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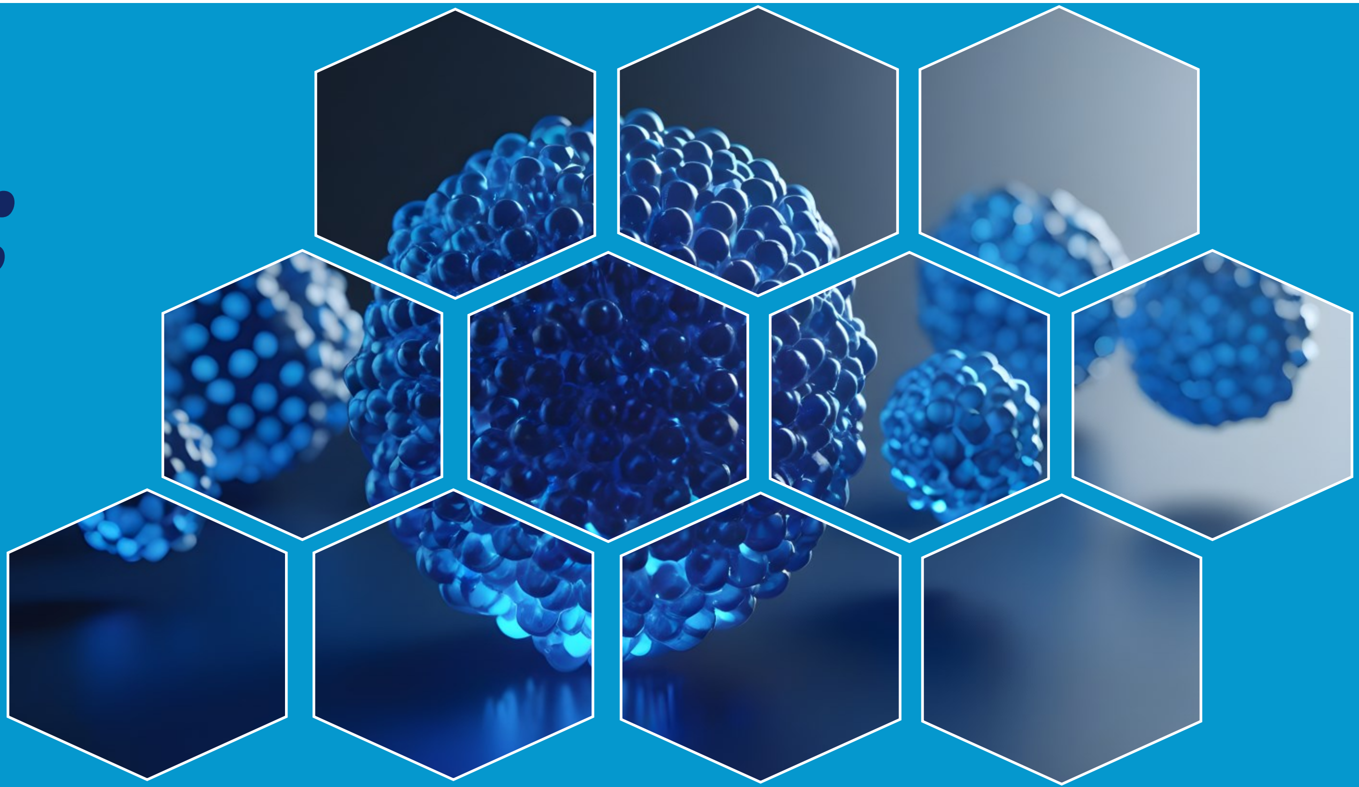
Nanomaterials: Introduction



Liliia Turovska, PhD

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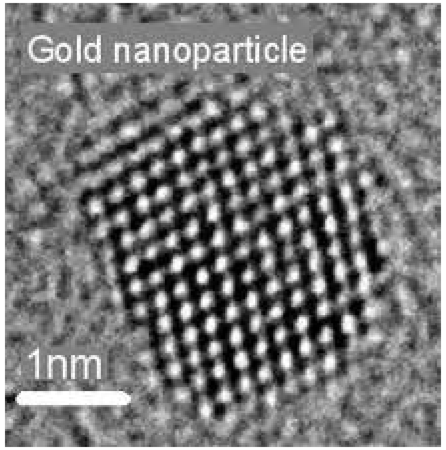
Outline

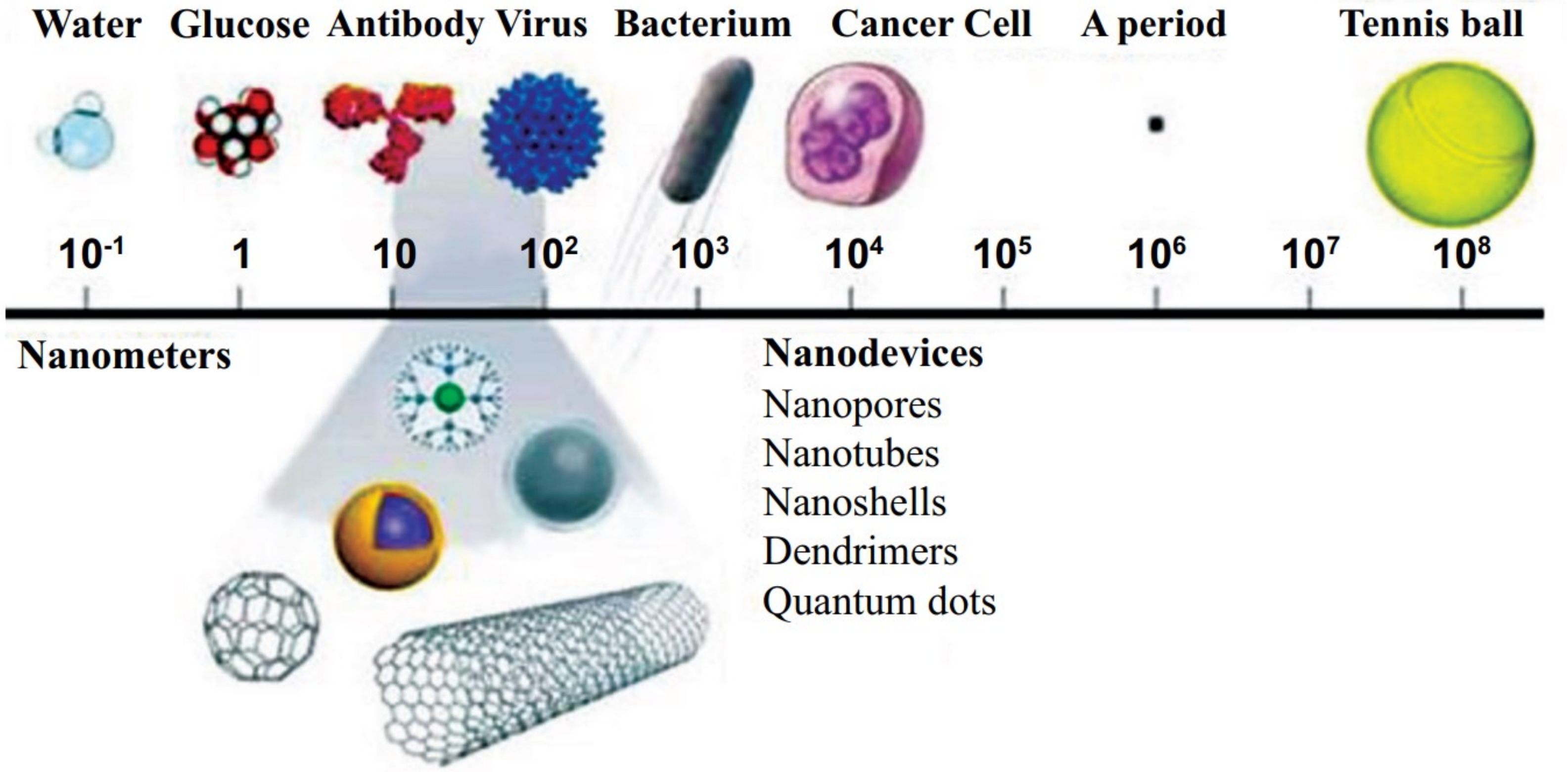
1. Nanotechnology and nanomaterials.
2. Classifications of nanomaterials, and their properties.
3. Historical overview of nanomaterials.
4. Reasons for special properties of nanoscale materials.
5. Classical and quantum size effects.
6. Basic concepts of quantum physics.
7. The energy of an electron in an atom.
8. Harmonic oscillator: transition from classical to quantum theory.
9. Wave-particle duality. Uncertainty principle.
10. Condensed matter physics. Electrons in crystals.
11. Quantum dots and their applications.
12. Applications of nanomaterials.

Nano

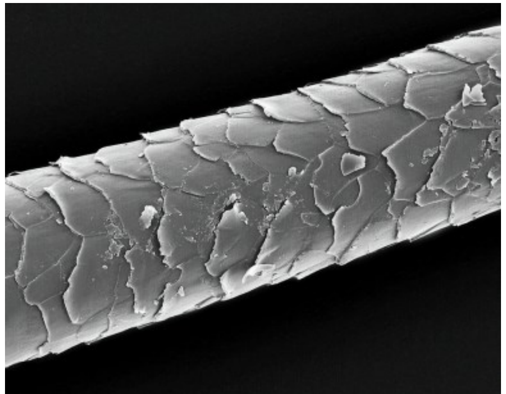
Nano is a millionth of a millimeter or a billionth of a meter, i.e. 1 nm = 10^{-9} m.

Atom is about 0.1 nanometer - 10 atoms side by side make up 1 nm.





Human hair:
50,000–100,000 nm in diameter.



Nanomaterials and Nanotechnology

According to the EU Commission Recommendation 2022/C 229/01, a nanomaterial is "a natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for from 1 to 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm".

Nanotechnology is the science of manipulating atoms and molecules to make advanced nanomaterials

Advanced nanomaterials are new materials with enhanced properties designed to provide superior performance.

Nanotechnology is the understanding and manipulation of matter in sizes ranging from approximately 1 to 100 nanometers, where unique phenomena enable new applications. It is an emerging, interdisciplinary field involving: Physics, Chemistry, Biology, Engineering, Materials Science, Computer Science

The main driving force of nanotechnology is the positive economic impact it can have.

The European Union, Japan and the USA have contributed the majority of all nanotechnology patents.

European Commission, Joint Research Centre, Rauscher, H., Rasmussen, K., Linsinger, T. et al., *Guidance on the implementation of the Commission Recommendation 2022/C 229/01 on the definition of nanomaterial*, Publications Office of the European Union, 2023, https://data.europa.eu/doi/10.2760/143118

Nanomaterials

Nanomaterials - in the range of 1-100 nanometers in at least one dimension.

Classification: based on the number of free dimensions

0D *nanomaterial*: all three dimensions are in the nanoscale.

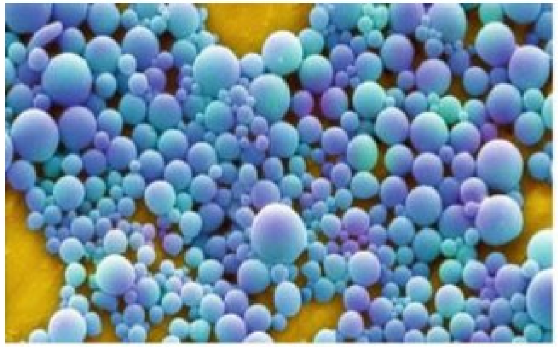
(nanoparticles, colloids, quantum dots)

1D *nanomaterial*: one dimension beyond the nanoscale and two other dimensions in the nanoscale. (nanowires, nanorods, nanotubes & biopolymers).

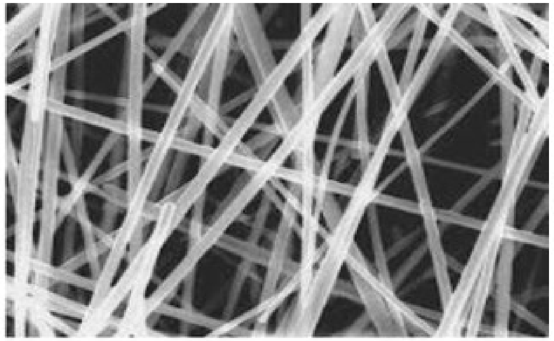
2D *nanomaterial*: any two dimensions can be outside of the nanoscale and one dimension in the nanoscale. (plate-like shapes - nanolayers, surface coatings and thin films).

3D *nanomaterial*: all three dimensions can be outside of the nanoscale. Made of nanomaterials.

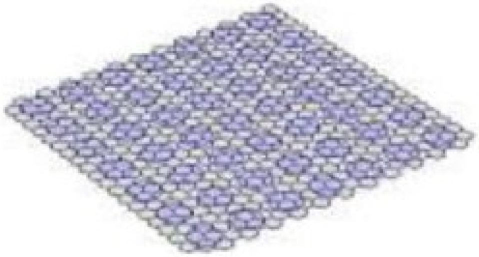
(nanoparticle dispersions, nanowire/ nanotube bundles & multiple nanolayers).



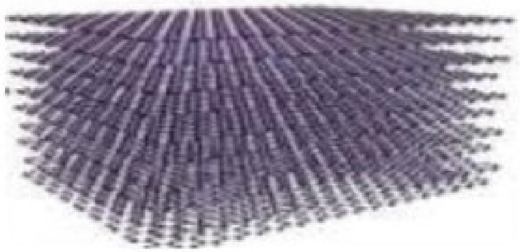
0D(Nanoparticle)



1D(Nanowire)

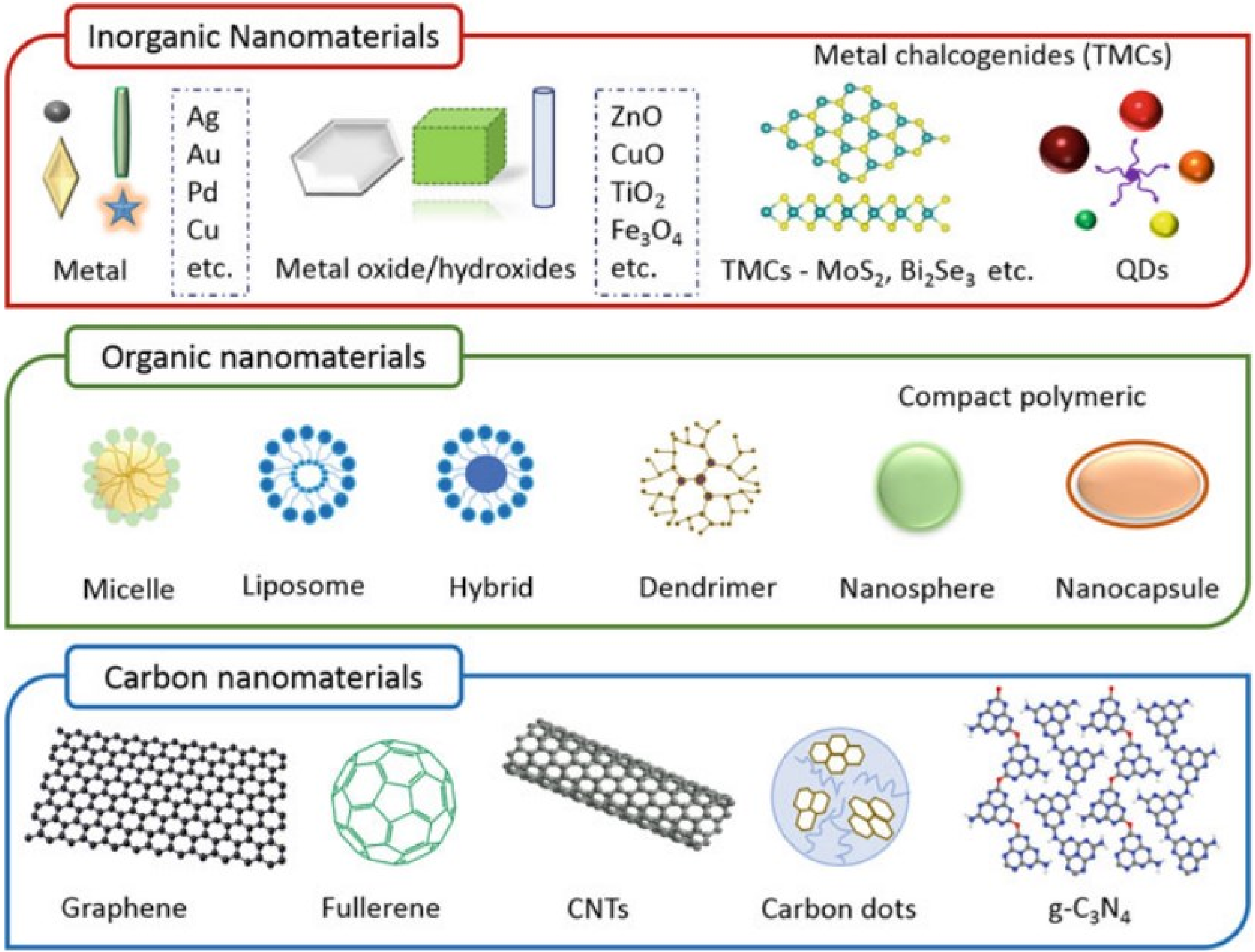


2D Nanomaterials (plate)

