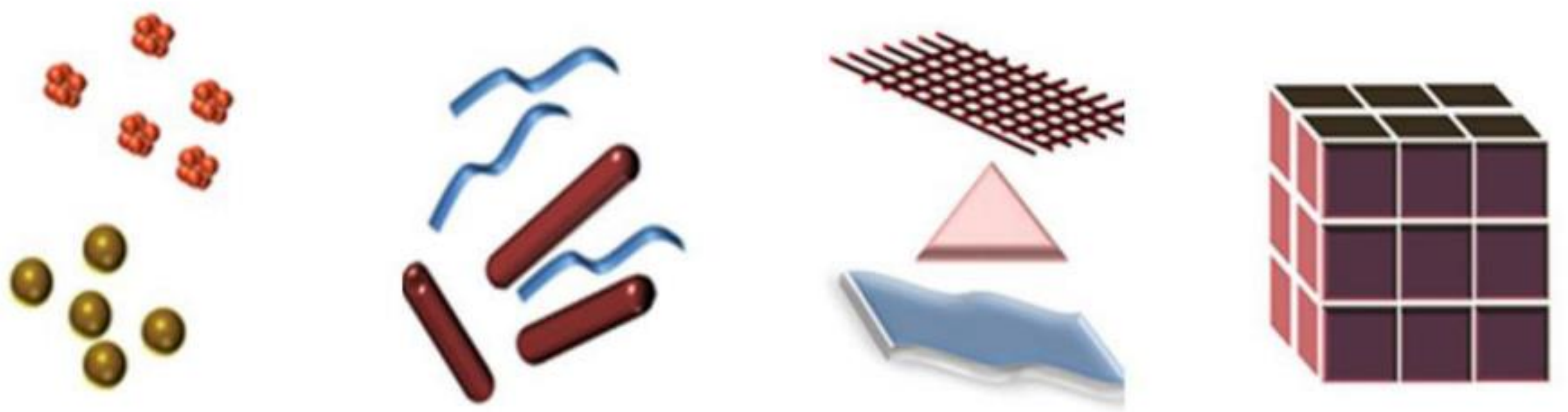
STM image of Au (110) surface (2014)