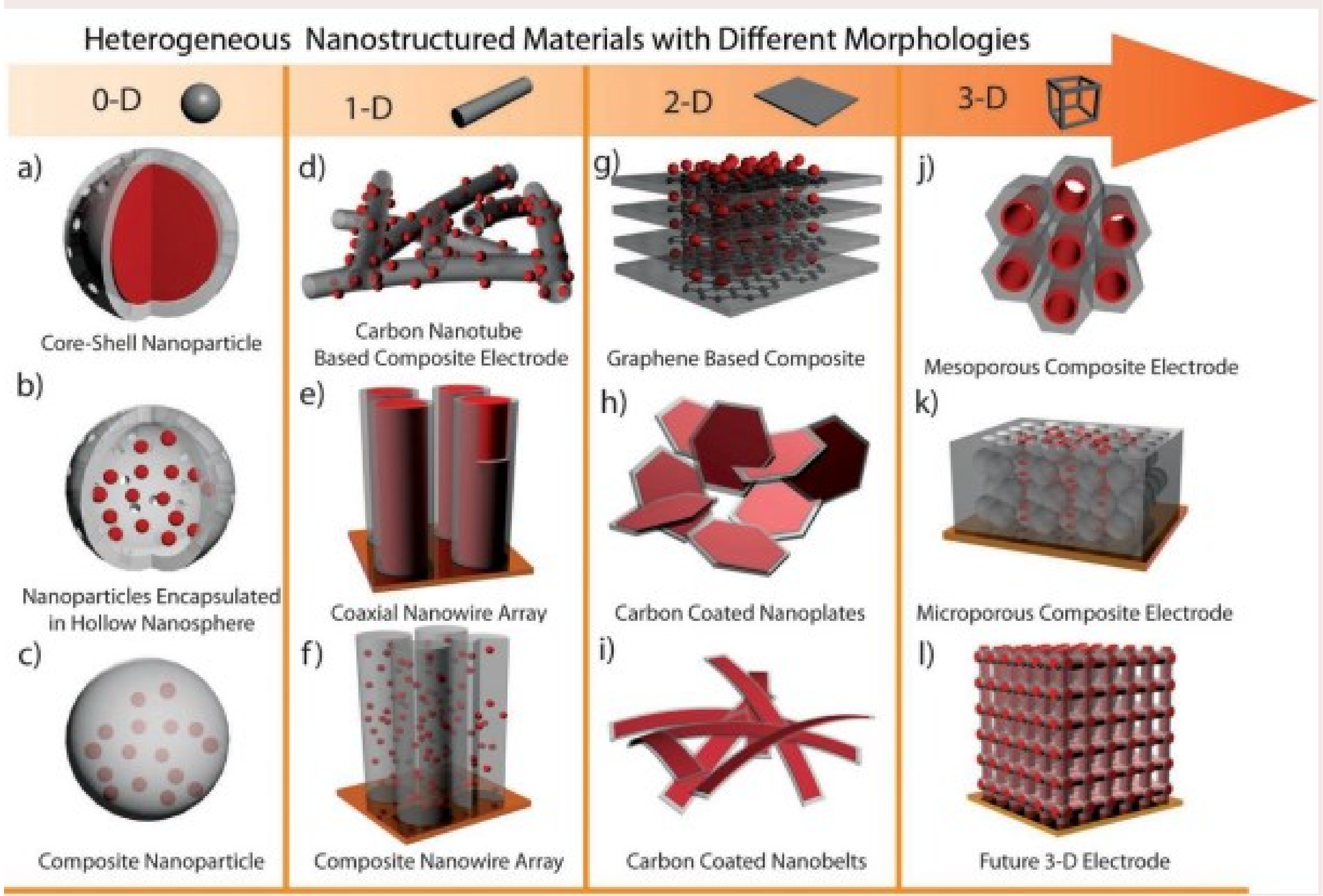


3D Nanomaterials

Nanomaterials: Main Types

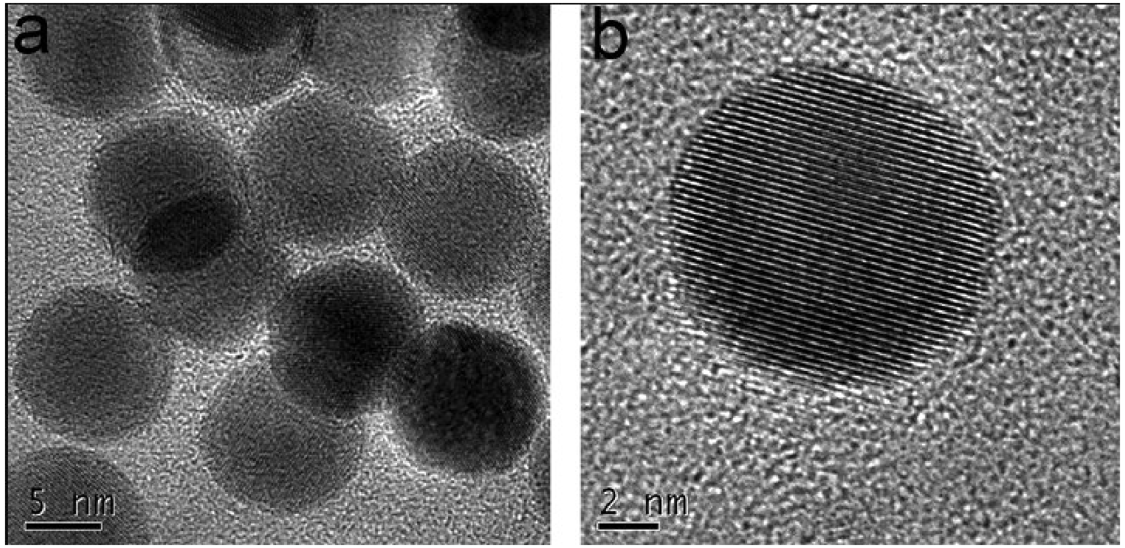


Nanomaterials: Compex Structures



There is a wide spectrum of different morphologies of NM.
The morphology can be explained as a combination of geometric characteristics.

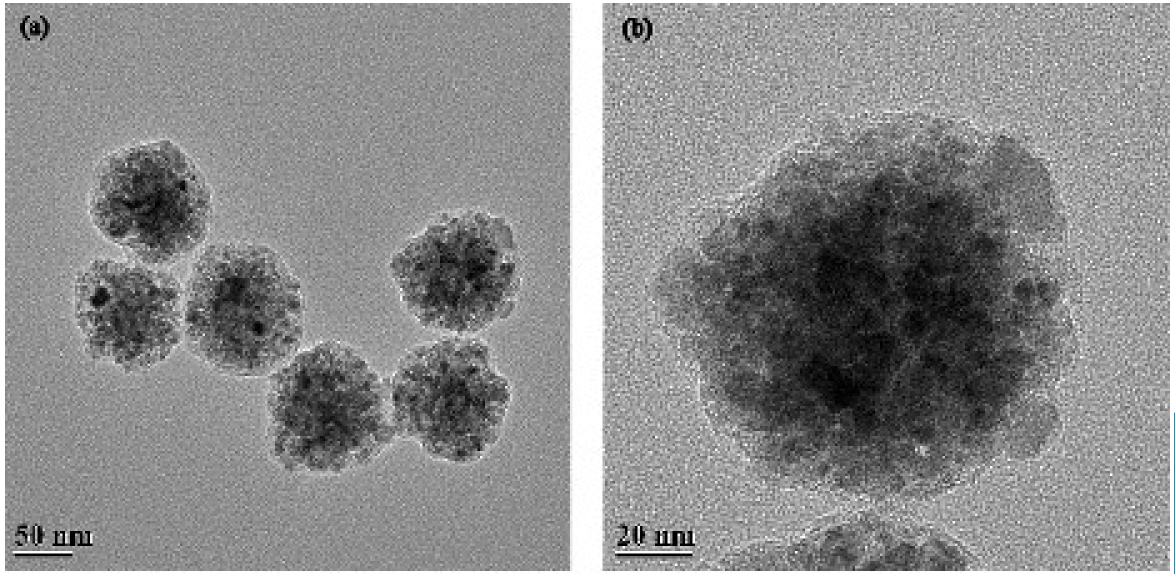
Nanomaterials: Gallery



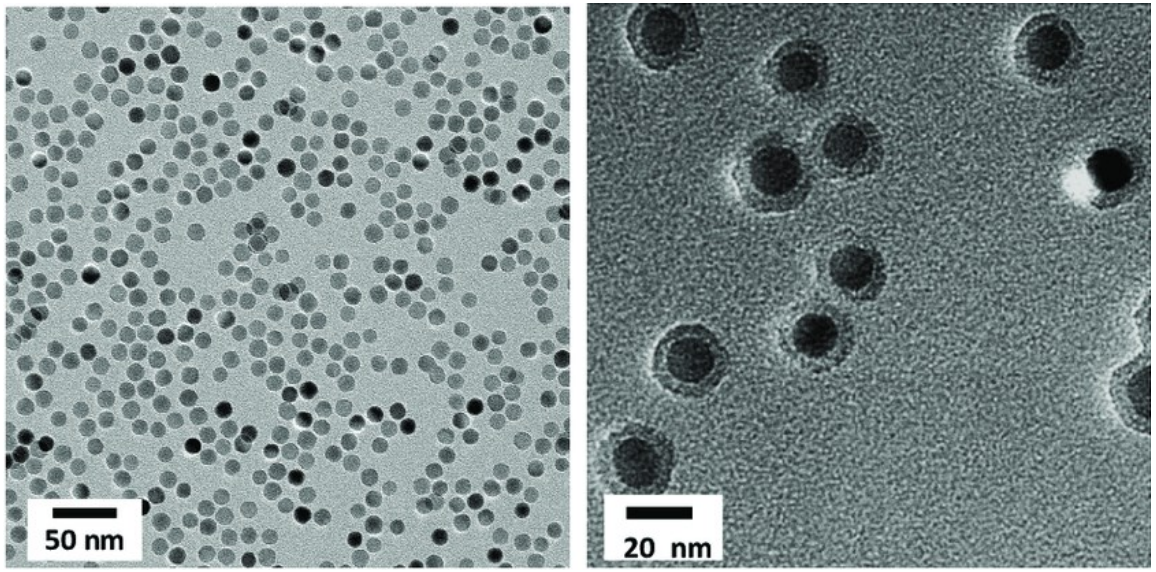
single

0D nanomaterials

single / composite / coated

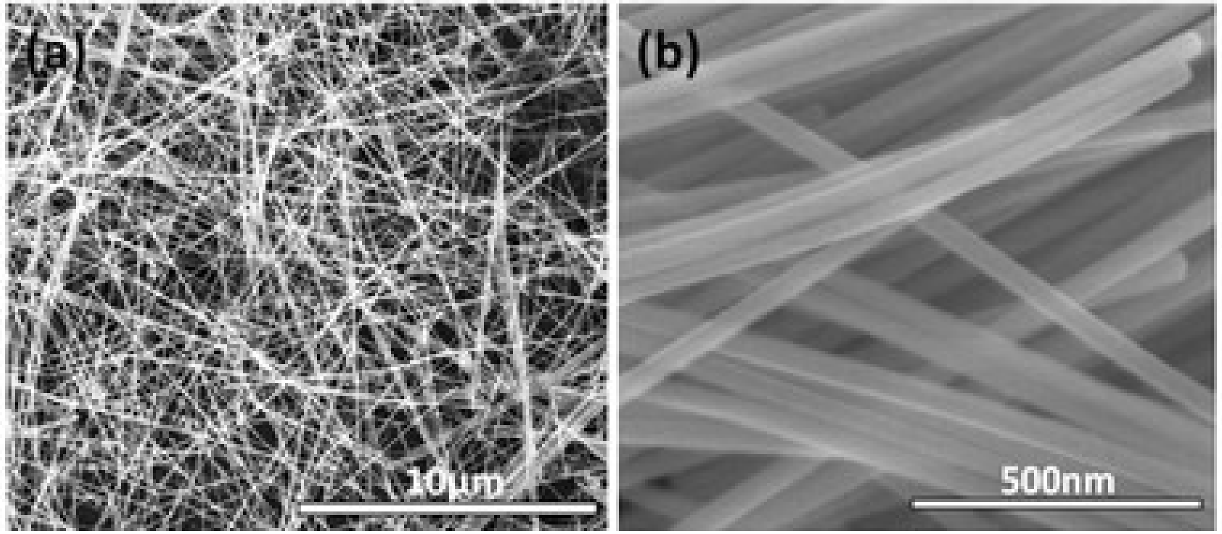


composite



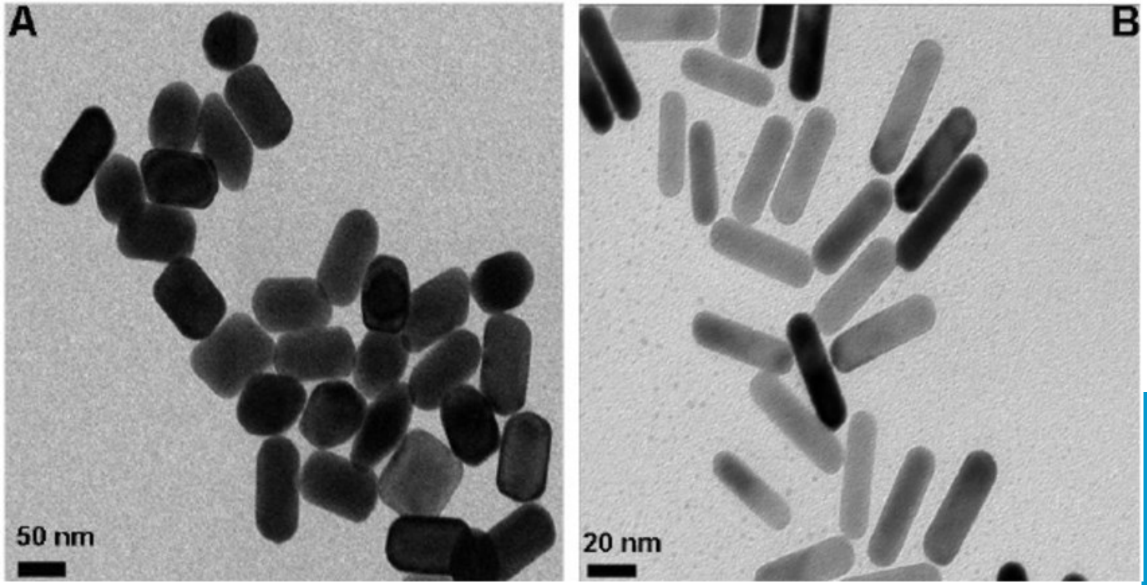
coated

Nanomaterials: Gallery

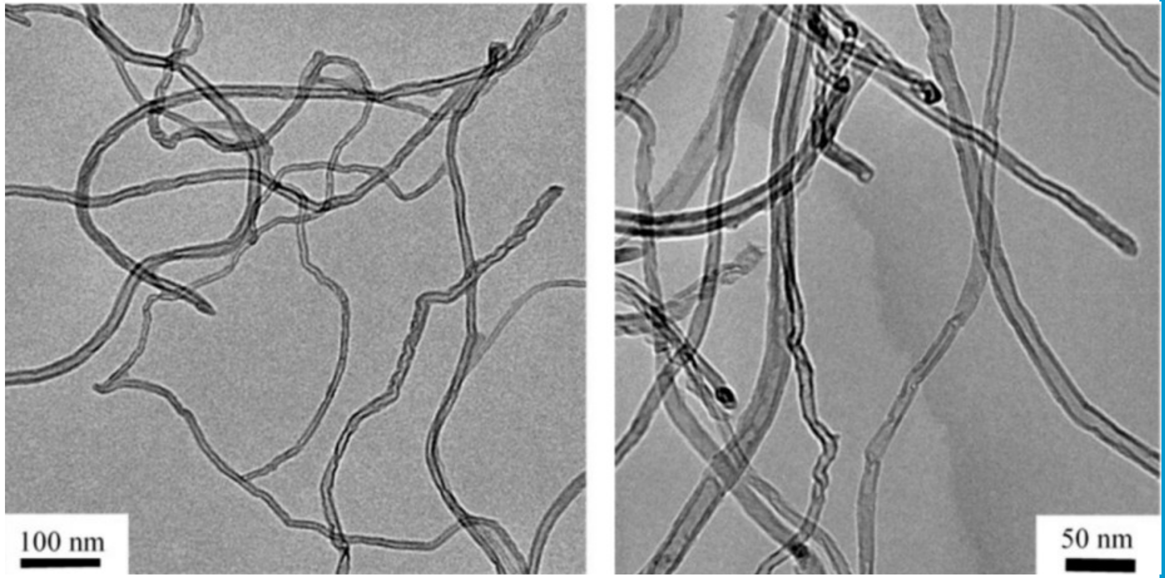


nanowires

1D nanomaterials
nanowires / nanorods / nanotubes

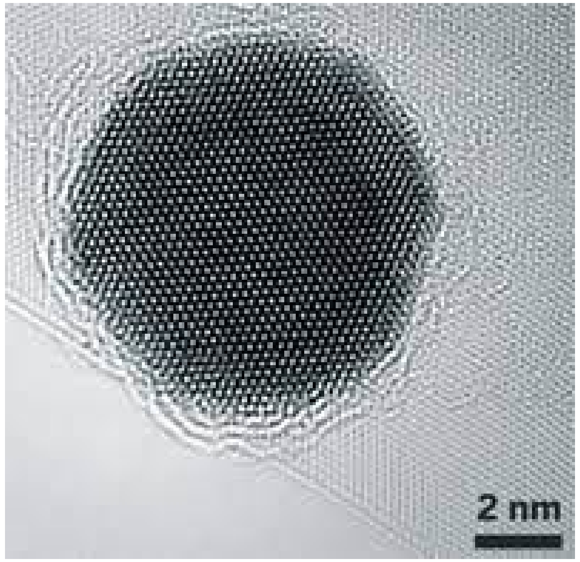


nanorods

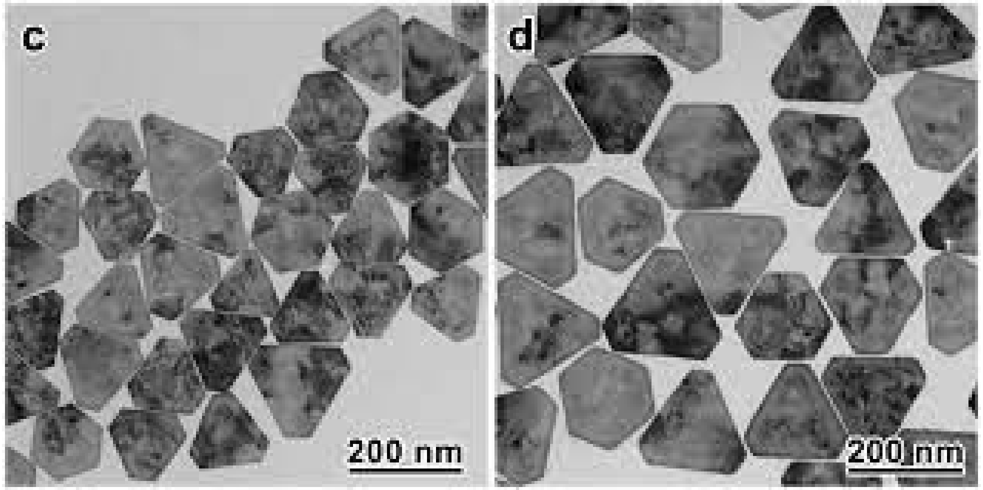


nanotubes

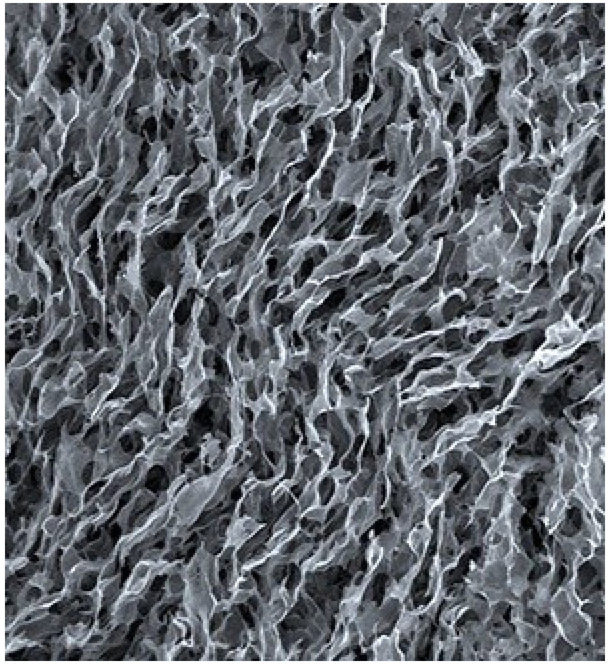
Nanomaterials: Gallery



nanosheets



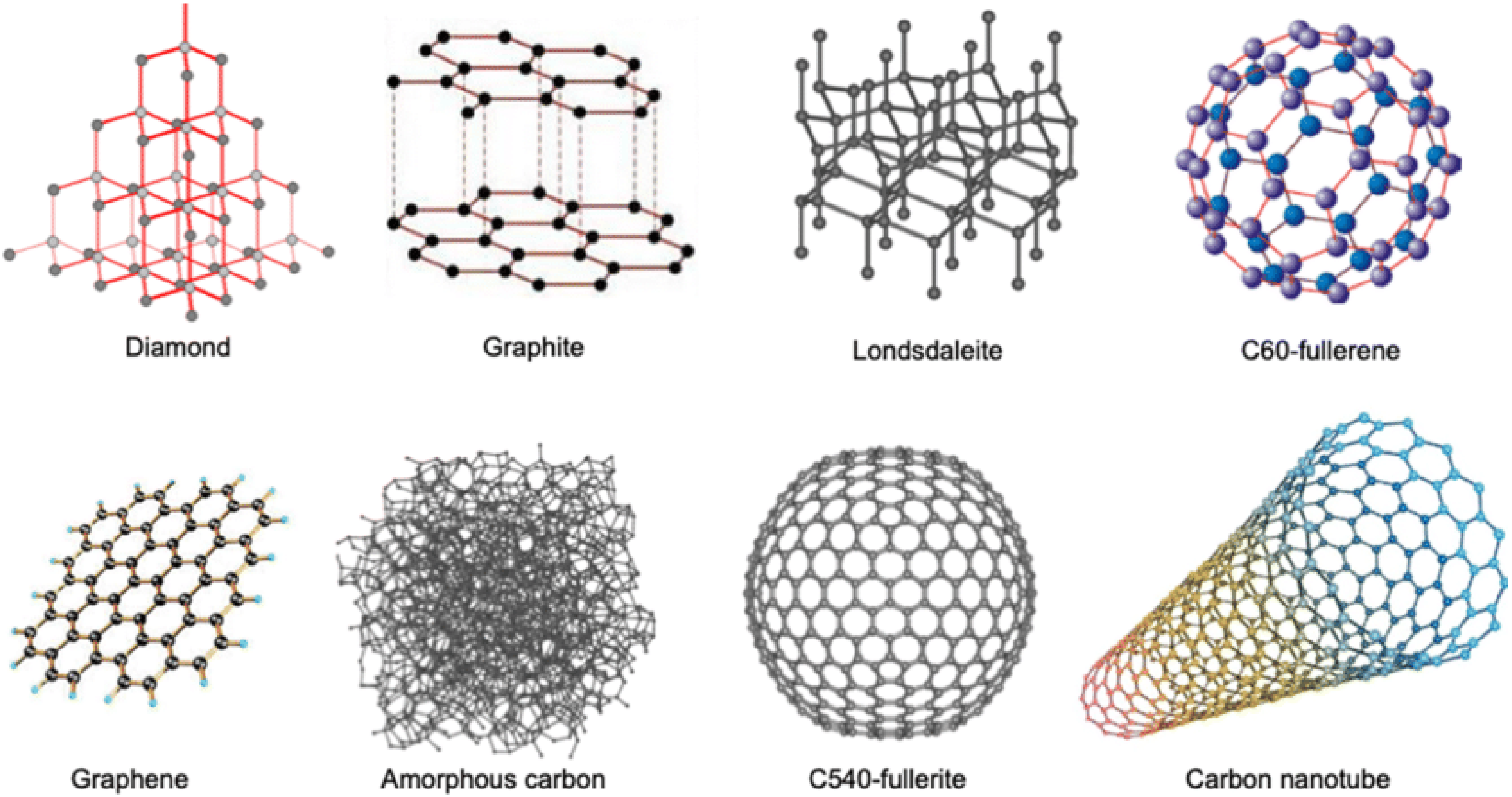
nanoplates



nanogrid

2D nanomaterials
nansheets / nanoplates / nanogrid

Nanomaterials: Gallery



Carbon: allotropes of carbon: 0D to 3D

Nanomaterials: History

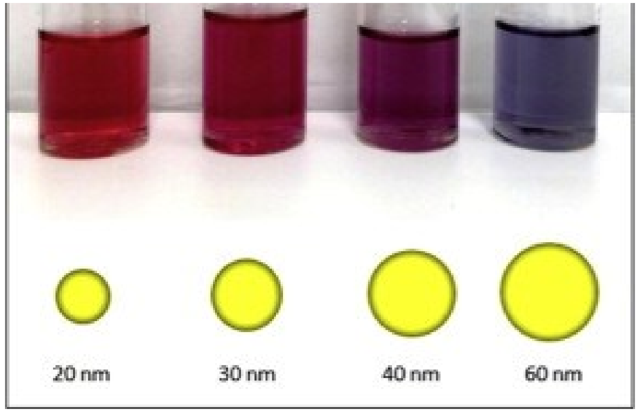
Roman glaziers (4th century) made a "Lycurgus cup" of soda-lime glass dyed with Au and Ag nanoparticles that appears green (in reflected light) and red (in transmitted light).

In the Middle Ages: multi-colored window panes of churches were stained with nanoparticles of various metals.

In the 16th and 17th centuries, an extremely strong yet flexible Damascus sword was made using carbon nanotubes and iron carbide (Fe_3C) nanowires. They were unusually strong, yet flexible enough to bend from hill to tip.

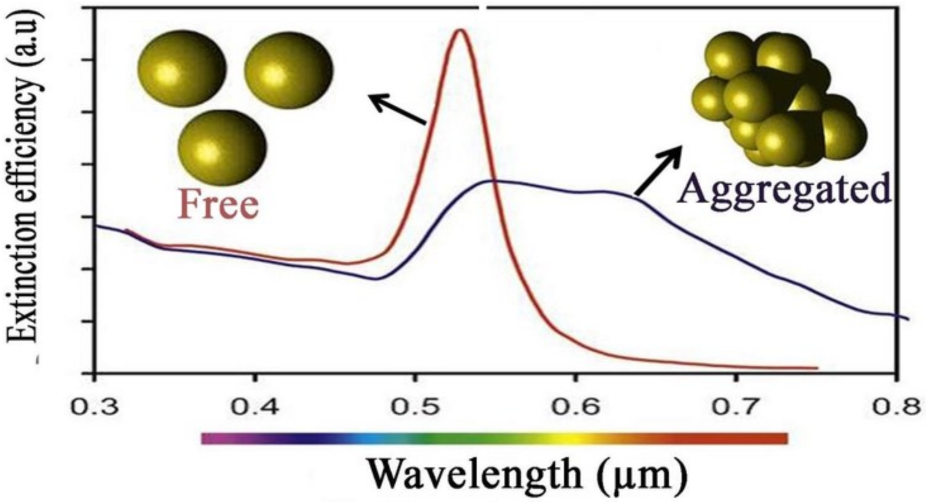
Nanomaterials: History - Optical Properties

Michael Faraday (1857) attributed the color of stained-glass windows to the presence of metallic nanoparticles. He prepared red gold nanoparticles (stored at the Royal Institution in London).



G. Mie (1908) explained the change in the color of glasses by the size of metal particles scattered in glasses.

R.A. Zsigmondy (first decade of the 20th century) studied the optical properties of gold and other nanoparticles and received the Nobel Prize in Chemistry in 1926.



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Nanomaterials: Persons

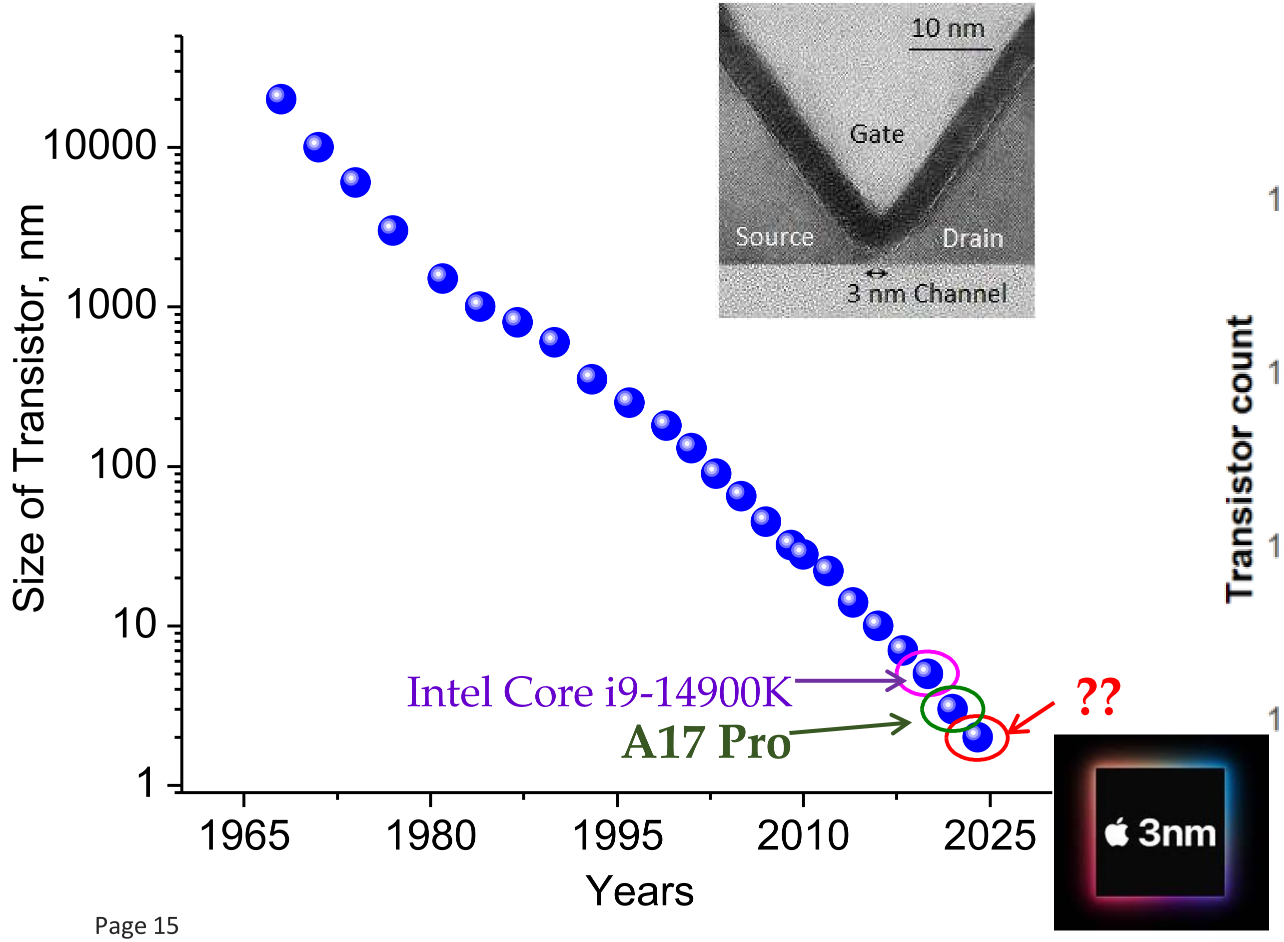
In 1959, the American physicist **Richard Feynman**, in his famous speech "**There's Plenty of Room at the Bottom**: An Invitation to Enter a New Field of Physics“ (a lecture at the annual American Physical Society meeting at Caltech) gave an idea of nanotechnologies, foresaw the possibilities and potentialities of nanotechnologies

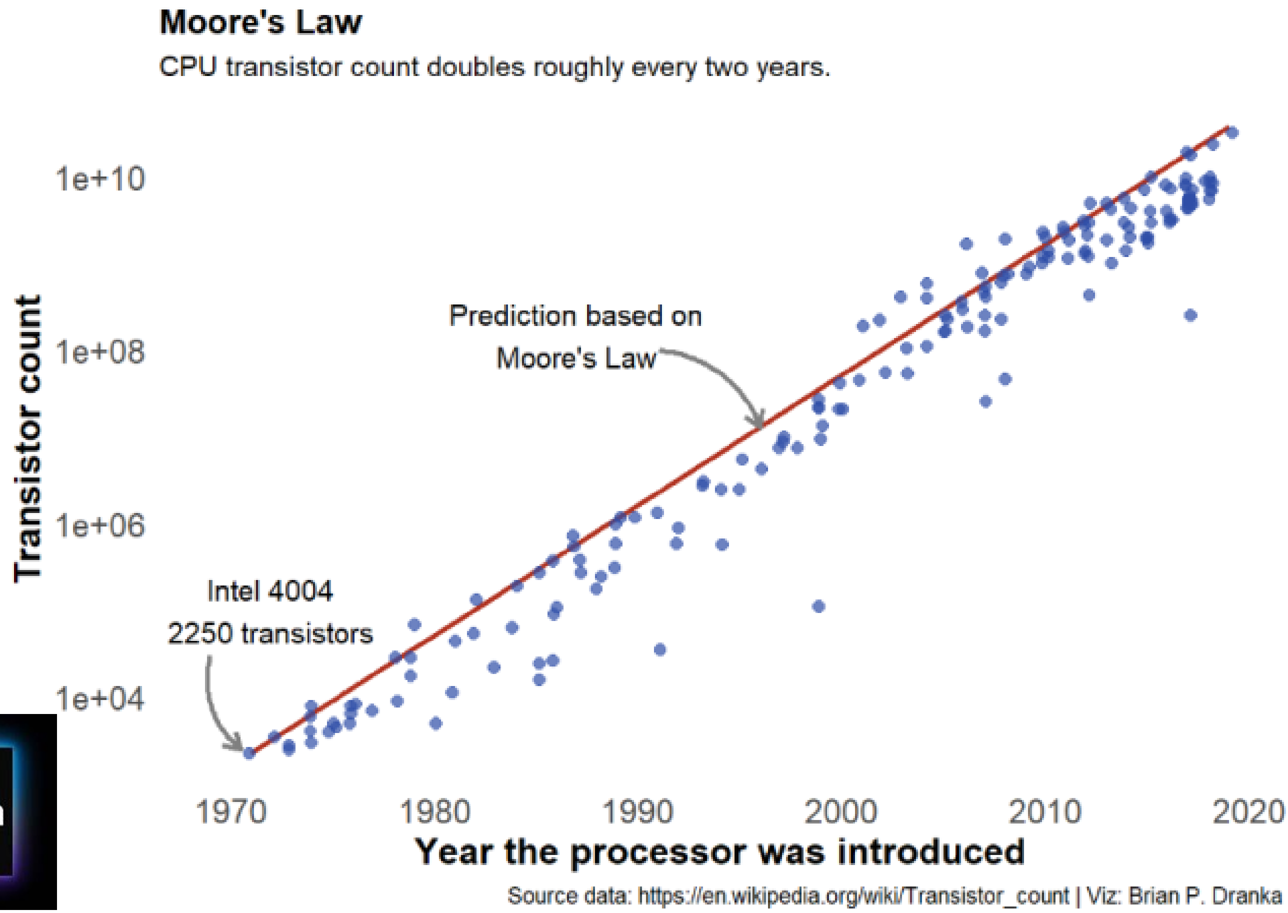
Feynman considered some ramifications of a general ability to manipulate matter on an atomic scale. He was particularly interested in the possibilities of denser computer circuitry and microscopes that could see things much smaller than is possible with scanning electron microscopes. These ideas were later realized by the use of the scanning tunneling microscope, the atomic force microscope and other examples of scanning probe microscopy.

He also presented the possibility of "swallowing the doctor". This concept involved building a tiny, swallowable surgical robot.

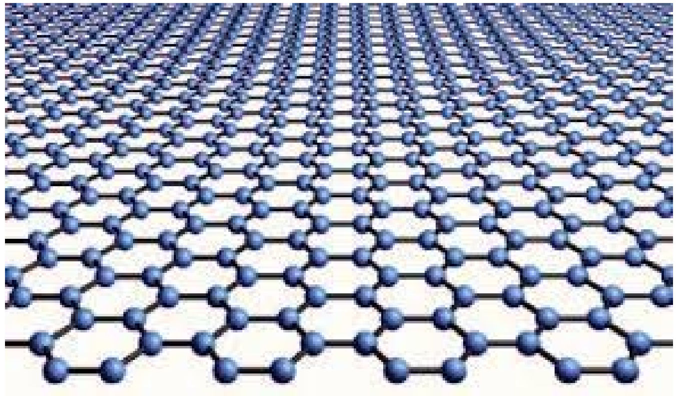
Nanomaterials: Persons

Gordon E. Moore (1965), co-founder of Intel Corporation, made an amazing prediction: the number of transistors on a chip of a given area will double every 1.5 years, that is, the size of a transistor decreases by 2 times every 1.5 years. The size of the transistor is reduced by 2 times every 1.5 years. His prediction indicated that today's transistors would be 1-2 nm in size (this is true, but we have some problems)

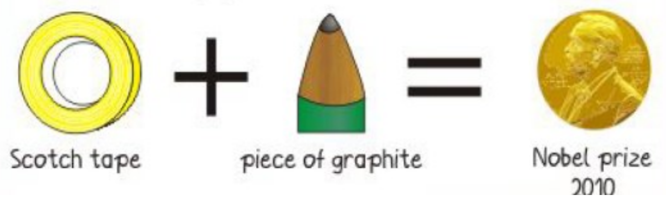




Nanomaterials: Persons



The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "**for groundbreaking experiments regarding the two-dimensional material graphene**"



Andre Geim

Prize share: 1/2

Konstantin Novoselov

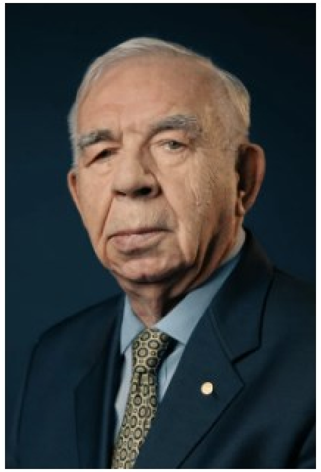
Prize share: 1/2

Moungi G. Bawendi

Prize share: 1/3

Louis E. Brus

Prize share: 1/3



Aleksey Yekimov

Prize share: 1/3

The Nobel Prize in Chemistry 2023 was awarded to Moungi G. Bawendi, Louis E. Brus, and Aleksey Yekimov "**for the discovery and synthesis of quantum dots**"

"**Quantum dots can be seen as one milestone for the whole field of nanotechnology**" said Professor Heiner Linke, a member of the Nobel Committee for Chemistry

A quantum dot is a crystal that often consists of just a few thousand atoms. In terms of size, it has the same relationship to a football as a football has to the size of the Earth.

Bulk vs. Nano

Material properties describe how a material behaves under certain conditions.

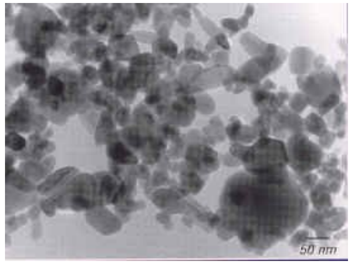
Optical Properties: Example:

Zinc Oxide (ZnO)

Large ZnO particles: block UV light, scatter visible light, appear white.