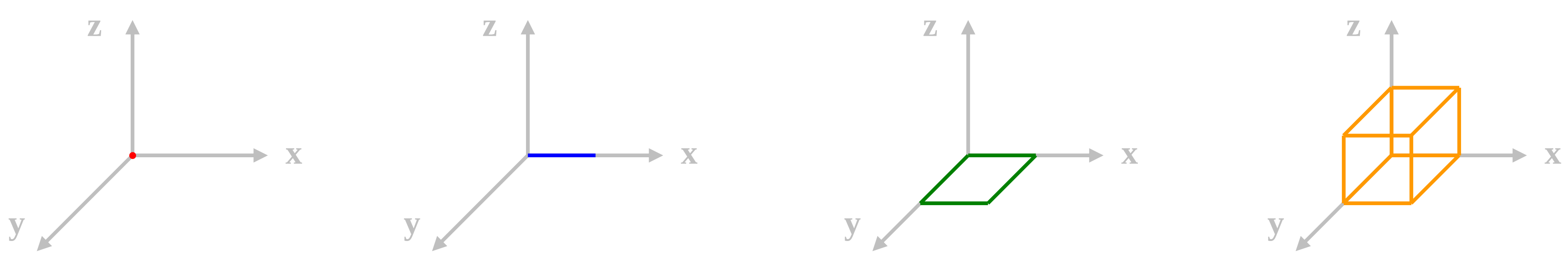
Nanomaterial Fabrication and Processing

Classification of nanomaterials

Dimensional classification



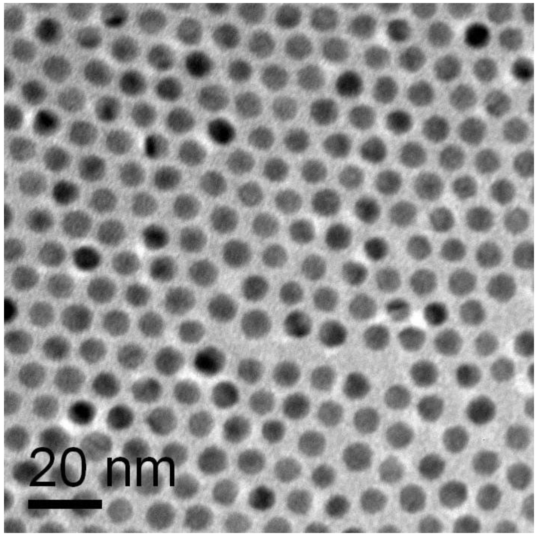
0-D **1-D** **2-D** **3-D**



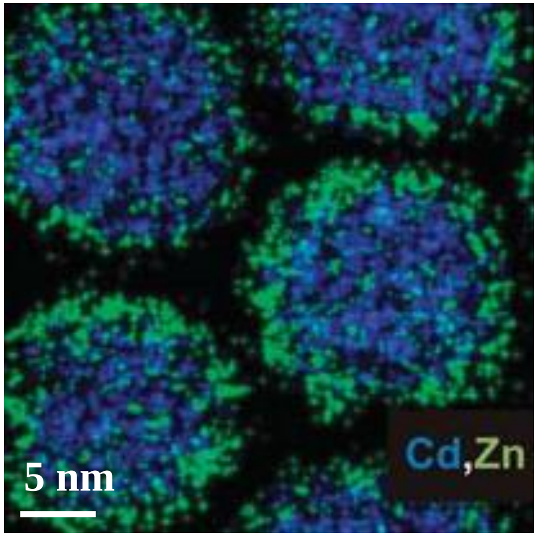
Classification of nanomaterials

Zero-dimensional (0-D) structures

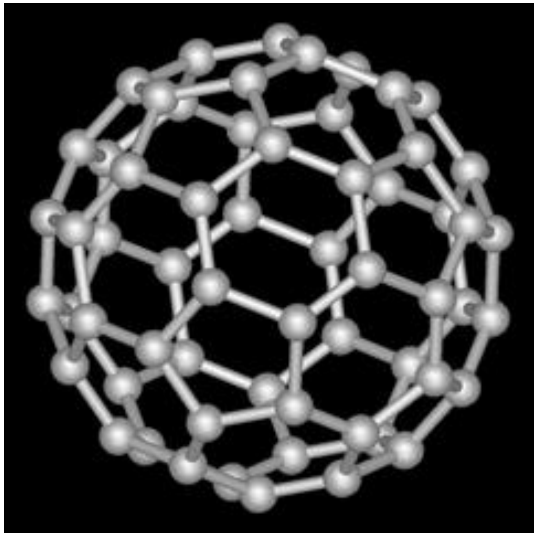
- Nanoparticles -



- Quantum dots -



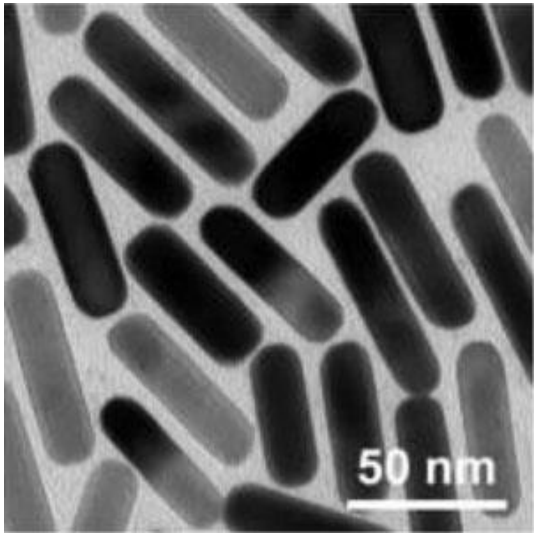
- Fullerenes -

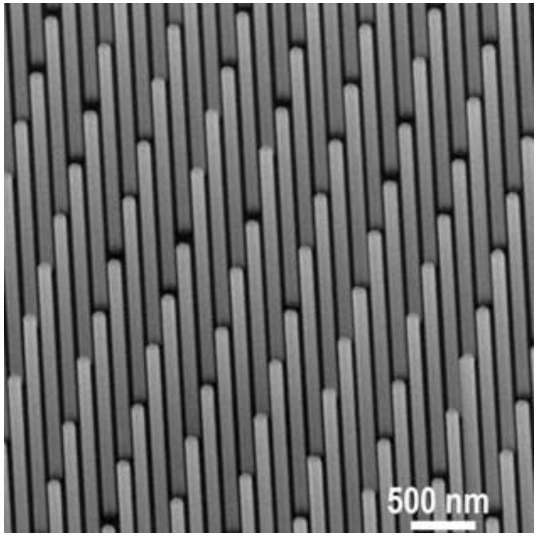


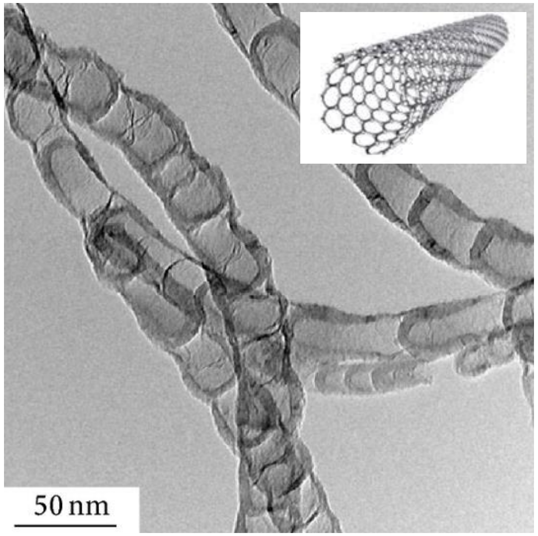
Classification of nanomaterials

One-dimensional (1-D) structures

- Nanorods - | - Nanowires - | - Nanotubes -





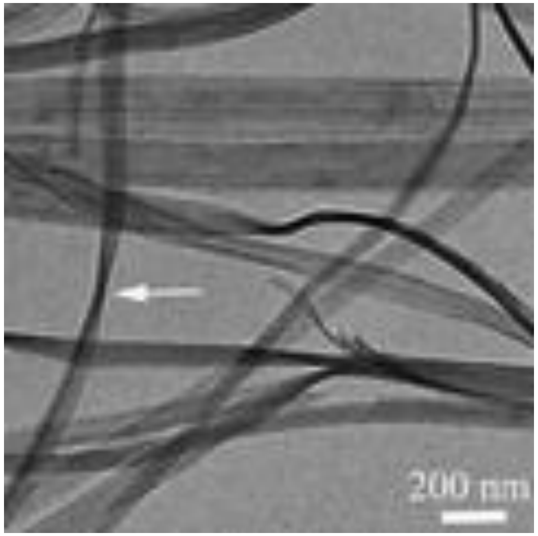


Nanoparticle Technology

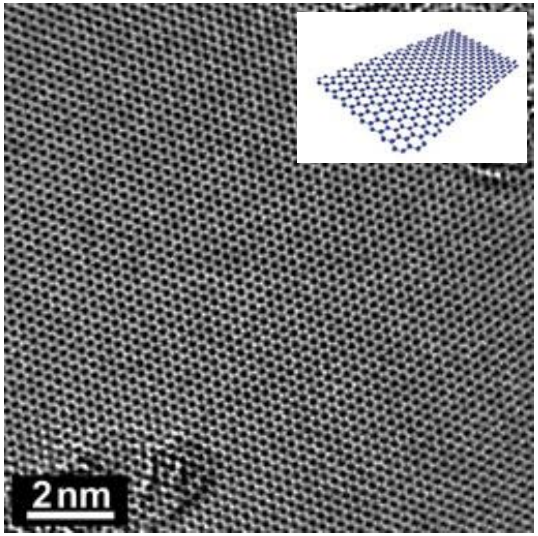
Classification of nanomaterials

Two-dimensional (2-D) structures

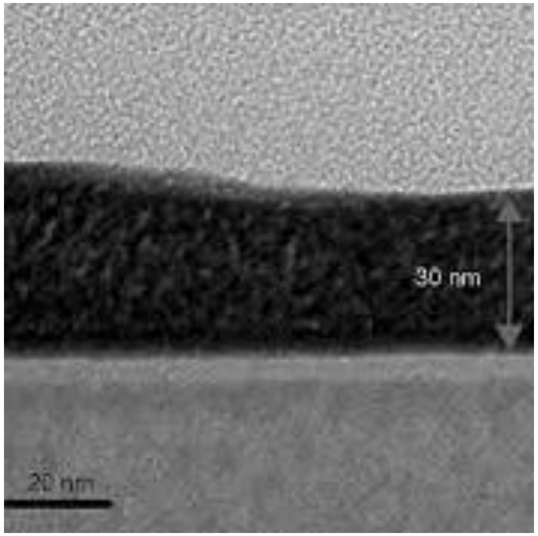
- Nanobelts -



- Graphene -



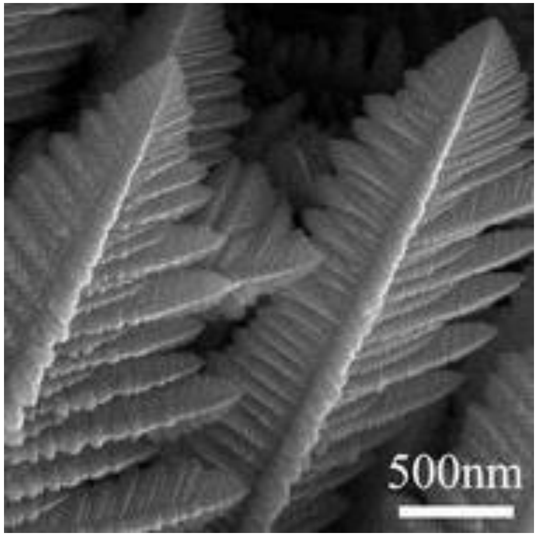
- Thin film -



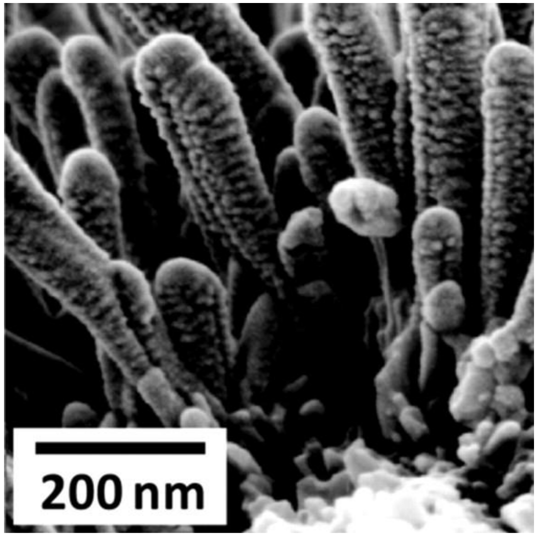
Classification of nanomaterials

Three-dimensional (3-D) structures

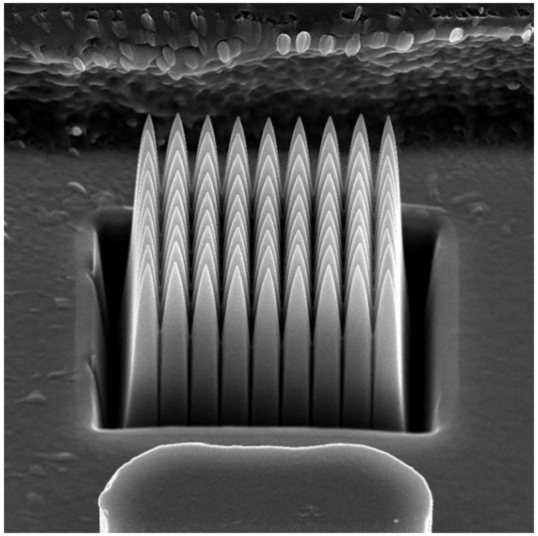
- Dendrite -



- Nanostructured thin film -



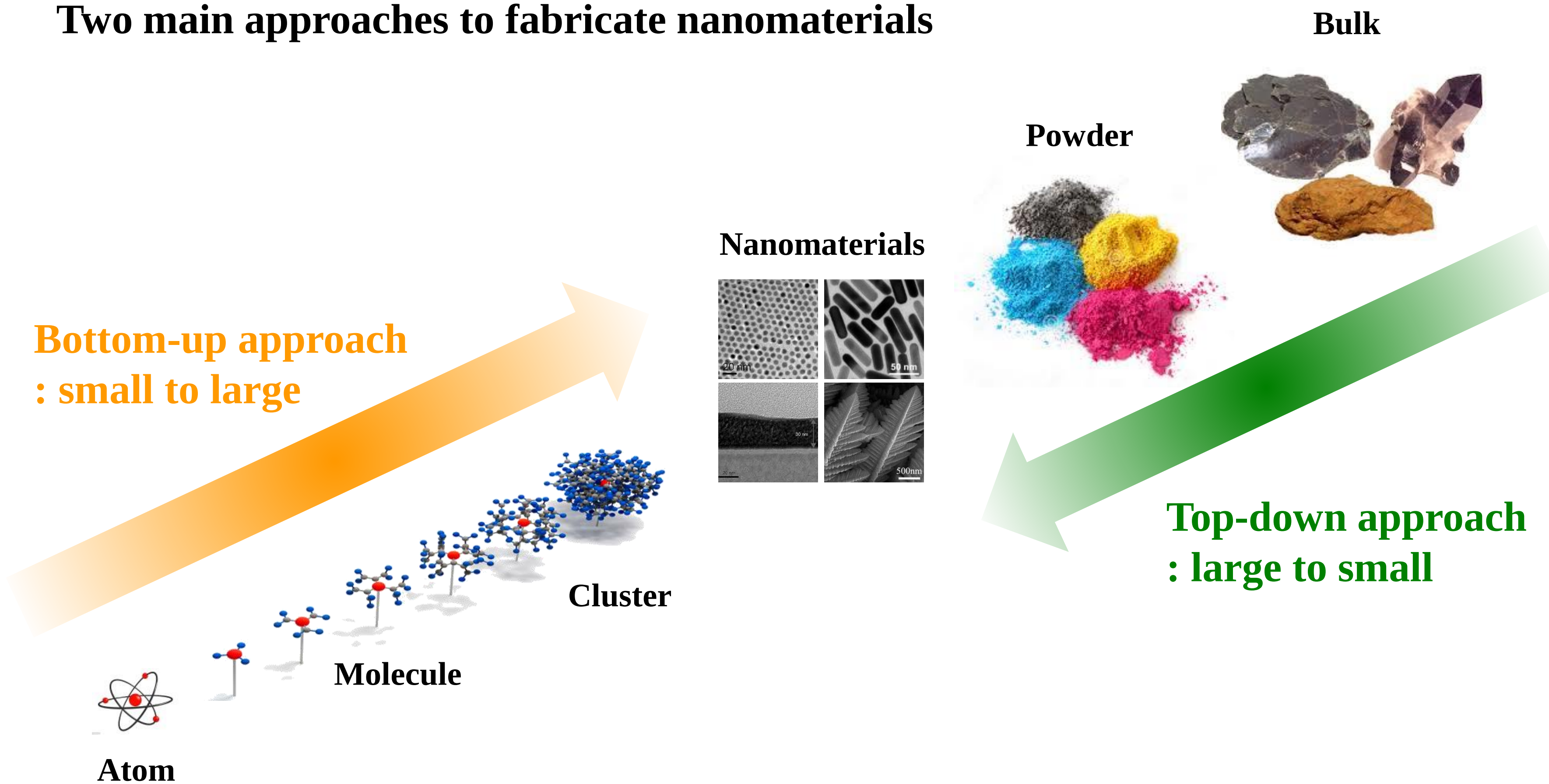
- Nanopattering -



Nanoparticle Technology

Fabrication strategy

Two main approaches to fabricate nanomaterials

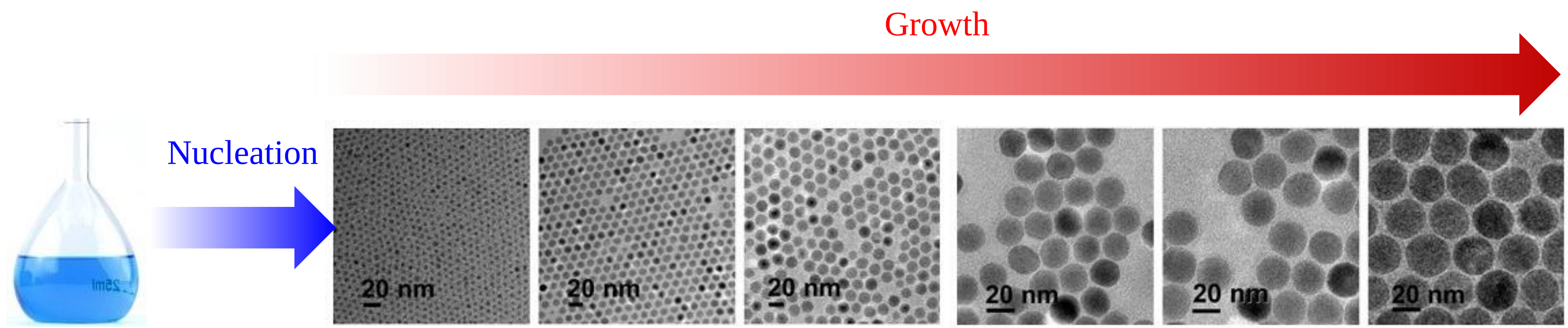


Fabrication strategy 1: bottom-up approach

Bottom-up approach

- Bottom-up approach refers to the construction of nanomaterial from the bottom, i.e. atom-by-atom, molecule-by-molecule or cluster-by-cluster.
- The atoms or molecules are used as the building blocks to produce nanoparticles, nanotubes, nanorods, thin films or layered structures.
- An advantage of the bottom-up approach is the better possibilities to obtain nanostructures with less defects and more homogeneous chemical compositions.
- For most materials, there is no difference in physical properties of nanomaterials compared with that of bulk.

Example: synthesis of nanoparticles and their growth

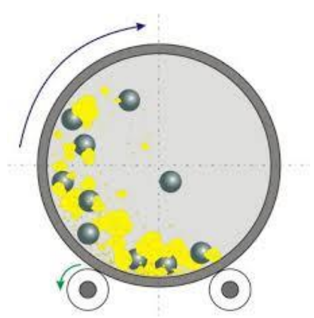


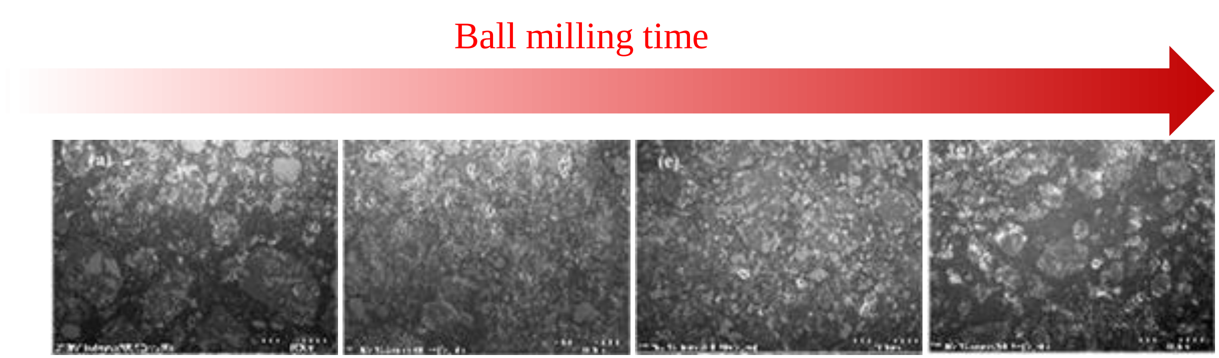
Fabrication strategy 2: top-down approach

Top-down approach

- The word "top-down" means starting from large pieces of material and producing the intended structure by mechanical or chemical methods.
- Cutting, grinding and etching are typical fabrication techniques, which have been developed to work on the nano scale.
- Top-down approach has proven unsuccessful with the problems originated from the defect of surface structure and incorporation of impurity.
- Even though there are problems connected to using a top-down approach, this is the method of choice when highly complex structures are made.