Nanosized ZnO particles: block UV radiation, are so small compared to the wavelength of visible light that they do not scatter it, appear transparent

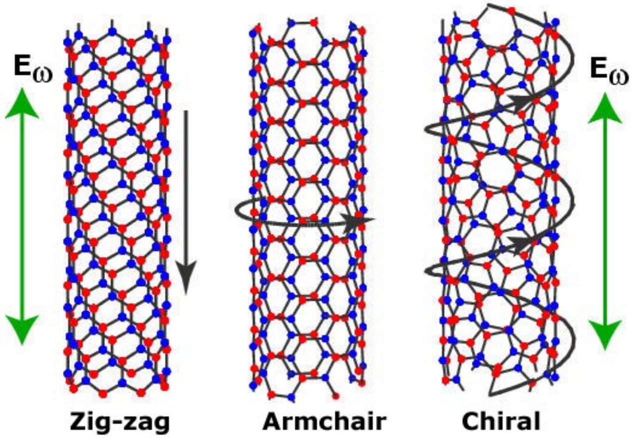
vs.



Application to sunscreen

Mechanical and Electrical Properties Example:

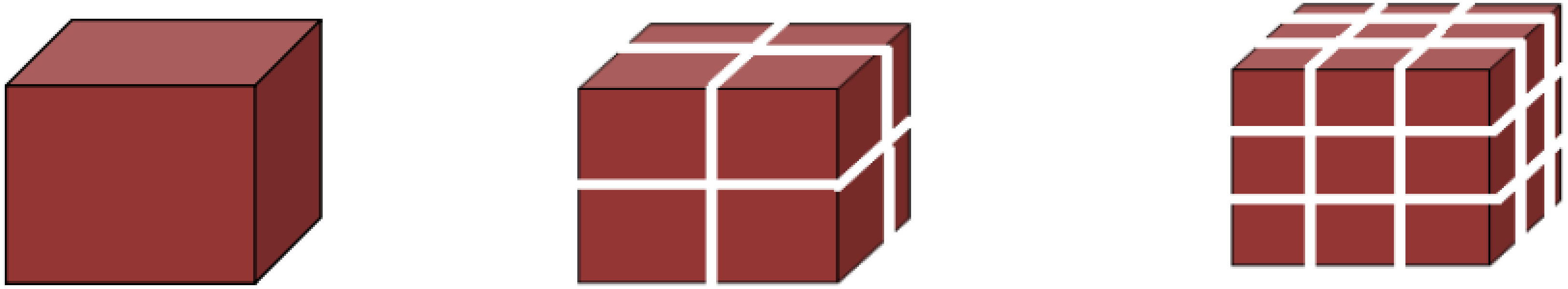
vs.



Nanotubes are long, thin cylinders of carbon. They are 100 times stronger than steel, very flexible, and have unique electrical properties. Their electrical properties change with diameter, "twist", and number of walls. According to their electrical behavior, they can be conducting or semi-conducting.

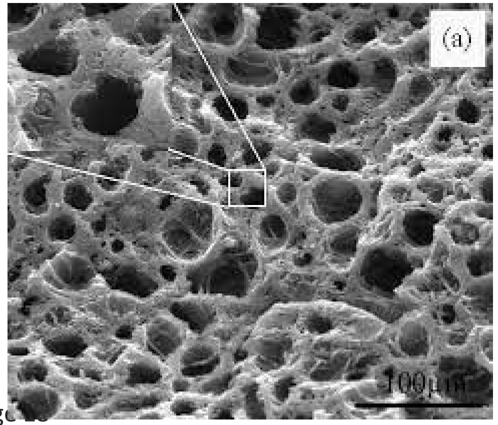
Reasons for Special Properties of Nanoscale Materials

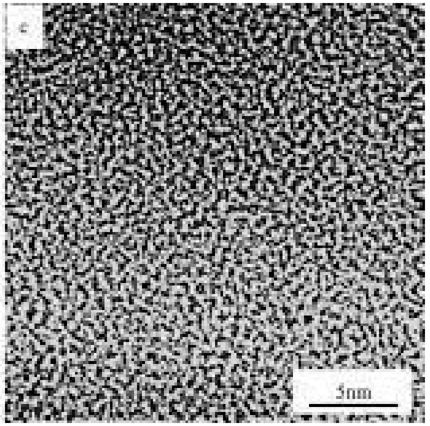
1 Increasing the surface area to volume ratio

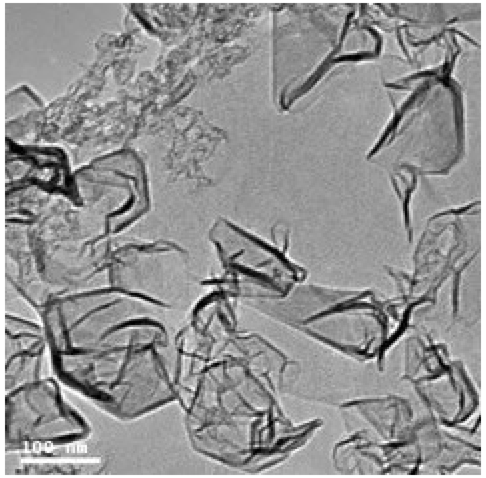


Area = 6 x 1cm^2 = 6 cm^2 Area= 6 x (1/2cm)^2 x 8 =12 cm^2 Area= 6 x (1/3cm)^2 x 27 =18 cm^2

Activated carbon – specific surface area up to 3550 m^2/g *Graphene – specific surface area up to 2630 m^2/g*







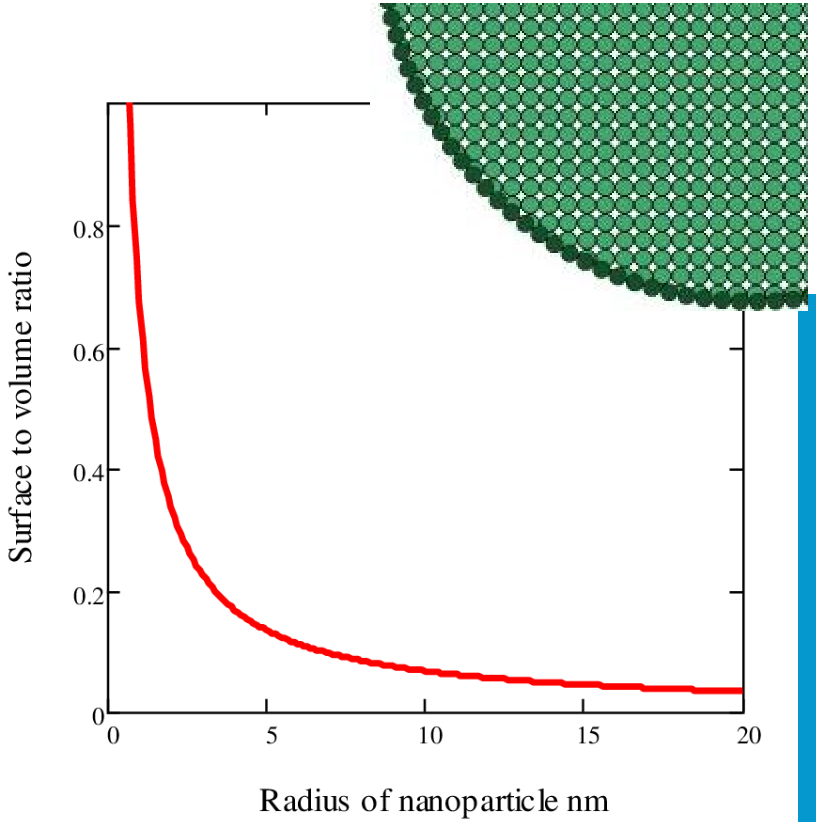
Reasons for Special Properties of Nanoscale Materials

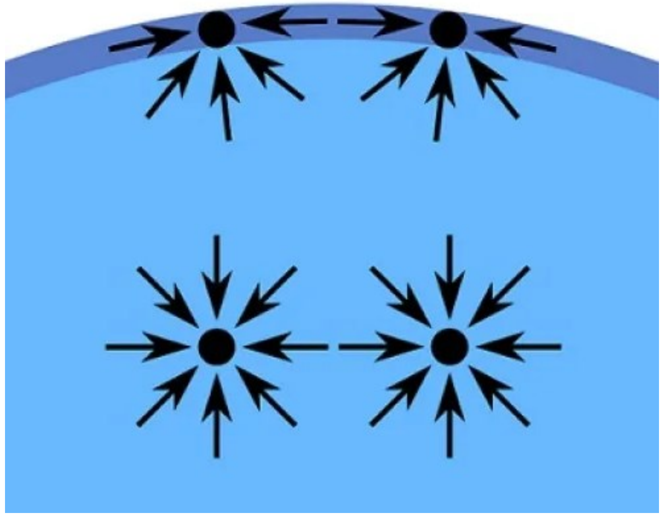
2. Surface tension effect

The larger the sample, the smaller the fraction of atoms on the surface.

Atoms on the surface have fewer neighbors than atoms inside (Students at the edge of the classroom have fewer neighbors than students at the center).

Only atoms on the surface can interact with another material and take part in a chemical reaction (increase in reactivity).





The surface layer has excess energy (surface free energy) compared to the bulk. Reducing the particle causes an increase in its surface energy, which leads to a change in properties.

Reasons for Special Properties of Nanoscale Materials

3. Size effect (particle sizes approached the characteristic length for this material)

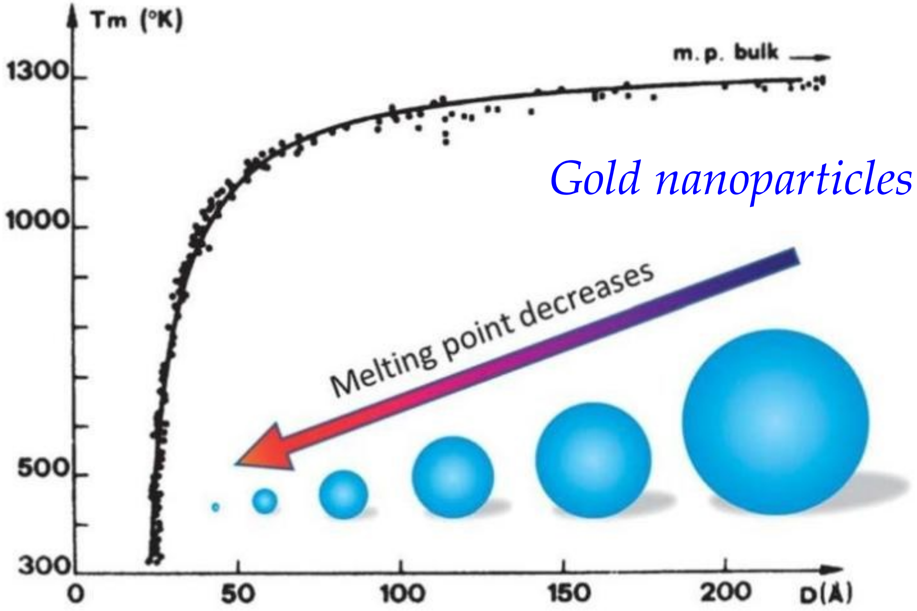
At the nanometer scale, properties become dependent on size.

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

Melting point example

MP is the temperature at which the atoms in a substance have sufficient energy to overcome the interatomic forces that hold them in a "fixed" position in a solid.

On a scale of macroscopic length, the melting point material does not depend on size - both the ice cube and the glacier melt at the same temperature.



Gold nanoparticles

- Surface atoms require less energy to move because they are in contact with fewer atoms of matter.

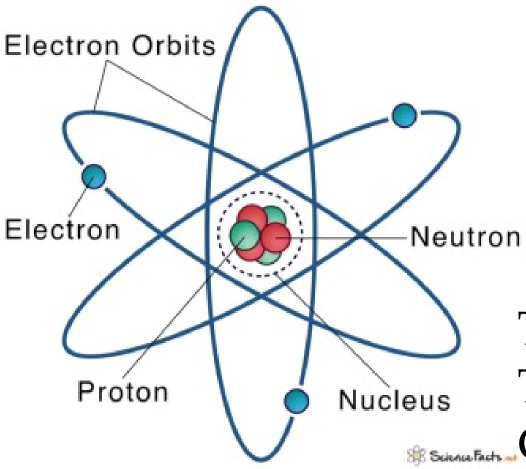
Size decreases → surface energy increases → → melting point decreases

Heat transfer in materials is carried out by two different mechanisms: lattice vibration waves (phonons) and free electrons. Size effects will be observed when the particle size becomes close to the phonon or electron free path.

Quantum Physics: Atom

To explain the effect of *quantum size*, we must take a small leap and imagine what quantum physics is dealing with.

Quantum Physics is a set of laws that explain observations of the tiny building blocks of all matter.
The quantum world should be able to explain the classical world we live in.
To understand the quantum world, we need to understand and believe in the equivalence of a single atom and an electromagnetic wave.



Rutherford’s classical model of atom

Observations show that the atom is basically an empty space with a dense central positively charged structure in the center. The electrons exist outside this nucleus and revolve around it like planets around the sun.

The problem with the classical model

The electron has a negative charge and revolves around a central positive nucleus.
The nucleus has a charge and therefore has a magnetic field.
Charged particles lose energy when passing through a magnetic field.
According to the classical electromagnetic theory, an electron must lose energy in its orbit and fall into the nucleus.

Observations

An atom is a stable structure made up of subatomic particles that do not normally decay during our lifetime.

Conclusion

Because the observation does not match the theory…. either classical physics is wrong, or Rutherford's model is wrong/incomplete.

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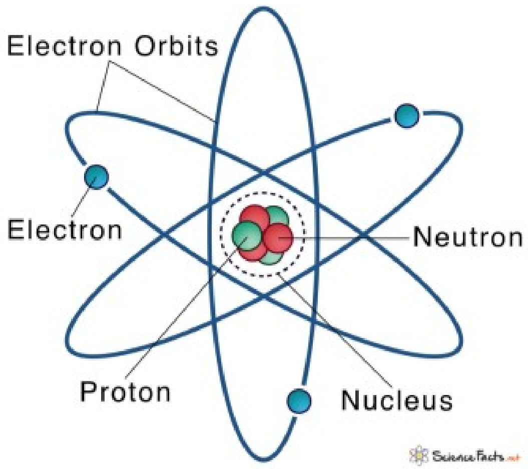
Quantum Physics: Atom



What is easier to believe?

Hundreds of years of laws and theories of physics are wrong.

OR

Rutherford's classical model of the atom of our atom is wrong.

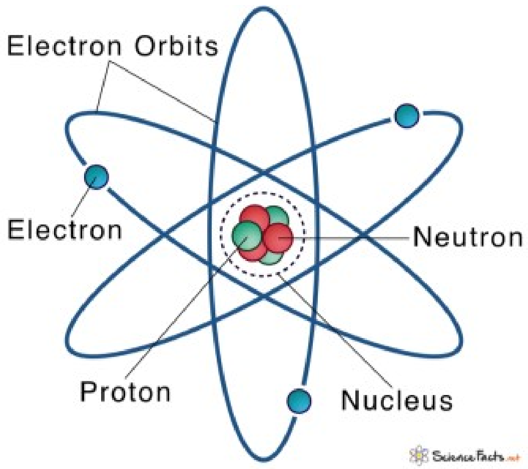
Answer:

Both classical physics and Rutherford's model have some flaws.

But this is our idea of the atom for the most part wrong ....

The ingenious ideas of Max Planck (1918 Nobel Prize for the discovery of the quantum nature of energy)

Quantum Physics: Atom



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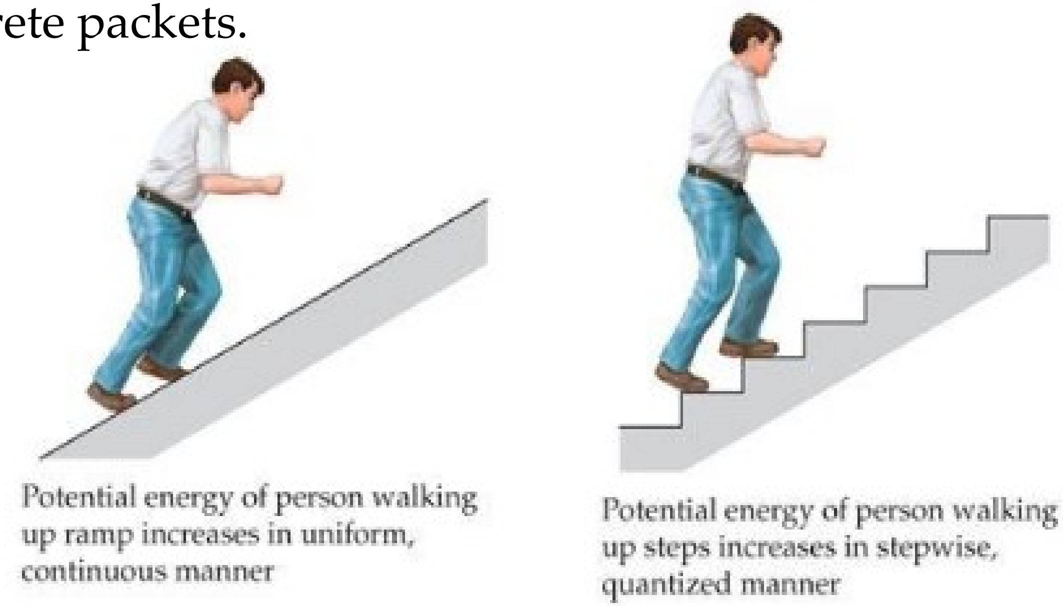
The ingenious ideas of Max Planck (1918 Nobel Prize for the discovery of the quantum nature of energy)

Energy is not a continuous stream but consists of chunks or discrete packets.
Energy is quantized (quanta flow)

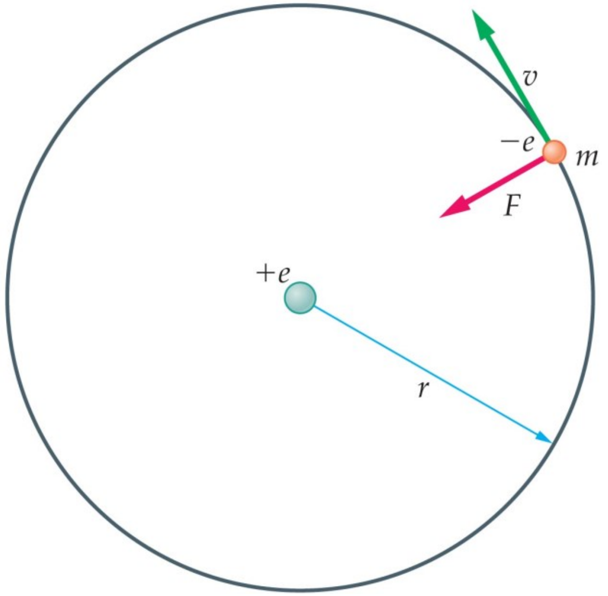
Electrons can only have a certain discrete amount of energy
Each energy quantum can be defined as $E = hf$

- E is the energy of the quanta (J or eV)
- f is the frequency of vibration
- h is Planck's constant (6.626×10^{-34} Js)

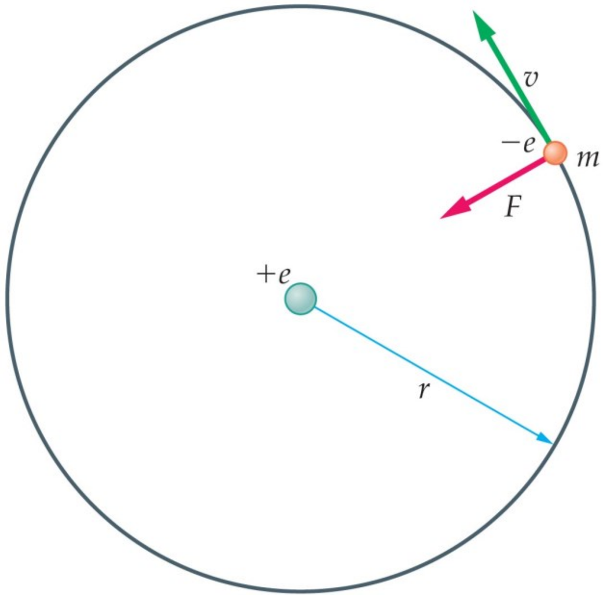


Quantum Physics: Atom

Bohr model of the atom



Quantum Physics: Atom



Bohr model of the atom

An electron in an atom moves in a circular orbit around the nucleus, m, υ and *e* are the mass of the electron, the speed in the orbit and the charge, r is the radius of the orbit

As a result, the electron experiences a centripetal acceleration towards the nucleus of magnitude $a = \upsilon^2/r$.

We know from Newton's second law that a force $F = ma$ is required to create an acceleration.

In this case, the electrostatic force is $F = ke^2/r^2$ (*k is constant*).

Combining these results, we have the following relation: $ke^2/r^2 = mv^2/r$

Bohr then suggested that the angular momentum in the allowed orbit should be an integer *n* (the quantum number) times $h/2\pi$, where *h* is Planck's constant. Since the electron moves with a speed *v* in a circular path of radius *r*, its angular momentum is $L = m\upsilon r$.

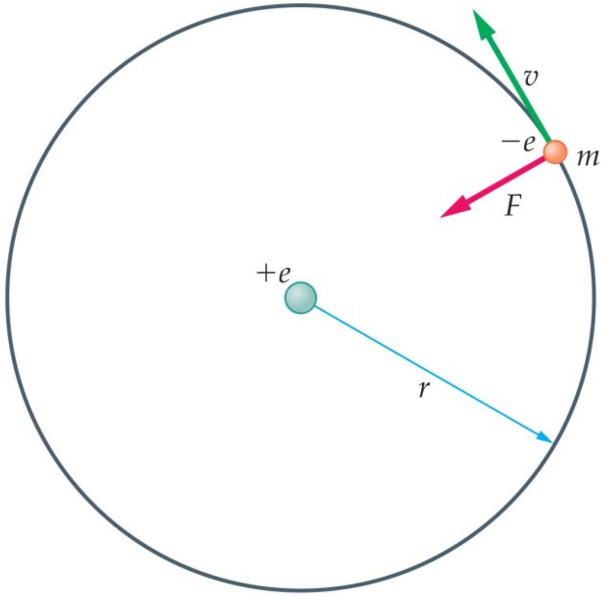
Thus, this condition is $m\upsilon r = n(h/2\pi) = n\hbar$

Combining the force and angular momentum equations, we can find the radii of the allowed orbits.

The result is $r_n = (h^2/(4\pi^2 mke^2))n^2 \quad n = 1, 2, 3, \ldots$

Conclusion : Only certain circular orbits are allowed

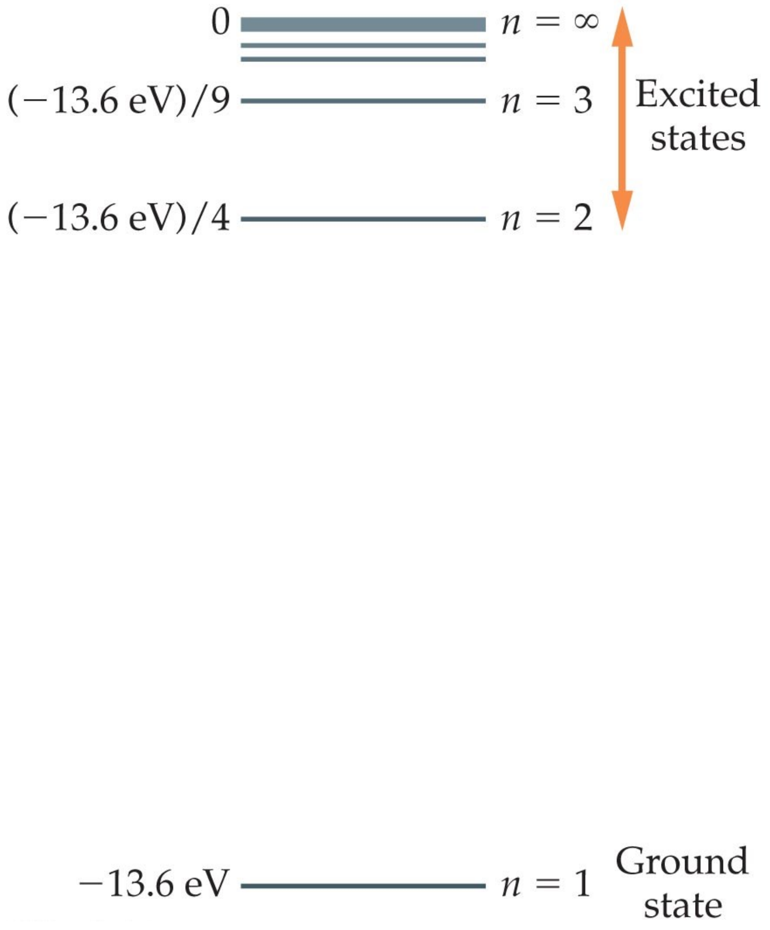
Quantum Physics: Energy of Atom

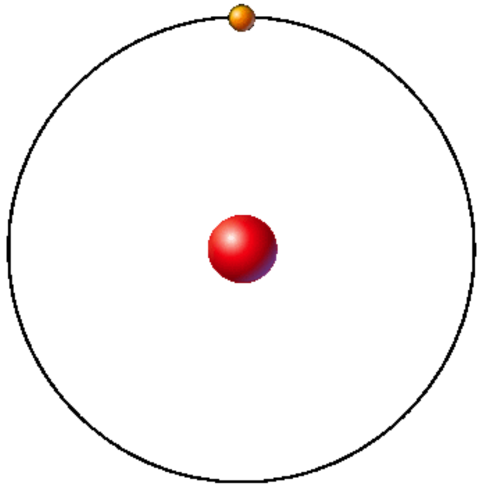


The total energy of the hydrogen atom is also quantized. In fact, a direct calculation combining the kinetic energy ($m\upsilon^2/2$) and potential energy ($-ke^2/r$) shows that the total energy of the n-th Bohr orbit is

$$E_n = -(2\pi^2 mk^2e^4/h^2)/n^2 = -constant/n^2$$

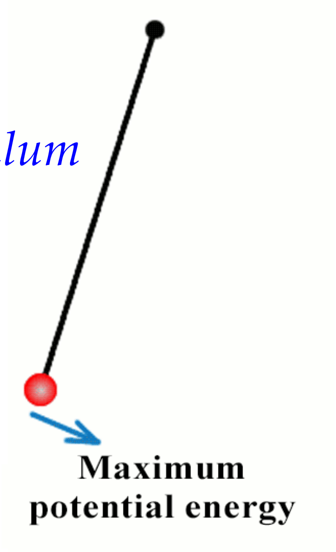
These energies are shown in the figure for various values of n



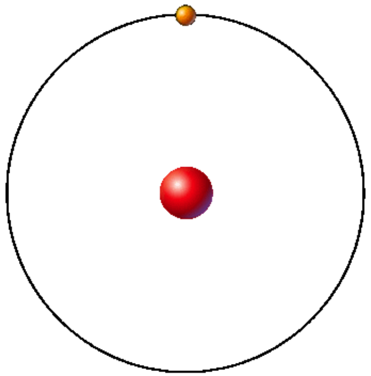


Oscillator

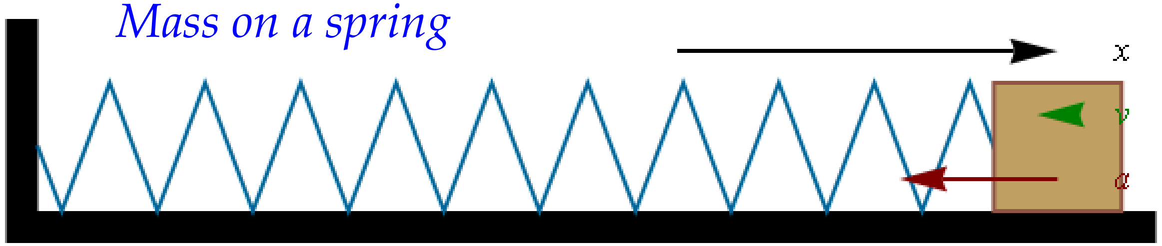
Pendulum



Electron in atom



Mass on a spring



Oscillation is a periodic movement in which the state of the system is repeated at regular intervals.

Description of Periodic Motion

The duration of one cycle is the period T

The reciprocal of the period is the frequency $f = 1/T$

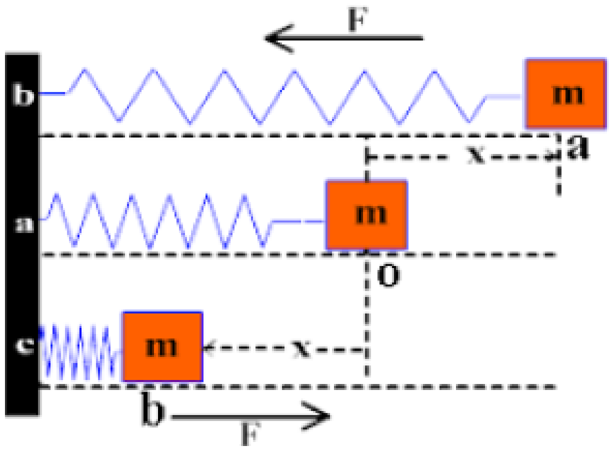
Frequency is how many cycles per unit of time (1 second) the system goes through

The maximum displacement is determined by the amplitude A

Angular frequency $\omega = 2\pi f = 2\pi/T$ is how many cycles the system goes through in 2π

Examples of harmonic oscillators. Yes, the orbiting electron is an oscillation

Oscillator: Classical Approach



Classical Harmonic Oscillator

If the spring is unbalanced and released, it will make a harmonic motion.

Pull the spring to the right and it will try to regain its length: For $\boldsymbol{x} > 0$, $\boldsymbol{F} < 0$ *(Left force)*
In equilibrium: $\boldsymbol{x} = 0$, $\boldsymbol{F} = 0$ *(No force)*
Move the spring to the left and it will try to regain its length: For $\boldsymbol{x} < 0$, $\boldsymbol{F} > 0$ *(Right force)*
This is summarized by Hooke's Law: $\boldsymbol{F} = -\boldsymbol{kx}$, *k is spring constant [N/m]*

$$F = -kx$$

$$F = ma = m\frac{d^2x}{dt^2}$$

$$m\frac{d^2x}{dt^2} = -kx$$

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x \equiv -\omega^2 x$$

$$\omega = \sqrt{\frac{k}{m}}$$

Natural angular frequency of a harmonic oscillator

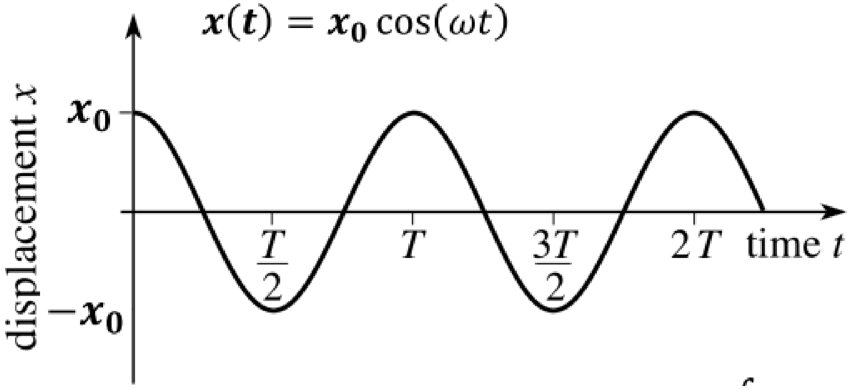
The solutions to this 2nd order differential equation are the sines and cosines

$$x(t) = A\sin(\omega t) + B\cos(\omega t)$$

Initial conditions

$$x(0) = x_0 \text{ and } \dot{x}(0) = 0$$

$$\mathrm{B} = x_0 \text{ and } \mathrm{A} = 0$$



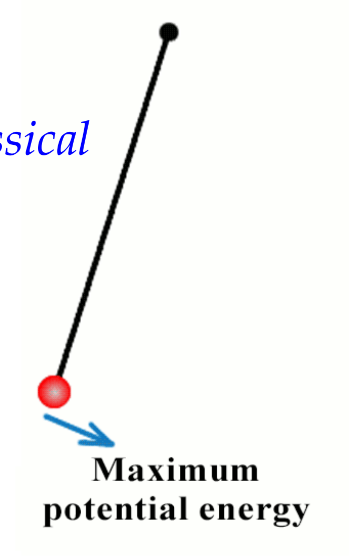
Mass on a spring

Potential energy (interaction) $V(x) = \frac{1}{2}kx^2$

Kinetic energy (motion) $T(x) = \frac{1}{2}m\dot{x}^2$

Harmonic Oscillator - Classical to Quantum Transition

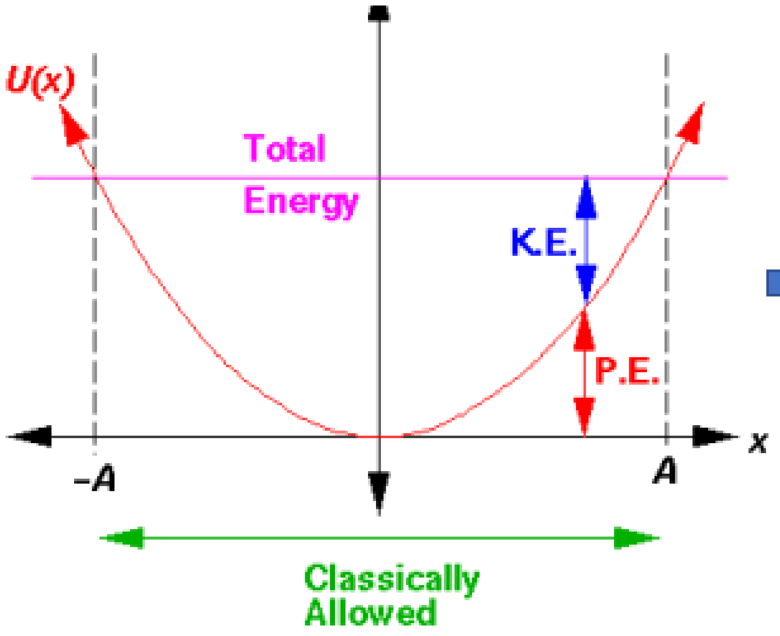
Classical



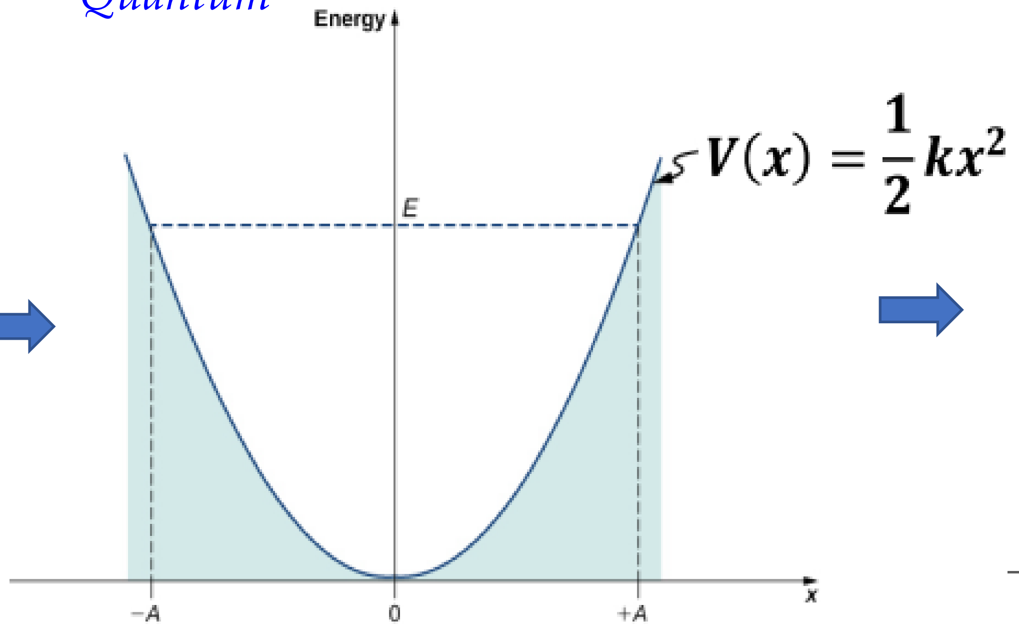
The energy of the pendulum (*harmonic oscillators*) at any time is equal to the *sum of the potential and kinetic components*

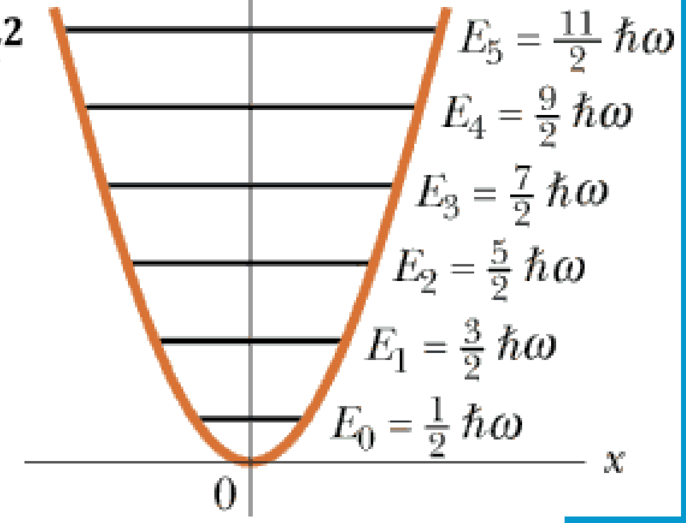
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \text{ where } n = \mathbf{0}, 1, 2, 3, \ldots$$