Example: ball milling of FeCo powder





Nanoparticle Technology

Fabrication methods

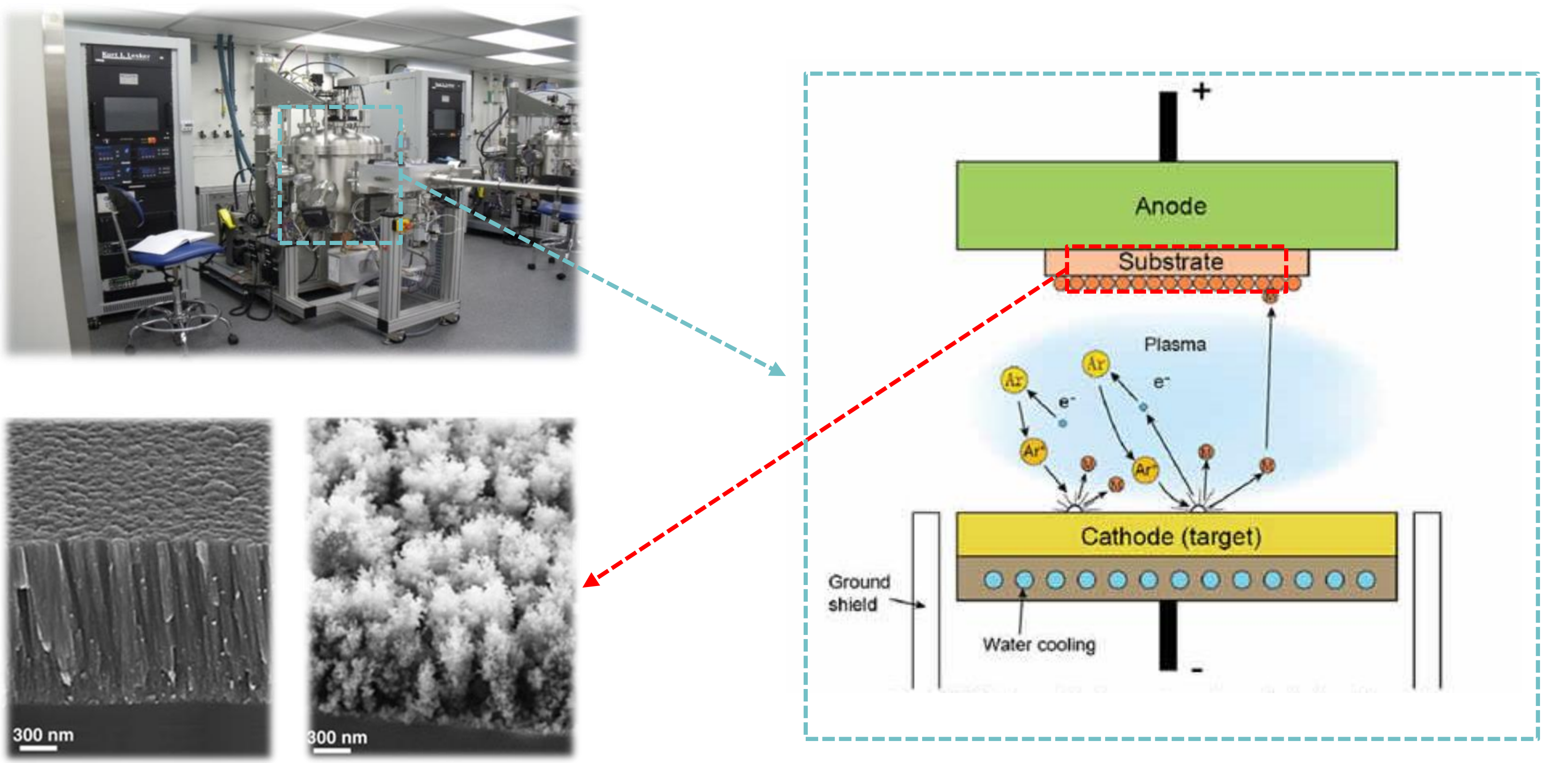
Nanomaterial fabrication methods

Physical methods	Chemical methods	Lithographic techniques
Ball milling	Chemical reduction synthesis	Photolithography
Inert gas condensation	Solvothermal synthesis	Electron-beam lithography
Arc discharge	Photochemical synthesis	Focused ion beam lithography
Ion sputtering	Electrochemical synthesis	Nanoimprint lithography
Laser ablation	Sonochemical synthesis	
Spray pyrolysis	Micelles and microemulsions	
Flame pyrolysis	Chemical vapor deposition	
Thermal evaporation	Sol-gel process	
Pulsed laser deposition		
Molecular beam epitaxy		

Fabrication methods 1: physical methods

Ion sputtering: direct current (DC) sputtering

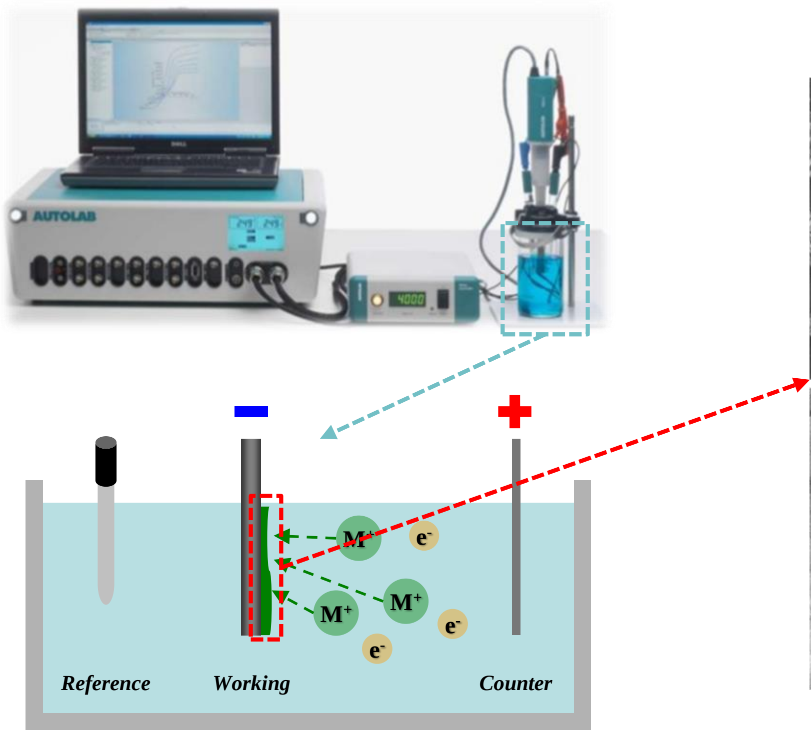
- Argon is ionized by a strong potential difference, and these ions are accelerated to a target. After impact, target atoms are released and travel to the substrate, where they form layers of atoms in the thin film.



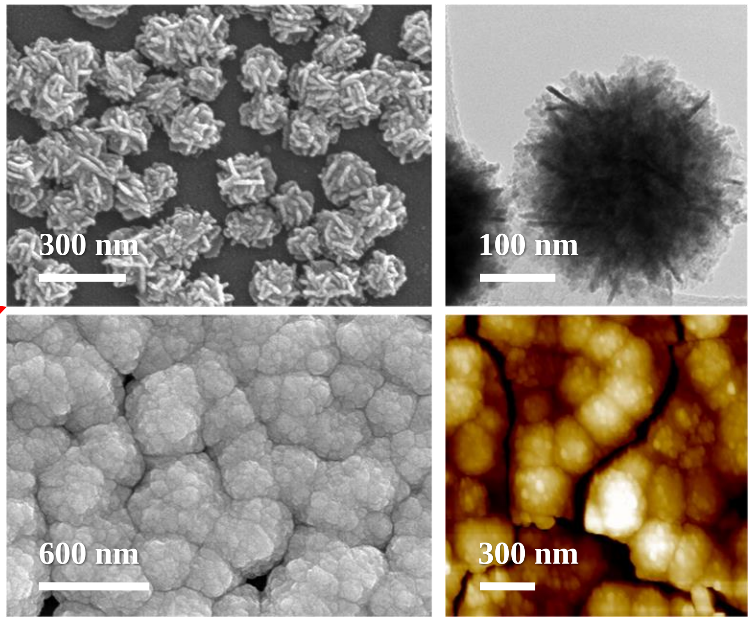
Fabrication methods 2: chemical methods

Electrochemical synthesis: electrodeposition

- Metal ions in solution can be electrochemically reduced by negative applied potential on the surface of substrate (working electrode).



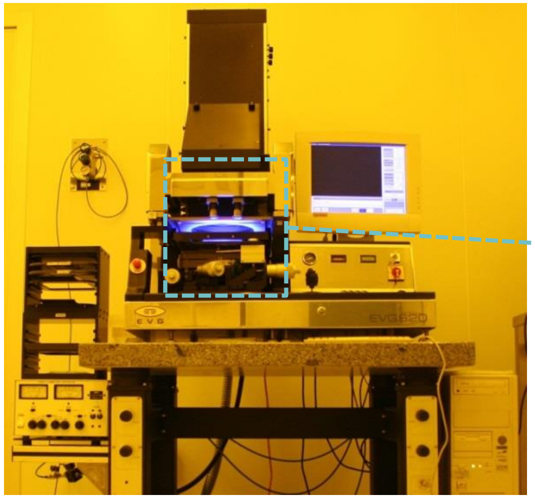
- Electrodeposited nanoparticles and thin films -

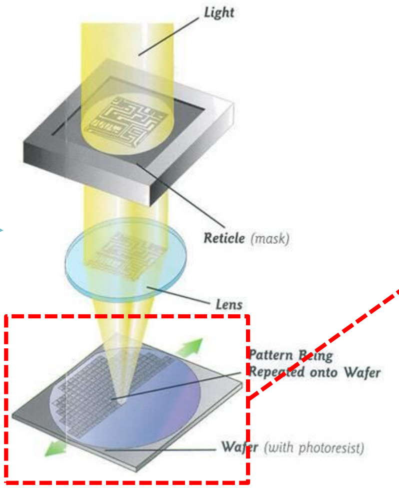


Fabrication methods 3: lithographic techniques

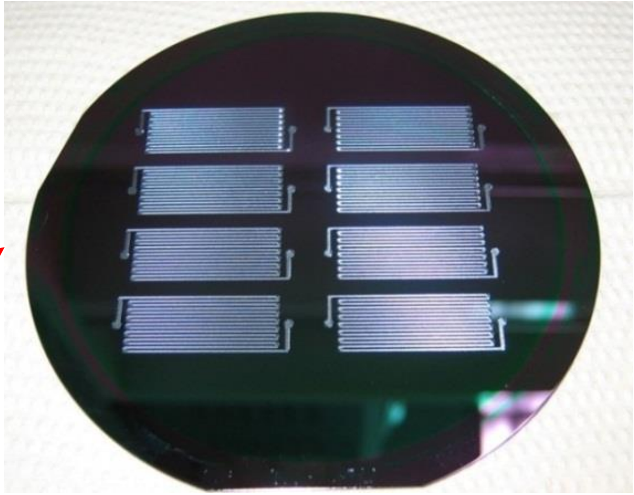
Photolithography

- Patterning on silicon wafer can be fabricated by using a mask with exposure of UV light .