*Note that **n** starts at 0*

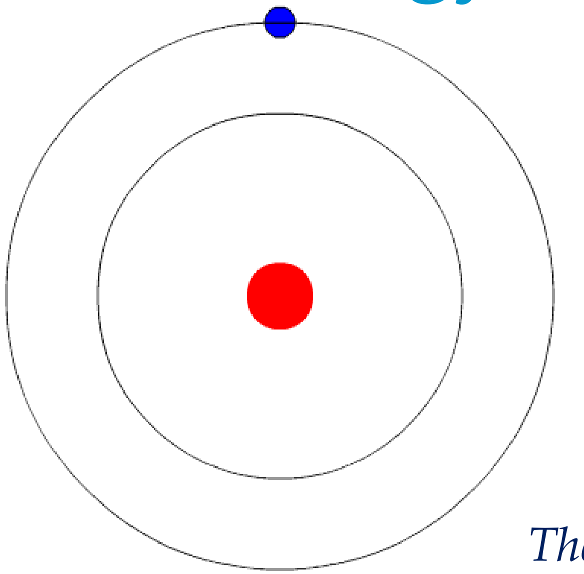


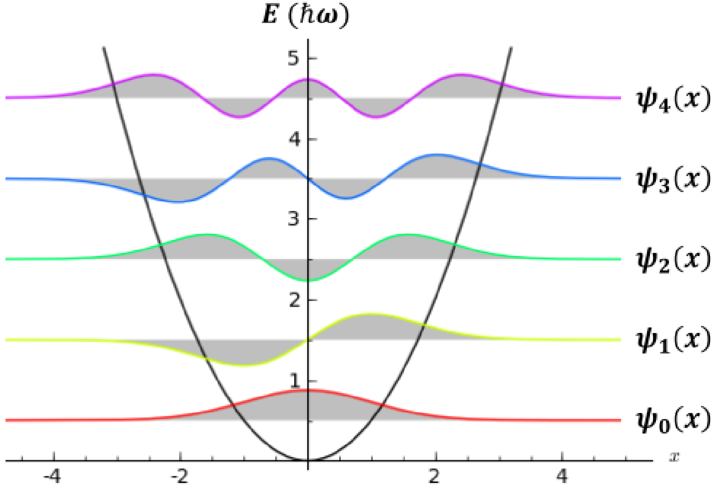
Quantum

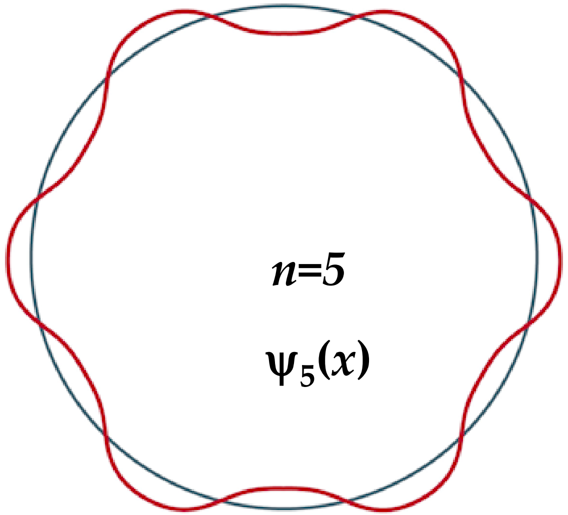




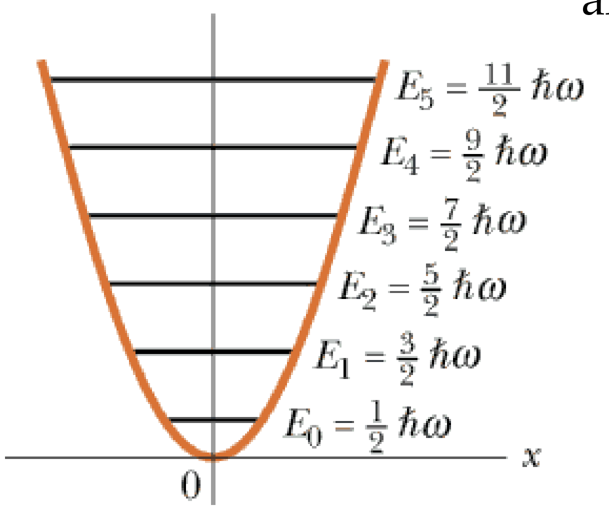
Energy of Electron in Atom







The energy of an oscillator (electrons in an atom) can only have certain discrete values of E_n
Energy is quantized, each discrete value of energy corresponds to different orbitals and different quantum states.



$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \text{ where } n = 0, 1, 2, 3, \ldots$$

Important conclusions

1. *An electron in an orbital is equivalent to a standing wave propagating along the orbital.*
2. *When electrons behave like standing waves, they no longer radiate energy in the form of radiation - as this applies to particles (de Broglie's idea).*
3. *A change in the energy of an electron is equivalent to a change in the quantum state.*
4. *A change in the energy of an electron is possible due to the emission or absorption of energy by an atom in the form of electromagnetic waves.*

Particle = Wave

Any piece of matter moving at any speed can exhibit wave properties.
Bridge between classical physics and quantum mechanics.
Effects for classical particles are too small to be observed.
A quantum particle, an electron, is not only a particle, but also exhibits a wave nature.

The de Broglie wavelength of the particle is $$\lambda = \frac{h}{m\upsilon}$$

$$E = mc^2 = hf$$

$$f = \frac{mc^2}{h}$$

TASK!

Find the de Broglie wavelength for a person with a mass of 70 kg traveling at about 1 m/s

$\lambda = 9.466 \times 10^{-36}$ *meters*

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Particle = Wave

Davisson-Germer Experiment

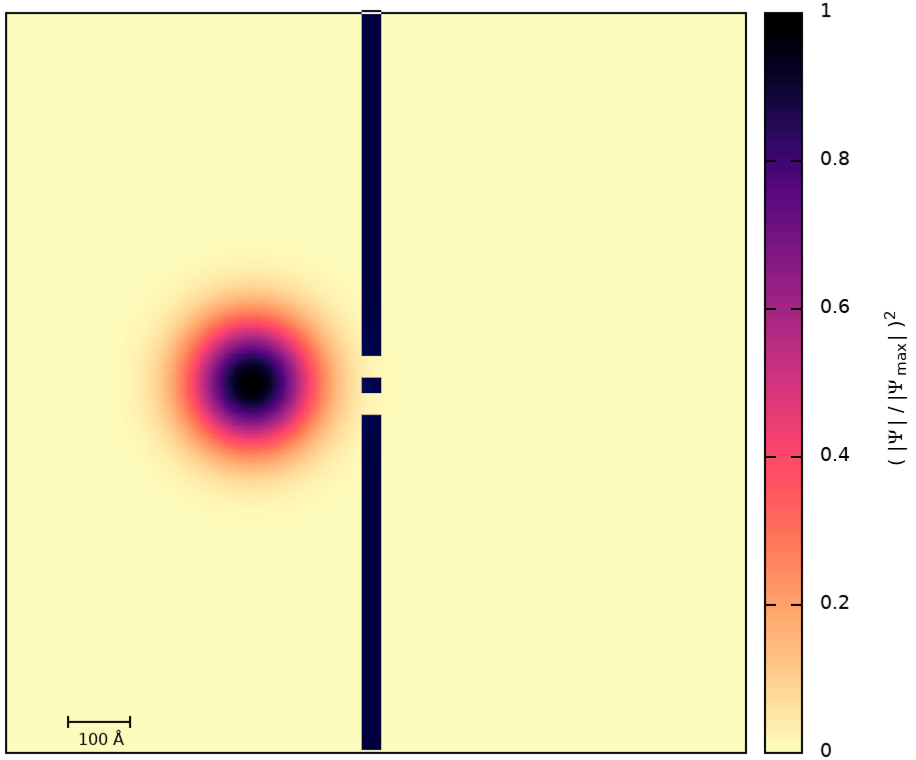
If the particles are of a wave nature, then under the right conditions they should exhibit diffraction effects.

Davisson and Germer measured the wavelength of electrons.

This confirmed the hypothesis, advanced by Louis de Broglie in 1924, of wave-particle duality

The principle of complementarity states that the wave and corpuscular models of matter or radiation complement each other.

None of the models can be used solely to adequately describe matter or radiation.



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The Uncertainty Principle

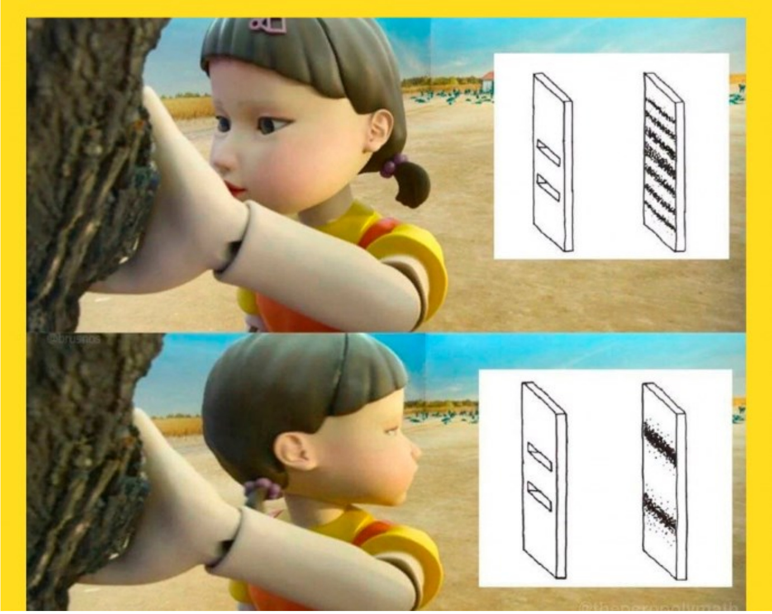
In classical mechanics, one can make measurements with an arbitrarily small uncertainty.
Quantum theory predicts the fundamental impossibility of simultaneous measurements of the position and momentum of a particle with infinite accuracy.

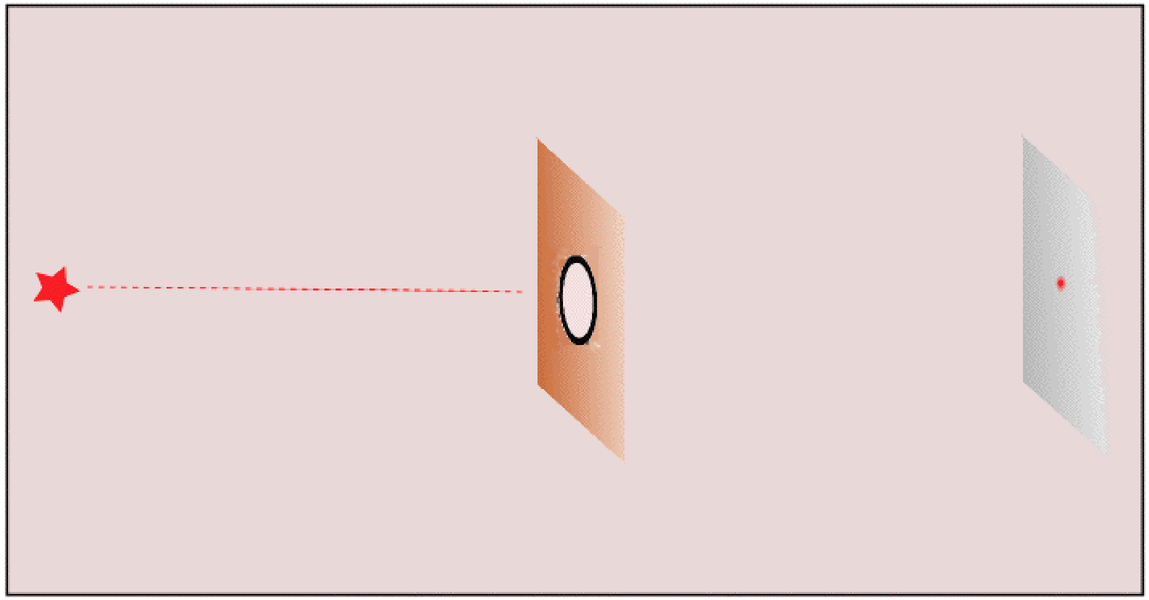
The Uncertainty Principle

The Heisenberg uncertainty principle states that if a particle's position is measured with an uncertainty Δx and x-component of its momentum is simultaneously measured with an uncertainty Δp_x, the product of this two uncertainties can never be less than $\hbar/2$

Classical system - electron trajectory after slit is *definite*
Quantum system - electron trajectory after diffraction is statistically *uncertain*

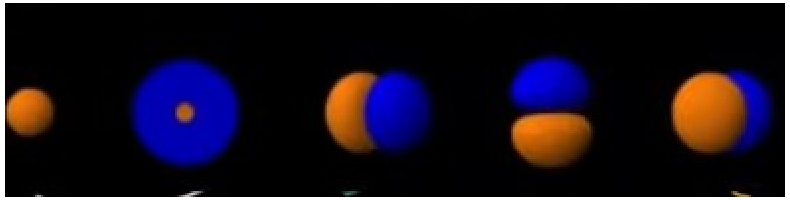
The combination of wave functions, uncertainty principle, probability distributions, and the wave-particle duality provide a powerful framework for understanding the behavior of particles at the quantum level.





Uncertainties arise from the quantum structure of matter.

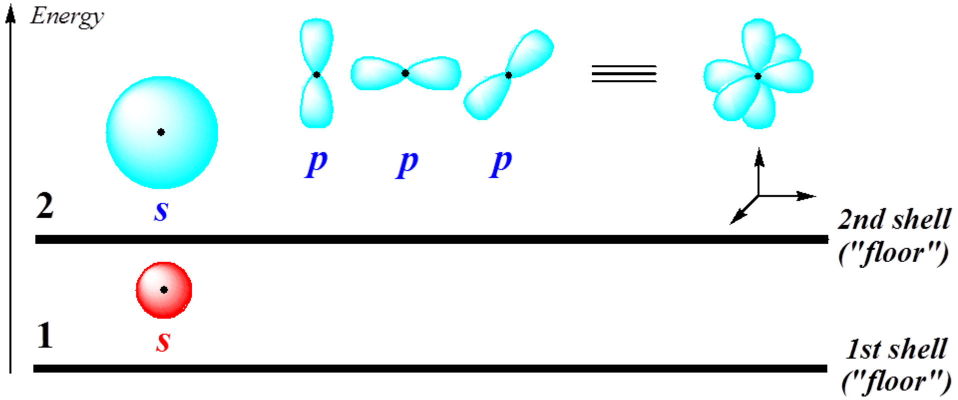
Electrons in Atom



Each electron shell is composed of ***subshells***, *which in turn are made up of* ***orbitals***. *The electronic system of the atom can be compared to a multistorey hotel building. Each floor of the hotel has rooms of different types (classes). All rooms within each class are identical, but different from rooms in another class.*

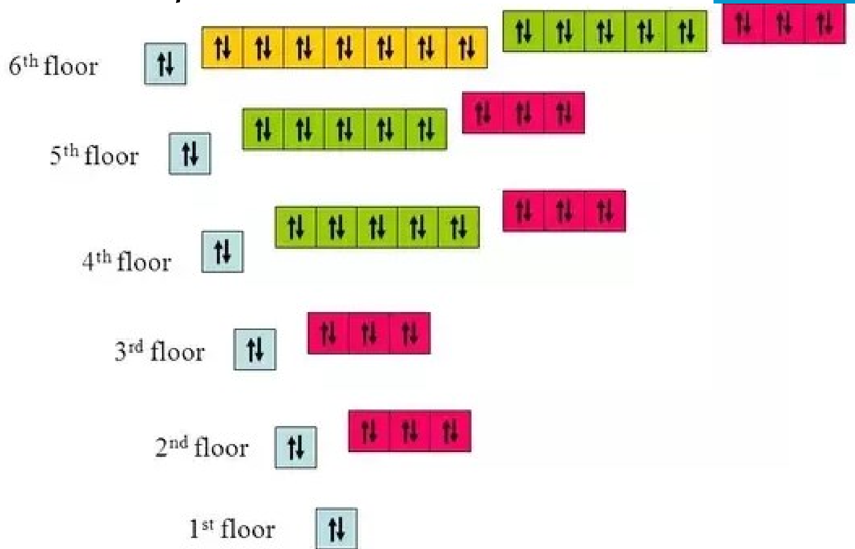
So, we think like this:

- The hotel building = *atom*
- Each floor of the building = *electron shell*
- Each set of identical rooms (of the same class) within a floor = *electron subshell*
- Each room, regardless of its type = *orbital*
- Each hotel guest = *electron*



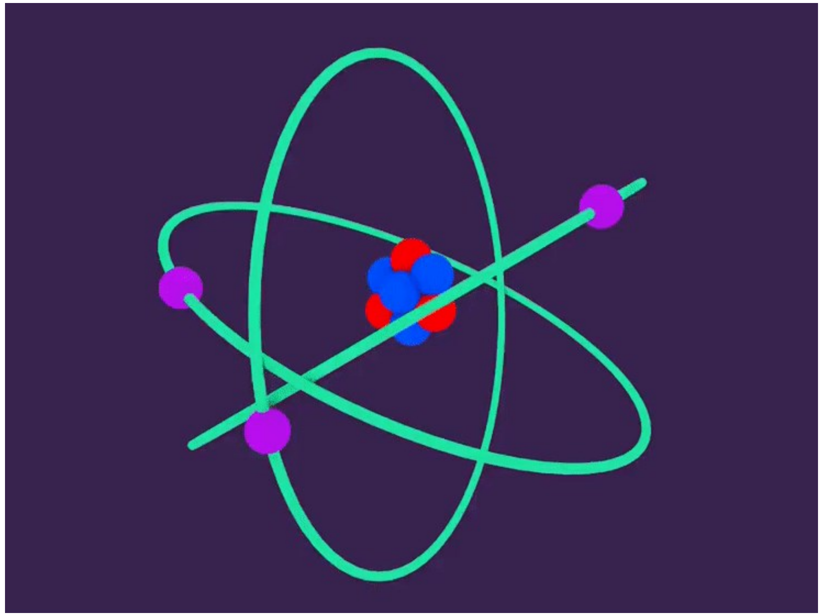
The "1st floor" (1st shell) is the first electron shell (n = 1), which is the lowest in energy (closest to the nucleus). This "floor" (shell) has only one "room" (orbital), which is spherical in shape (s-orbitals).

The "2nd floor" (2nd shell) has a total of four "rooms" (four orbitals) of two different "classes" (two subshells). One of the four is another spherical orbital (s-orbital). The remaining three orbitals of the 2nd shell are slightly higher in energy and have a "dumbbell" shape. Orbitals of this shape are referred to as p-orbitals. All three p-orbitals are identical, except for their orientation in space - three are perpendicular to each other.