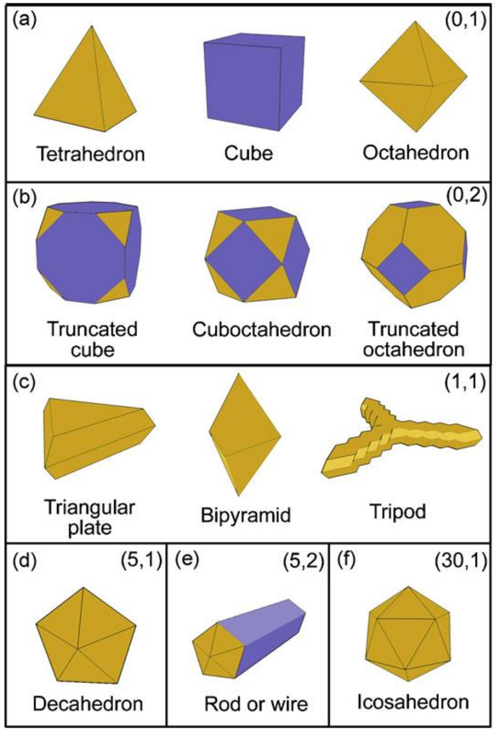


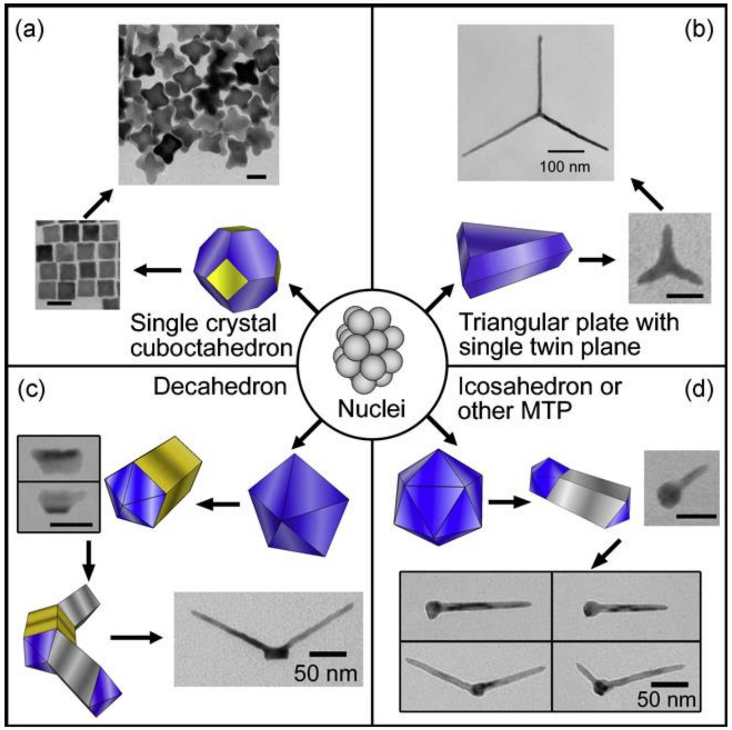
- Patterned silicon wafer -

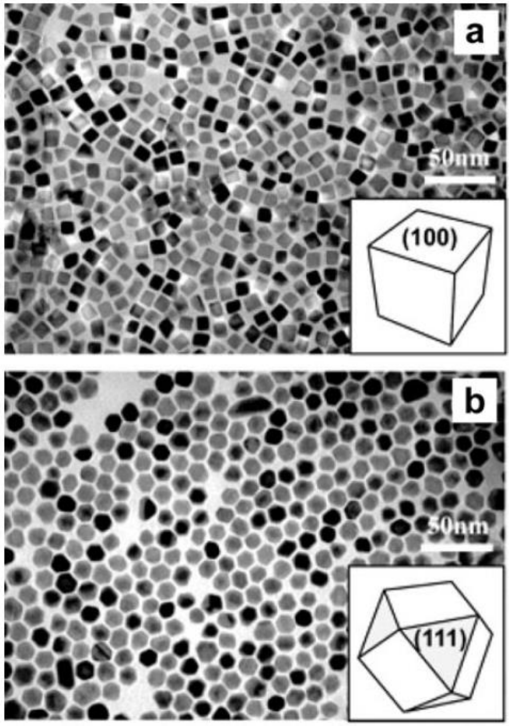


Nanostructure processing 1: shape control

Crystal orientation

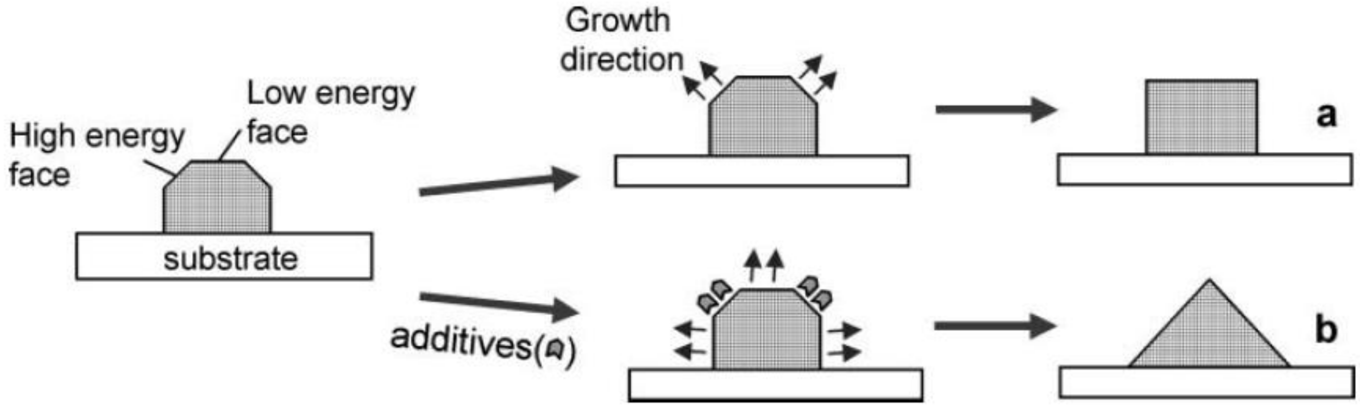


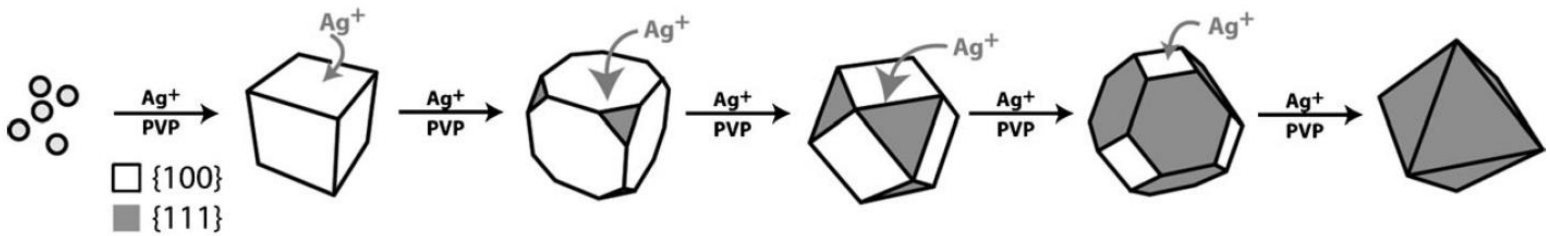




Nanostructure processing 1: shape control

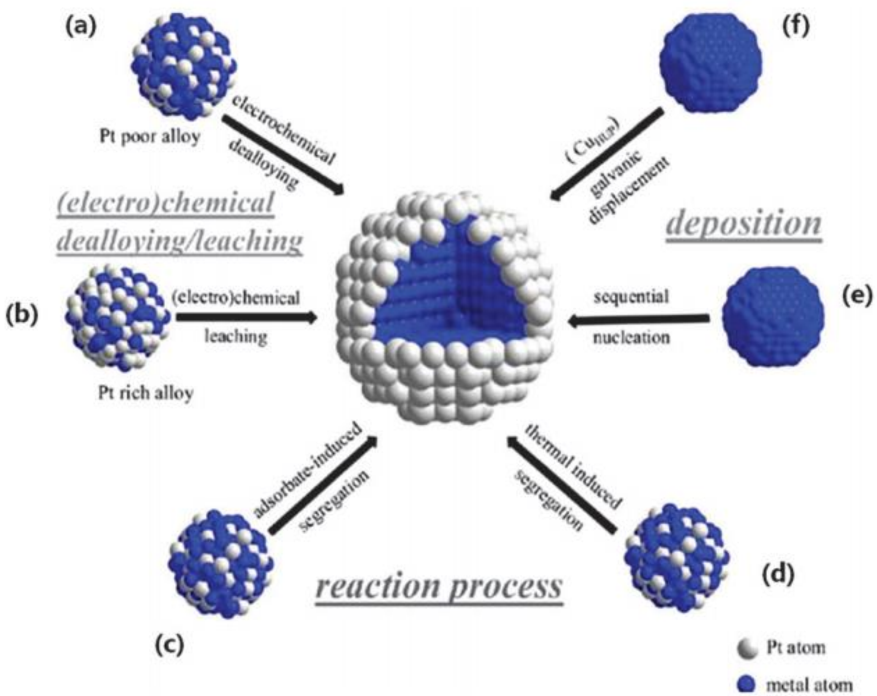
Crystal orientation





Nanostructure processing 2: core-shell

Core-shell synthesis



Methods for Pt bimetallic core-shell synthesis

(a) Electrochemical dealloying

(b) Electrochemical leaching

(c) Adsorbate-induced segregation

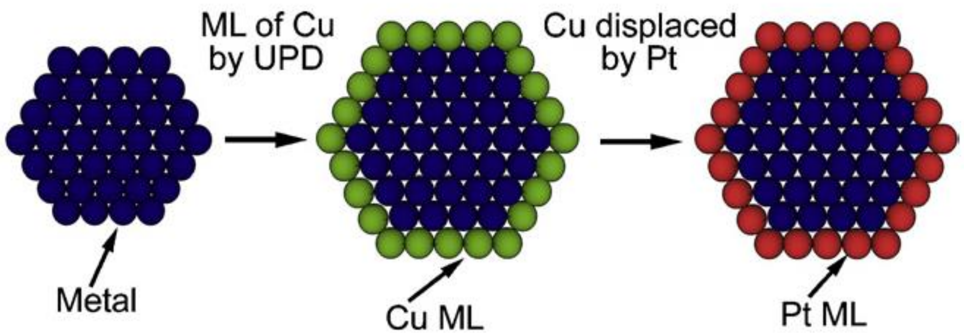
(d) Thermal induced segregation

(e) Heterogeneous colloidal nucleation

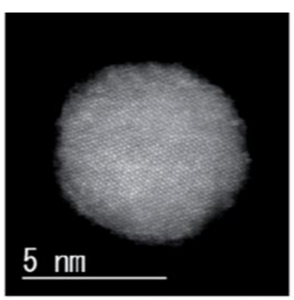
(f) Underpotential deposition - displacement

Nanostructure processing 2: core-shell

Core-shell synthesis (Pt-Pd core-shell)

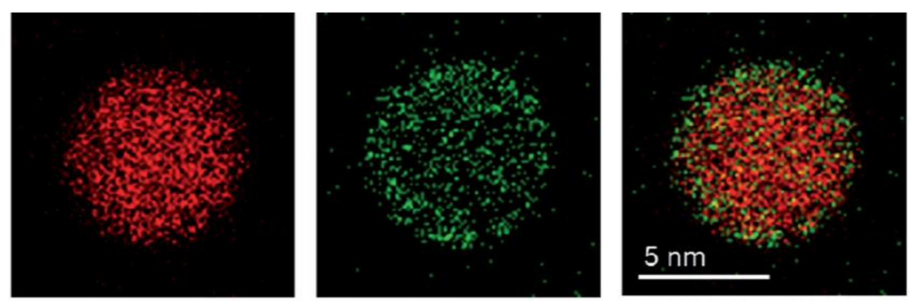


- Image -



- Composition -

Pd Pt Pd+Pt



Nanomaterial Characterization

Characterization methods

Nanomaterial characterization methods

Structural characterization

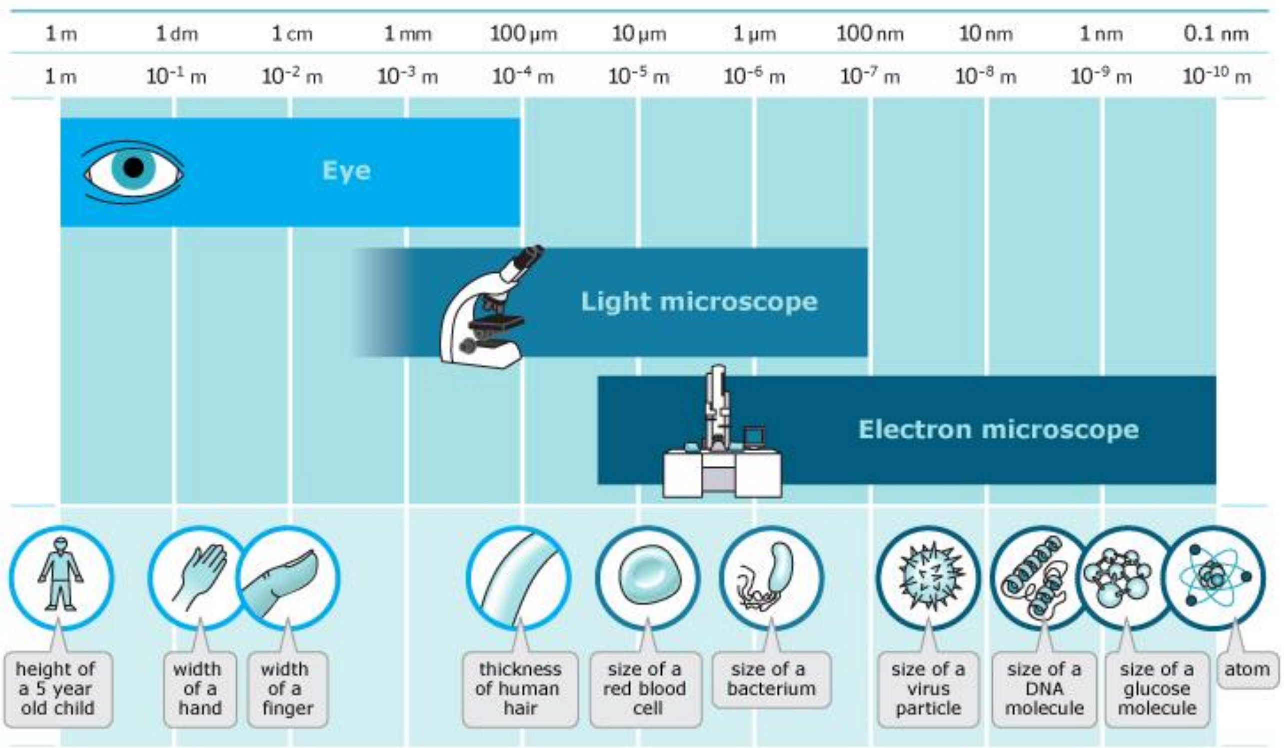
- X-ray diffraction
- Small angle X-ray scattering
- Electron microscope
  - Scanning electron microscope
  - Transmission electron microscope
- Scanning probe microscope
  - Scanning tunneling microscope
  - Atomic force microscope
- Gas physical and chemical adsorption

Chemical characterization

- Optical spectroscopy
  - UV-visible spectroscopy
  - FT-IR spectroscopy
  - Raman spectroscopy
- Electron spectroscopy
  - Energy dispersive spectroscopy
  - Electron probe micro analyser
  - Electron energy loss spectroscopy
  - Auger electron spectroscopy
  - X-ray photoelectron spectroscopy

Characterization methods

Resolution of microscope

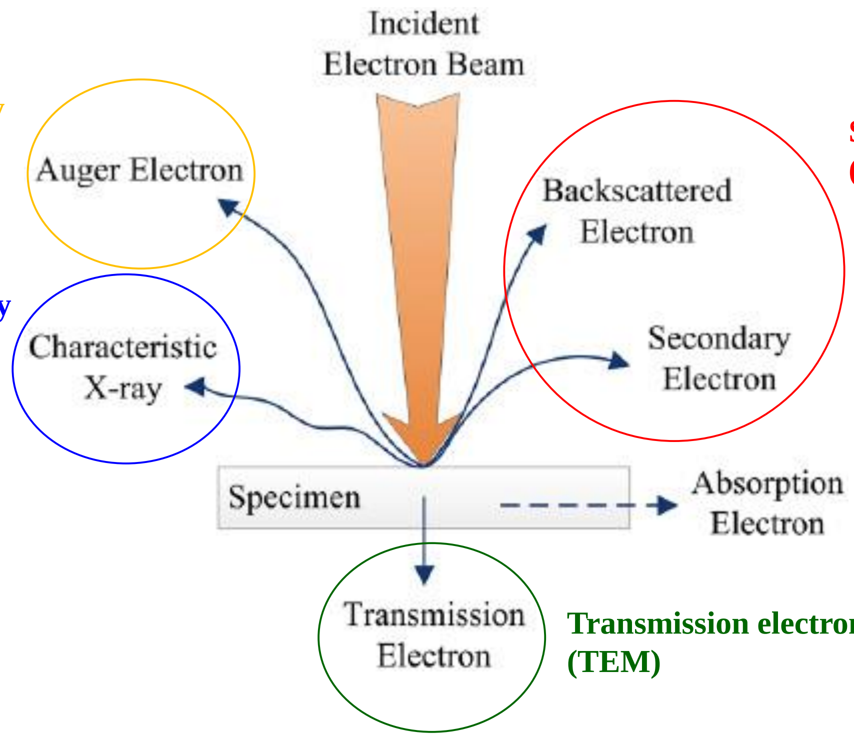


Characterization methods

When the incident electron beam meet specimen…

Auger electron spectroscopy (AES)

Energy dispersive spectroscopy (EDS)

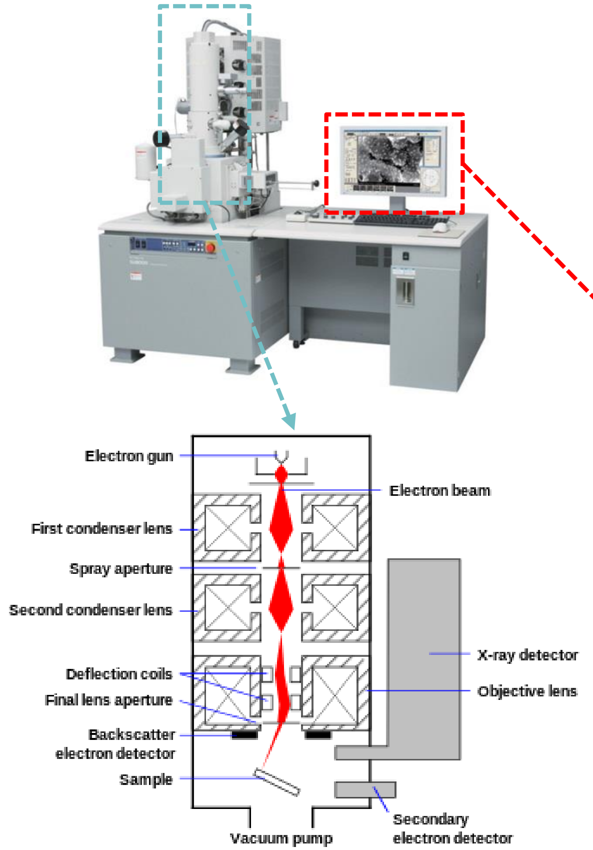


Scanning electron microscope (SEM)

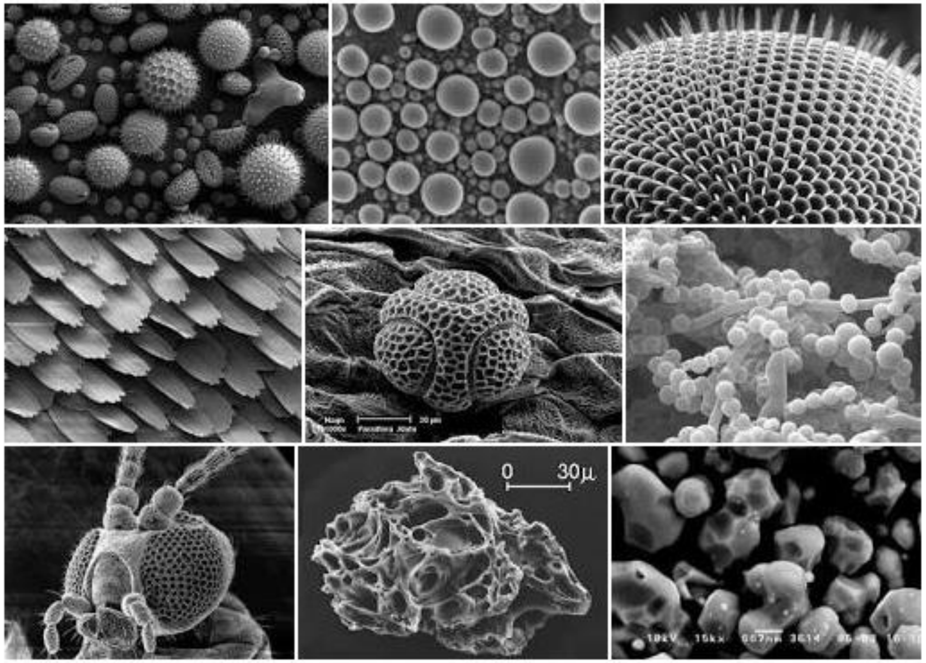
Transmission electron microscope (TEM)

Characterization methods 1: structural characterization

Scanning electron microscope (SEM)

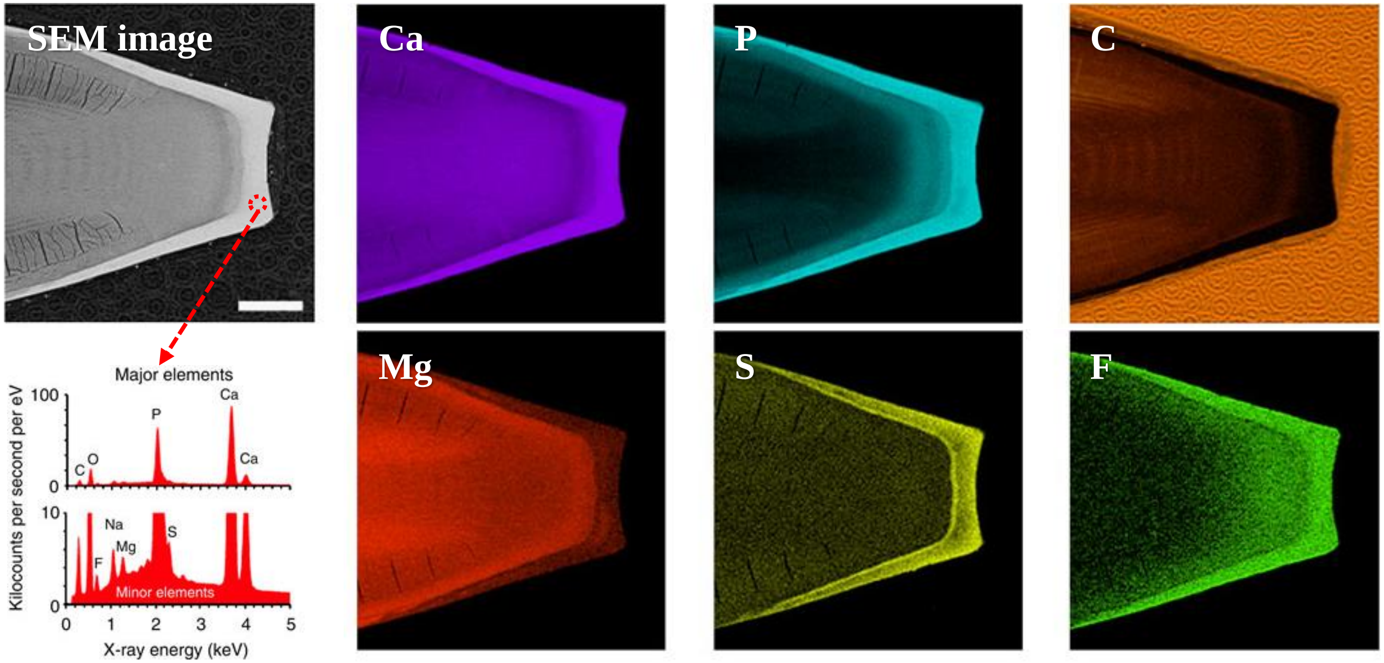


- Several examples of SEM images -



Characterization methods 2: chemical characterization

Energy dispersive spectroscopy (EDS)