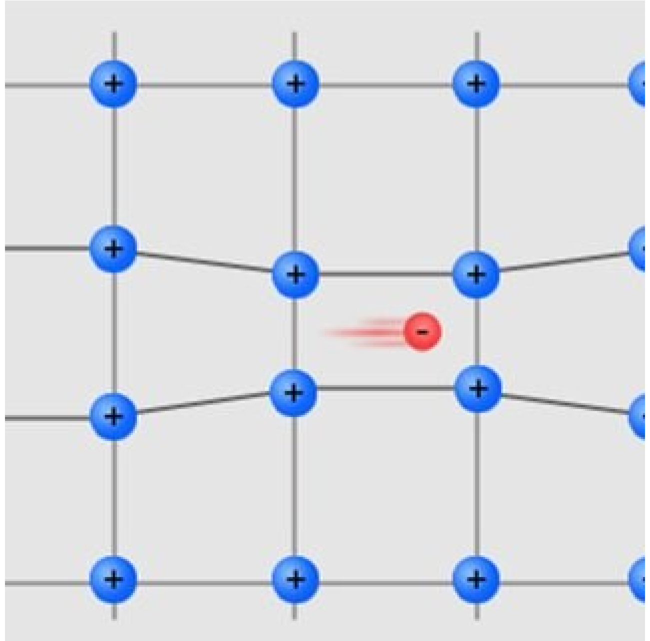
The orbital of an electron is a part of space where the probability of finding an electron is non-zero.

Electrons in Atom



We are still preparing to explain the quantum size effect

Now we can imagine electrons in an atom and realize that this visualization is not quite correct



The next leap - an electron in a crystal

Quantum Particle

A quantum particle has both corpuscular and wave characteristics.

An ideal particle has zero size

Therefore, it is localized in space

An ideal wave has a single frequency and is infinitely long

Therefore, it is unlocalized in space

A localized entity can be built from infinitely long waves

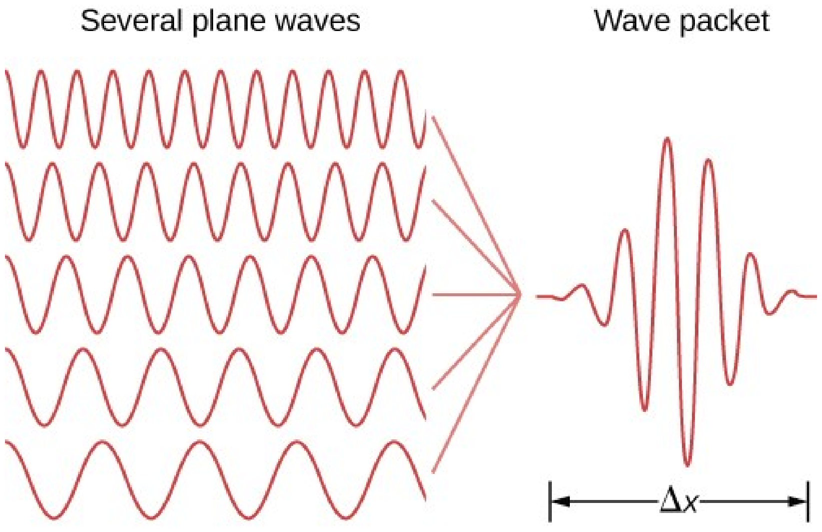
Multiple waves are superimposed so that one of its crests is at $x = 0$

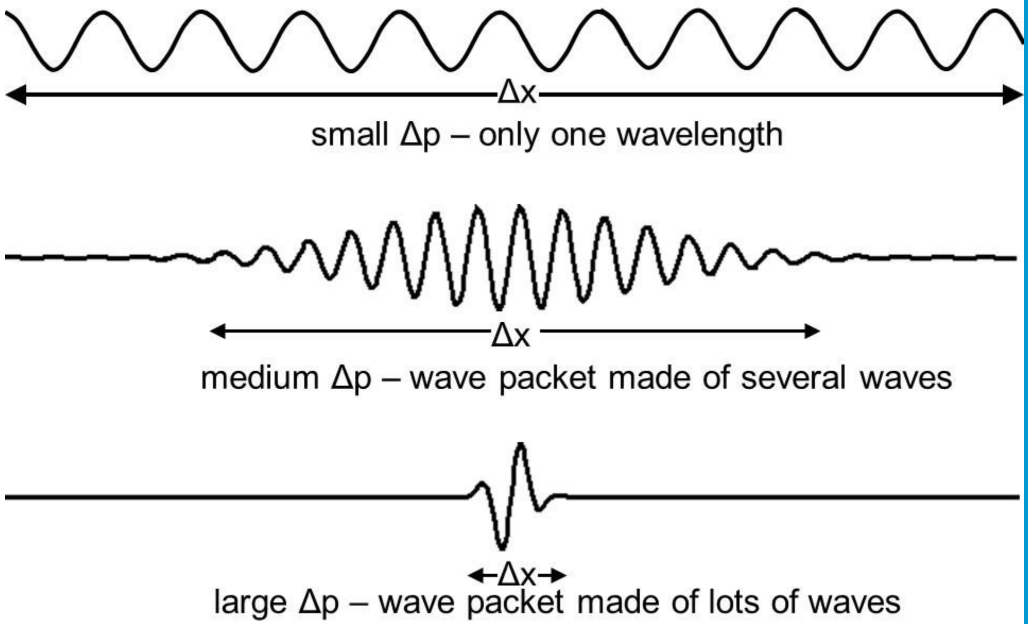
The result is that all the waves add constructively at $x = 0$

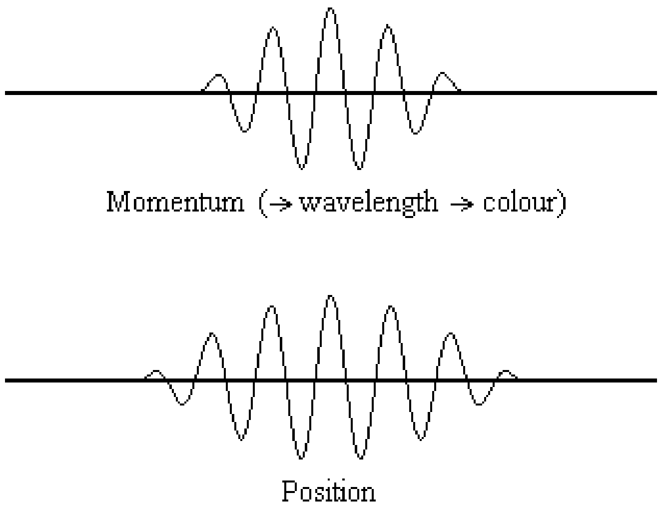
There is destructive interference at every point except $x = 0$

The small region of constructive interference is called a wave packet

The wave packet can be identified as a particle



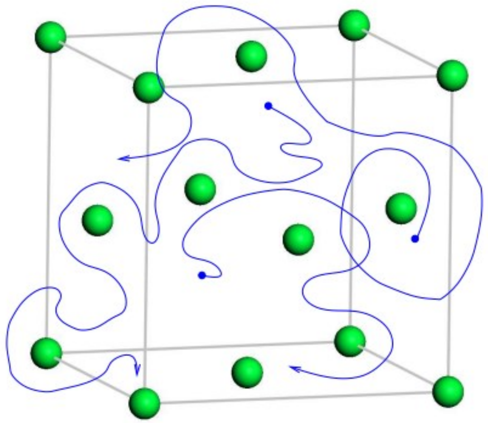




Electrons in Crystals

An electron in a crystal is in a periodic electric field, which is created by the nuclei of atoms (positively charged) and electrons in the shells of atoms (negatively charged)

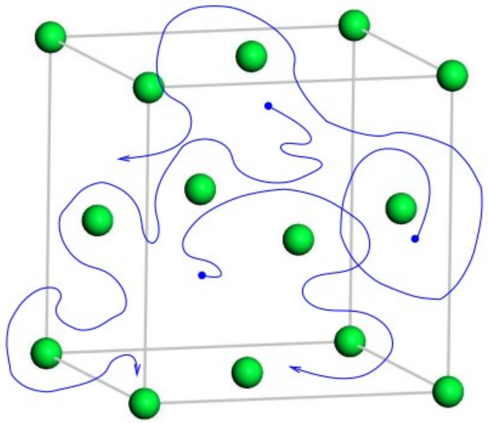
The periodicity scale is of the order of the de Broglie wavelength of an electron, about 0.1 nm. *Periodicity is idealization: impurities, defects, thermal fluctuations*



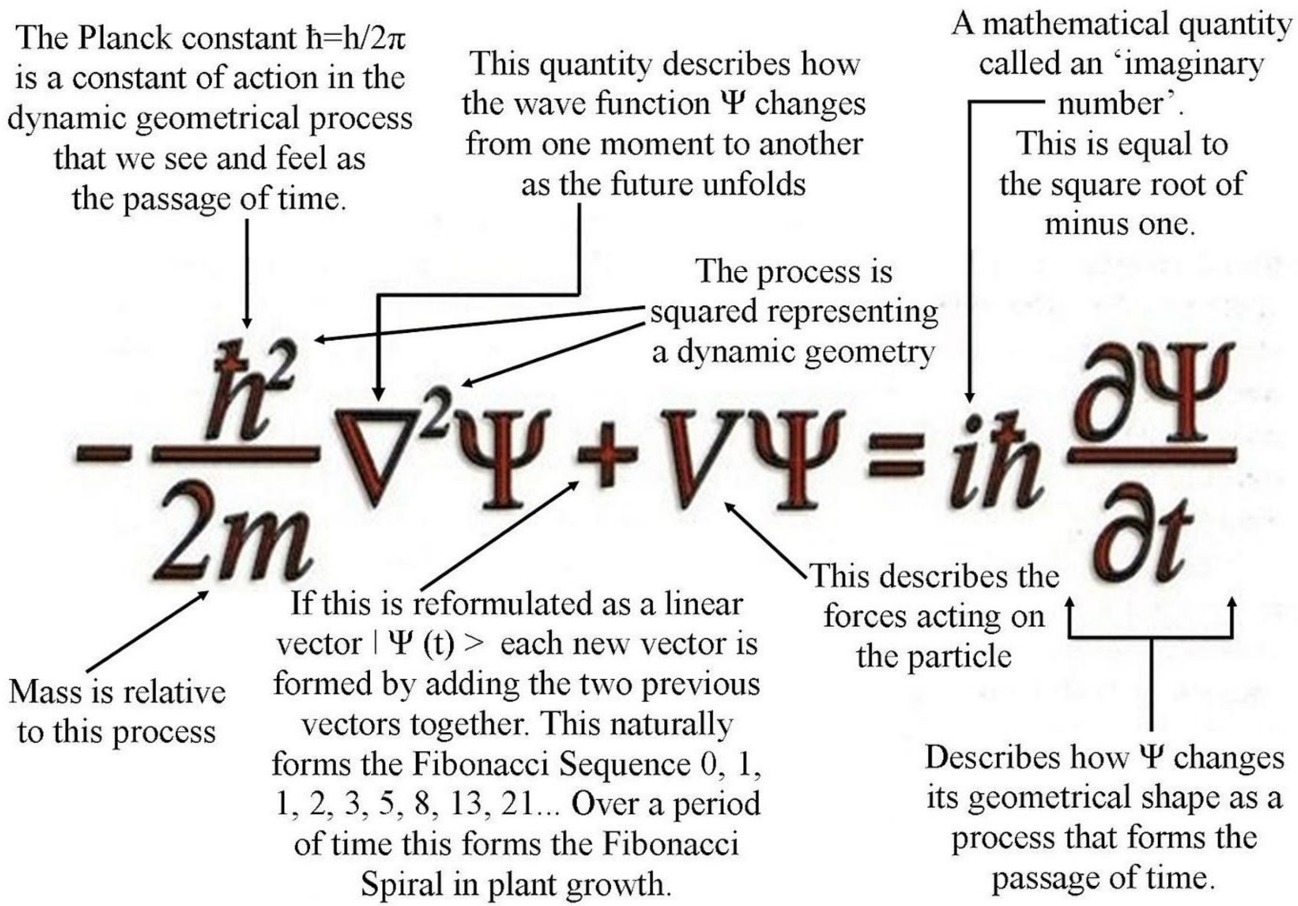
The Schrodinger equation defining the position of the electron is both energy and time dependent.

Electrons in Crystals

The solution to the Schrödinger equation is a wave function that gives the probability of finding an electron in a given location.
This can be considered a law of energy conservation.



Independent electronic approximation:



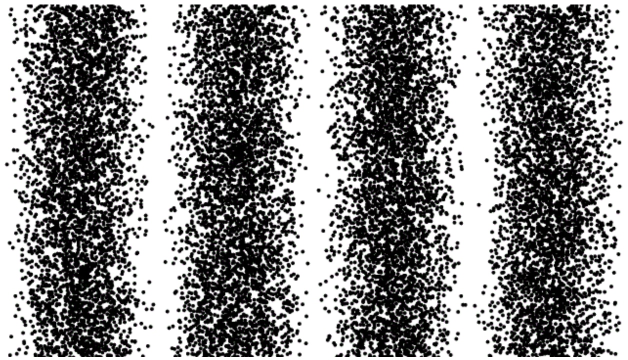
Schrödinger equation for a single electron:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\mathrm{r}) + V(r)\Psi(\mathrm{r}) = E\Psi(\mathrm{r})$$

Kinetic Energy + *Potential Energy* = *Total Energy*

Electrons in Crystals

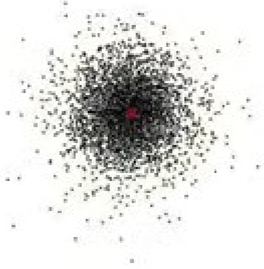
The wave function doesn't tell you where the electron is - as in the case of classical physics - it tells you the probability that the electron is here, or there, or somewhere else.



To visualize a wave function, think of it as a probability cloud.

The wave function can be interpreted as the probability amplitude of finding a particle at a specific point in space at a specific moment in time.

Max Born was awarded the 1954 Nobel Prize in Physics for his "**fundamental research in quantum mechanics, especially in the statistical interpretation of the wave function**".

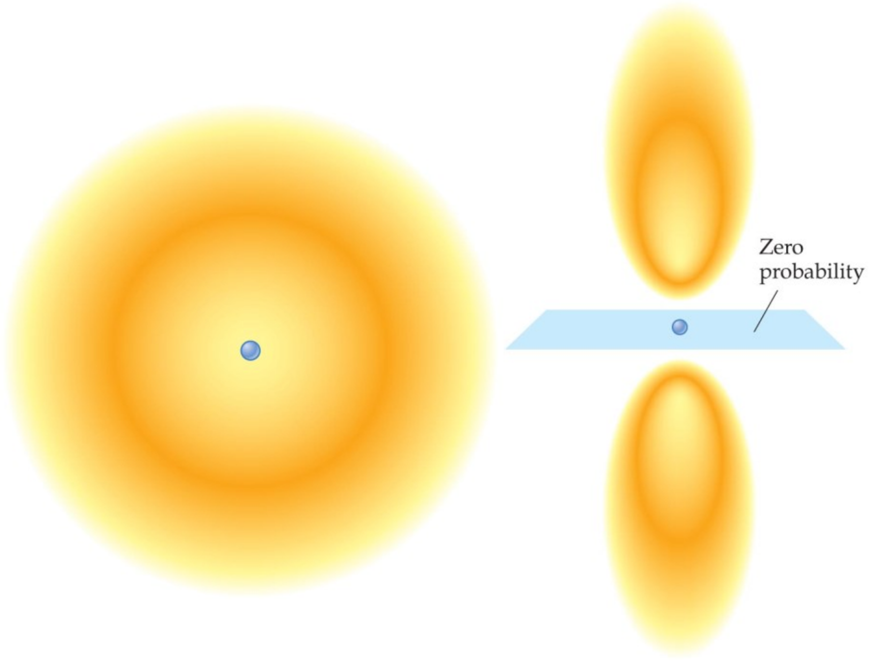


Electrons in Crystals

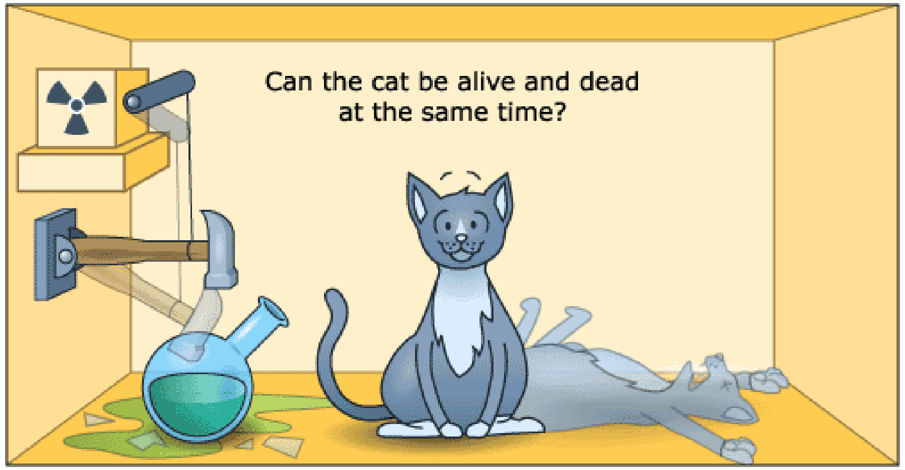
The interpretation of the probability cloud is simple: the electron is most likely to be found where the cloud is densest.

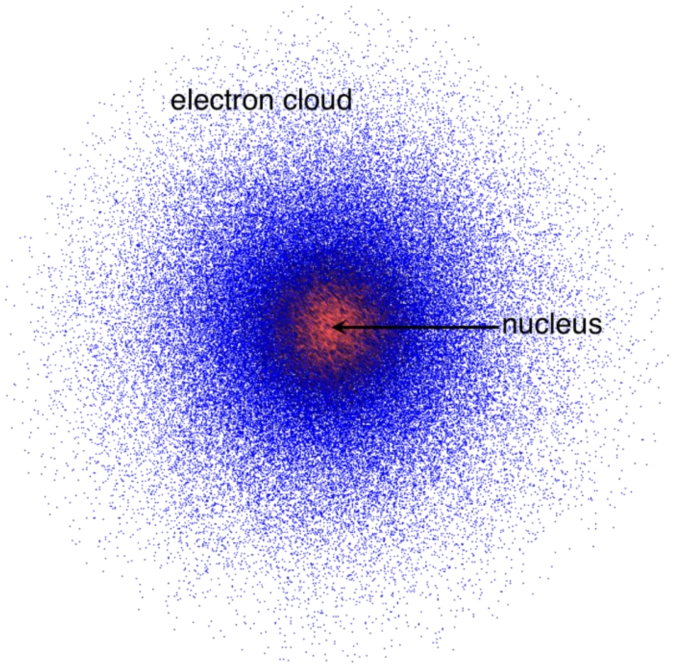
The probability of finding an electron near the nucleus or far from it is small.

The probability clouds for the excited states of hydrogen have the same interpretation as for the ground state, but their shape is more interesting.



In quantum mechanics, Schrödinger's cat is a thought experiment that illustrates the paradox of quantum superposition. In the thought experiment, a hypothetical cat can be considered simultaneously both alive and dead, while not being observed in a closed box, since its fate is tied to a random subatomic event that may or may not occur.