Nanomaterial Application

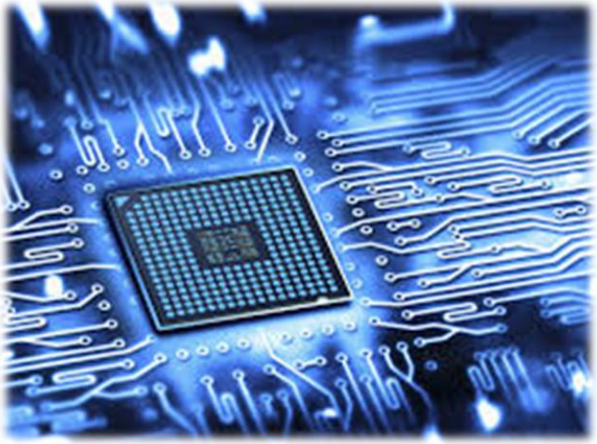
Nanoparticle Technology

Applications

Energy

Bio

Electronic



Optic

Nanoparticle Technology

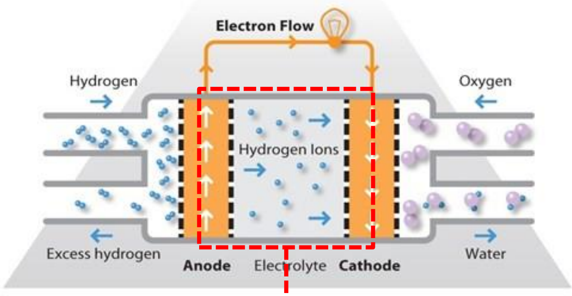
Application 1: energy

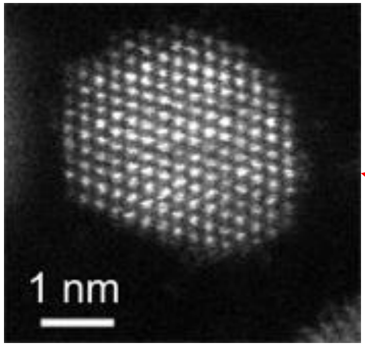
Fuel cell

Fuel cell car

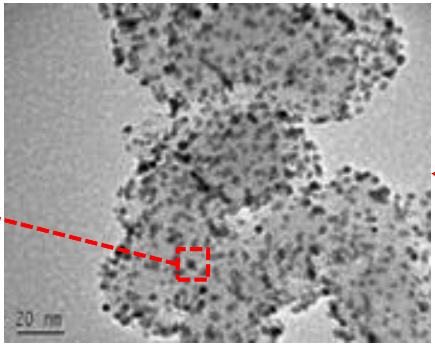
Fuel cell engine (stack)

Single fuel cell

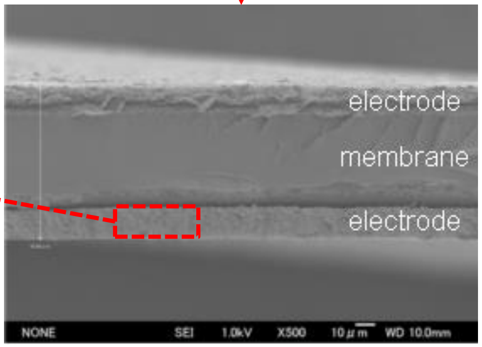




Single Pt nanoparticle



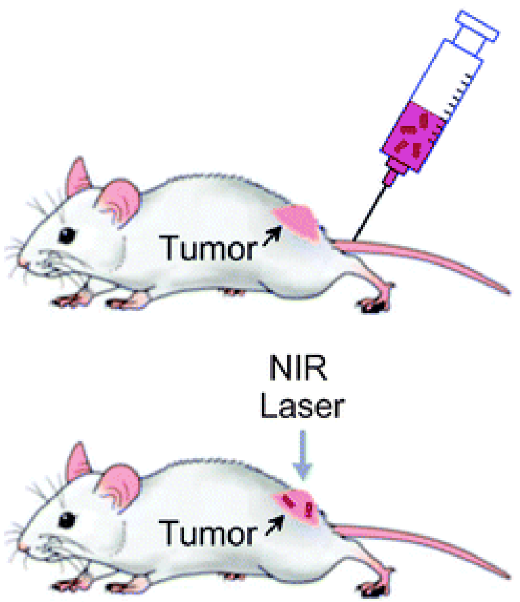
Pt/C catalysts

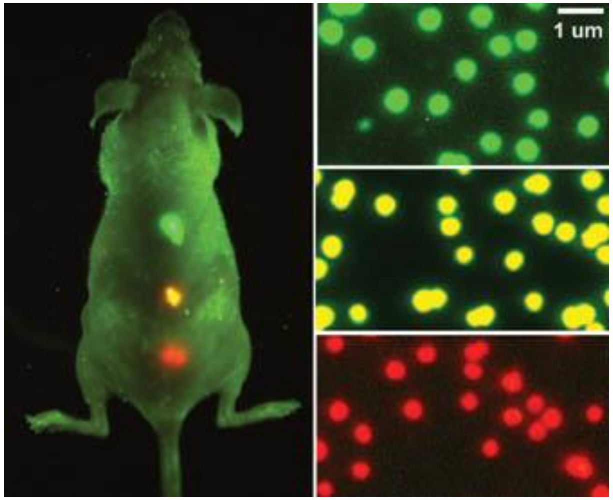


Membrane electrode assembly

Application 2: bio

Biological imaging

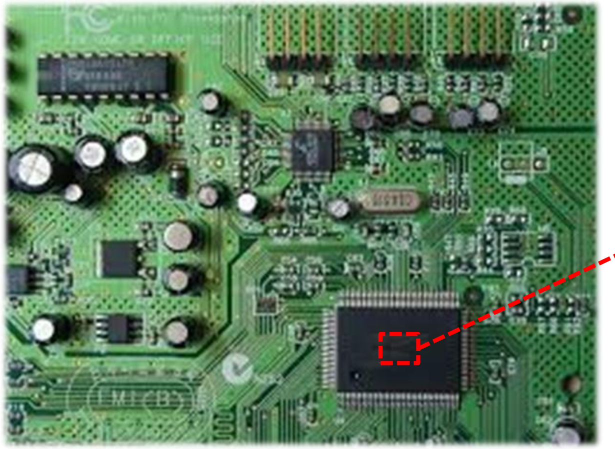




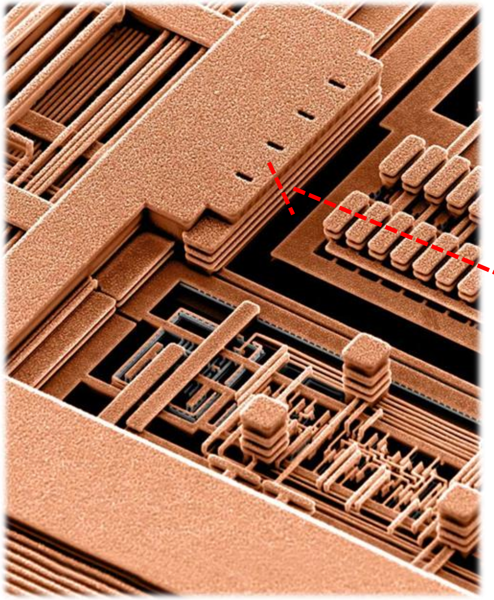
Application 3: electronics

Cu interconnection

Integrated circuit (IC)



Cu interconnection



Cu interconnection
(cross-section)

Application 4: optics

Quantum dot display