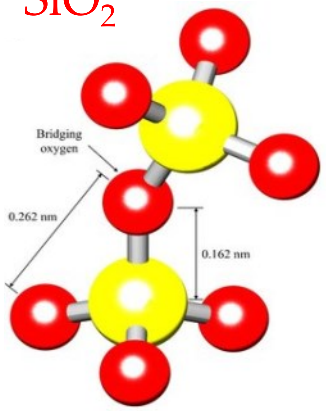


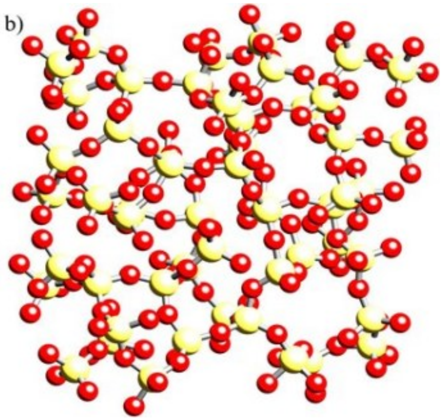


Crystals

Crystalline materials are characterized by the long-range ordered periodic arrangements of atoms.

SiO_2



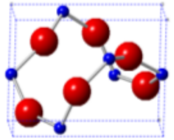


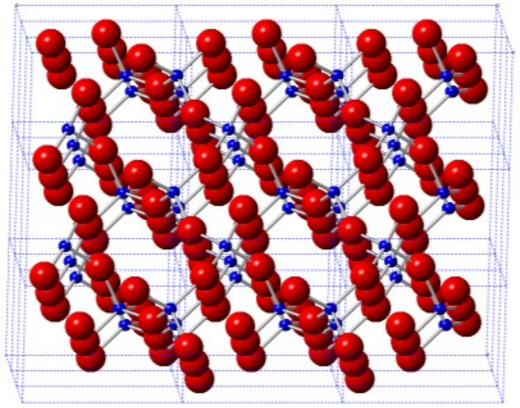
The unit cell is the basic repeating unit that defines the crystal structure. The unit cell contains the symmetry elements necessary for the unambiguous determination of the crystal structure.

The unit cell might contain more than one molecular unit (not molecules!).

The crystal system describes the shape of the unit cell.

The lattice parameters describe the size of the unit cell





SiO_2 crystals consist of periodically ordered atoms Si and O with certain symmetry of the spatial distribution.

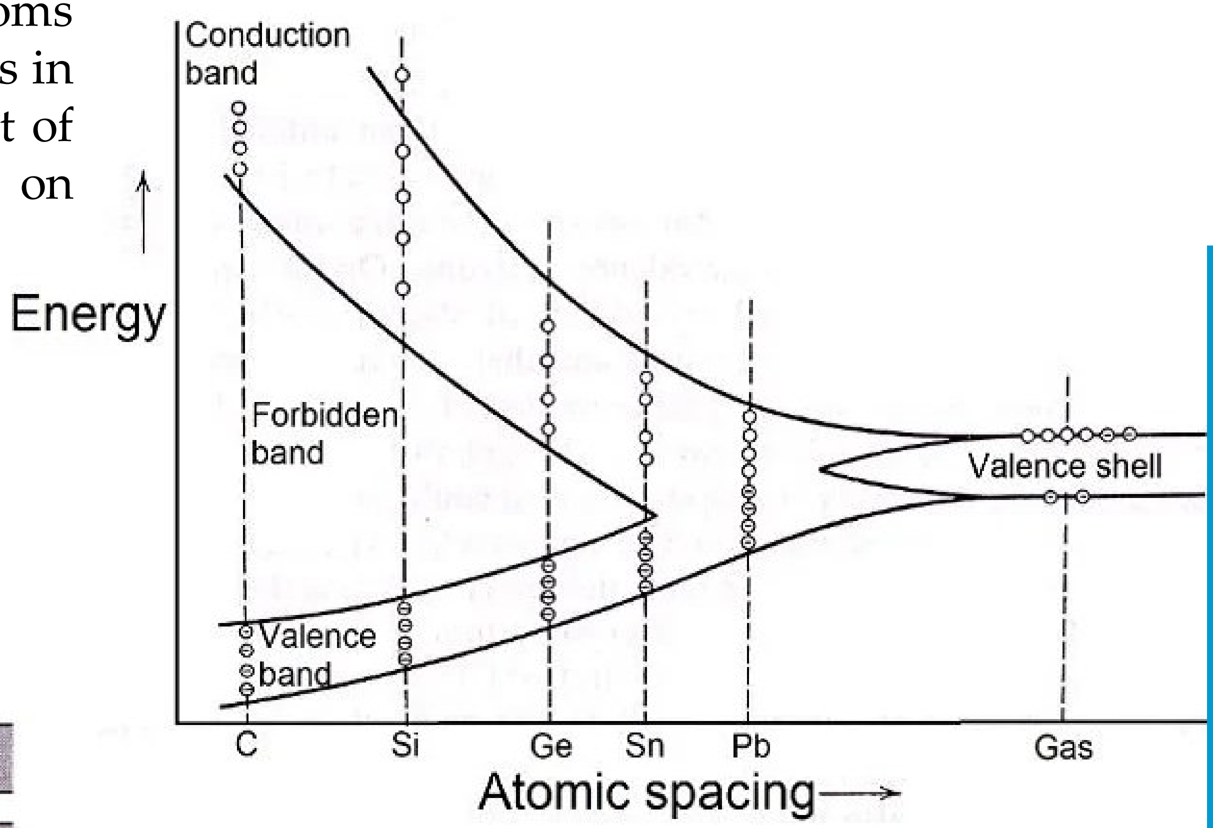
Crystal System: hexagonal
Lattice Parameters:
4.9134 x 4.9134 x 5.4052 Å (90 x 90 x 120°)

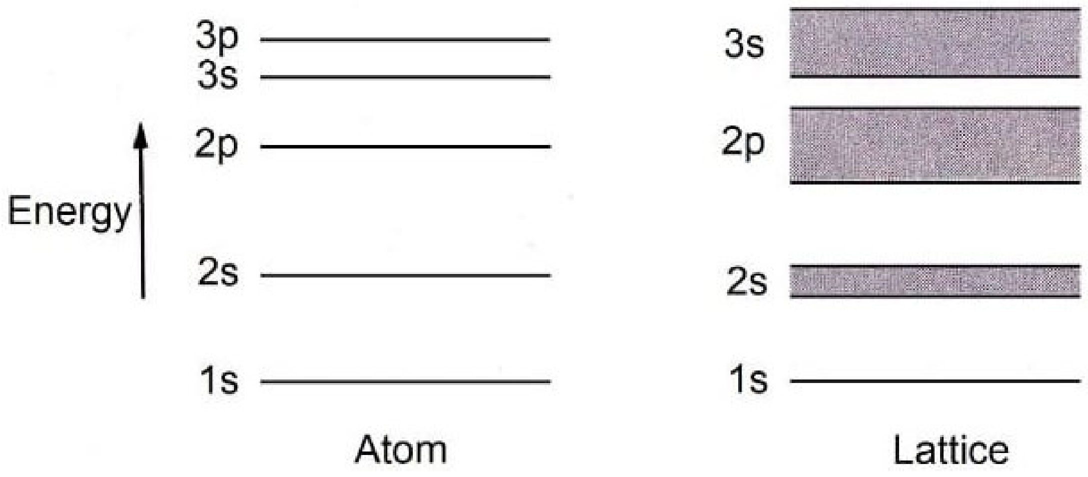
Band Structure Formation

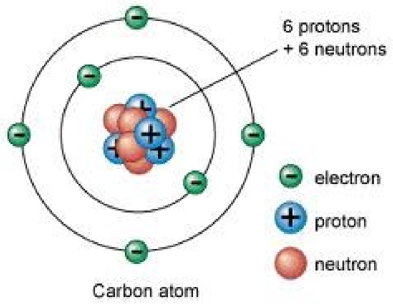
The magnitude of the influence of neighboring atoms depends on the type of atoms (the number of electrons in atomic shells and protons in nuclei), the environment of each atom (lattice symmetry and distance), and also on the location of an electron within a group of atoms.

Following the Pauli exclusion principle, when a system consists of many identical atoms, the individual energy levels of the electrons of individual atoms turn into energy bands.

An energy band is an energy range with many allowed adjacent energy levels very close to each other.





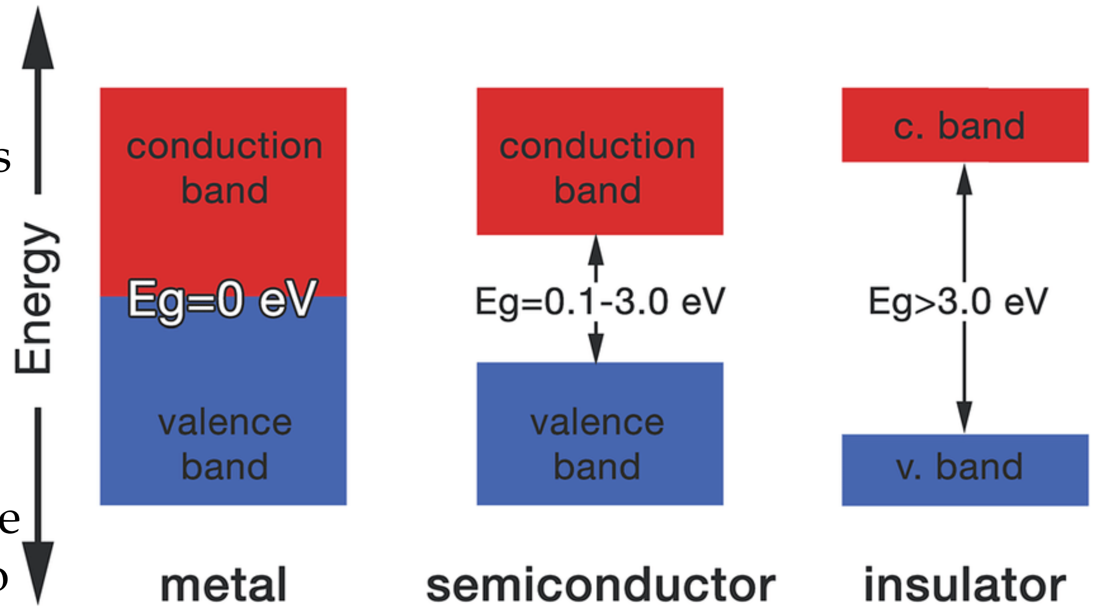


Energy Bands

Electrons in the same orbit have different energy levels. The grouping of these different energy levels is known as an ***energy band***.

There are three types of bands:
Valance band: represents the range of energy levels occupied by the valence electrons, which are the outermost electrons in an atom and are involved in bonding between atoms. The valence band is typically the highest energy band filled with electrons at absolute zero temperature.

Conduction band: contains energy levels that electrons can access when they gain sufficient energy. Electrons in the conduction band are free to move and contribute to electrical conductivity.



One electron volt is defined as the energy gained by an electron when it is accelerated through a potential difference of 1 volt.

$1eV = 1.6\times10^{-19}$ Joules

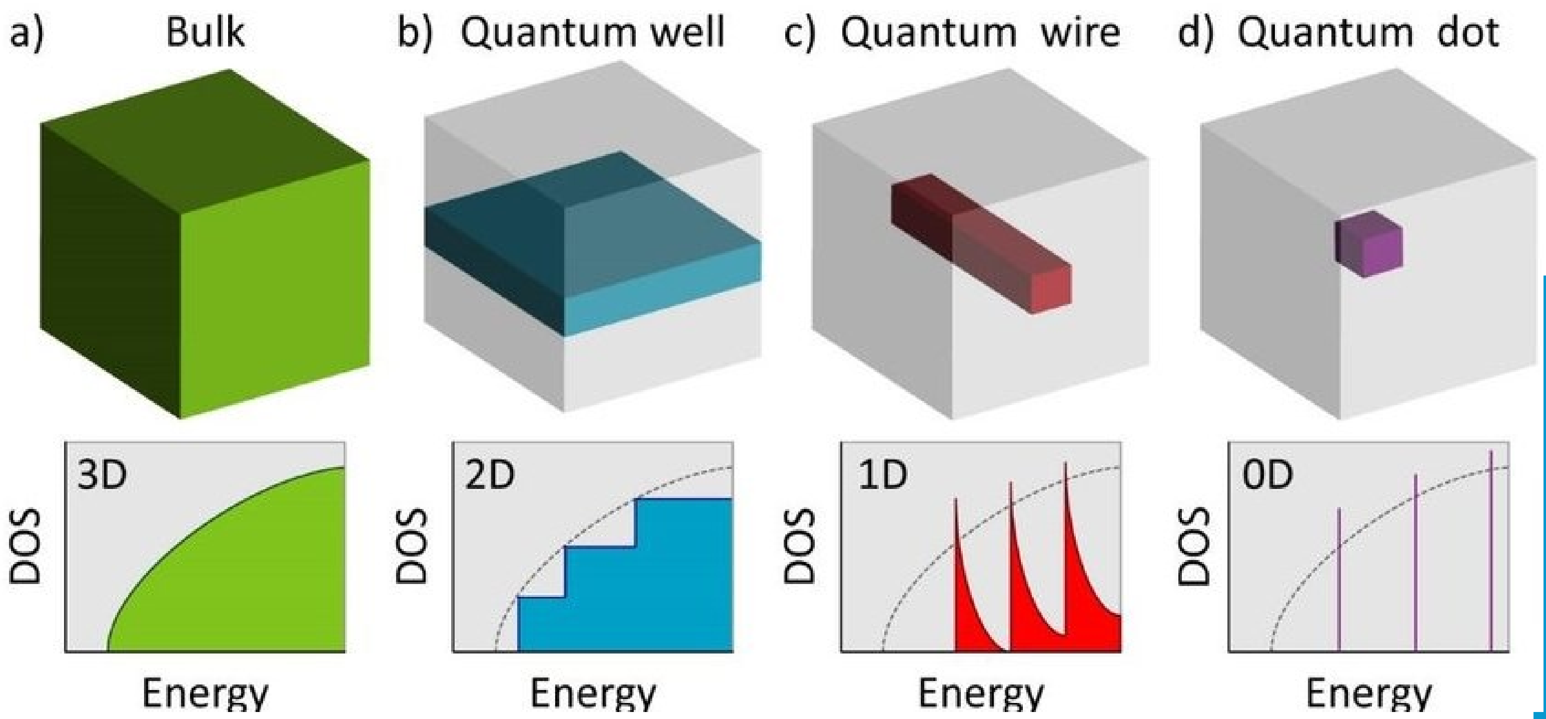
Forbidden energy gap: the energy gap between the valence band and the conduction band.
The energy difference between the valance band and the conduction band is known as the **band gap**.

Due to the band gap, materials can be divided into three groups:
Conductor: The valence band and conduction band overlap.
Semiconductor: There is a small band gap between the valence band and the conduction band.
Insulator: There is a large band gap between the valence band and the conduction band.

Quantum Confinement in Nanomaterials

When the length of a particle is reduced to the same order as ***the wave packet***, i.e., to a few nanometers, the quantum confinement effect occurs, and the material properties are altered. This confinement leads to discrete energy levels, rather than continuous bands, resulting in quantization of energy states.

Depending on the dimension of the confinement, three kinds of confined structures are defined: *quantum well*, *quantum wire,* and *quantum dot*



The density of states (DOS) is the number of different states at a certain energy level that electrons can occupy, that is, the number of electron states per unit volume per unit energy.

The dimensionality reduction caused by the confinement of electrons from bulk (3D) to a thin crystal layer (2D) leads to a sharp change in their behavior and transformation of DOS. A further decrease in the dimension of the electron environment to a one-dimensional quantum wire (1D) and eventually to a zero-dimensional quantum dot (0D) leads to the formation of an ***atom-like system***.

The energy distribution of electrons in a quantum dot is similar to the energy level of atoms – there is no band structure, but the density of single levels is greater.

Quantum Confinement in Nanomaterials

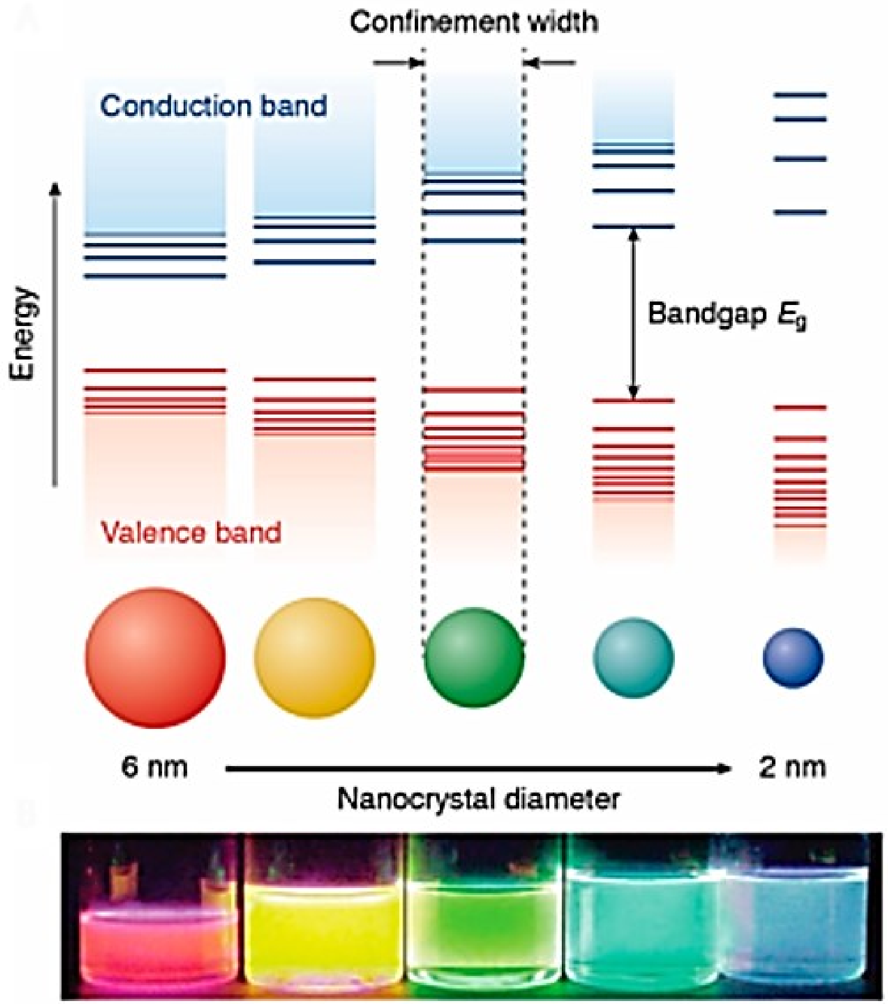
Quantum confinement is responsible for increasing the energy difference between the energy states and the band gap.

A phenomenon tightly related to the optical and electronic properties of the materials.

The size of the nanoparticle decreases from left to right, and the corresponding increase in the band gap is reflected in the change in the color of the photoluminescence from red to violet.

For instance, as the size of semiconductor nanoparticles decreases, their bandgap widens, leading to a shift in the wavelengths of light they absorb or emit. This property is exploited in various applications such as *quantum dot displays, solar cells, and biological imaging.*

Bulk of Semiconductor (CdSe single crystal)



Nanocrystal of Semiconductor (CdSe Quantum Dots)

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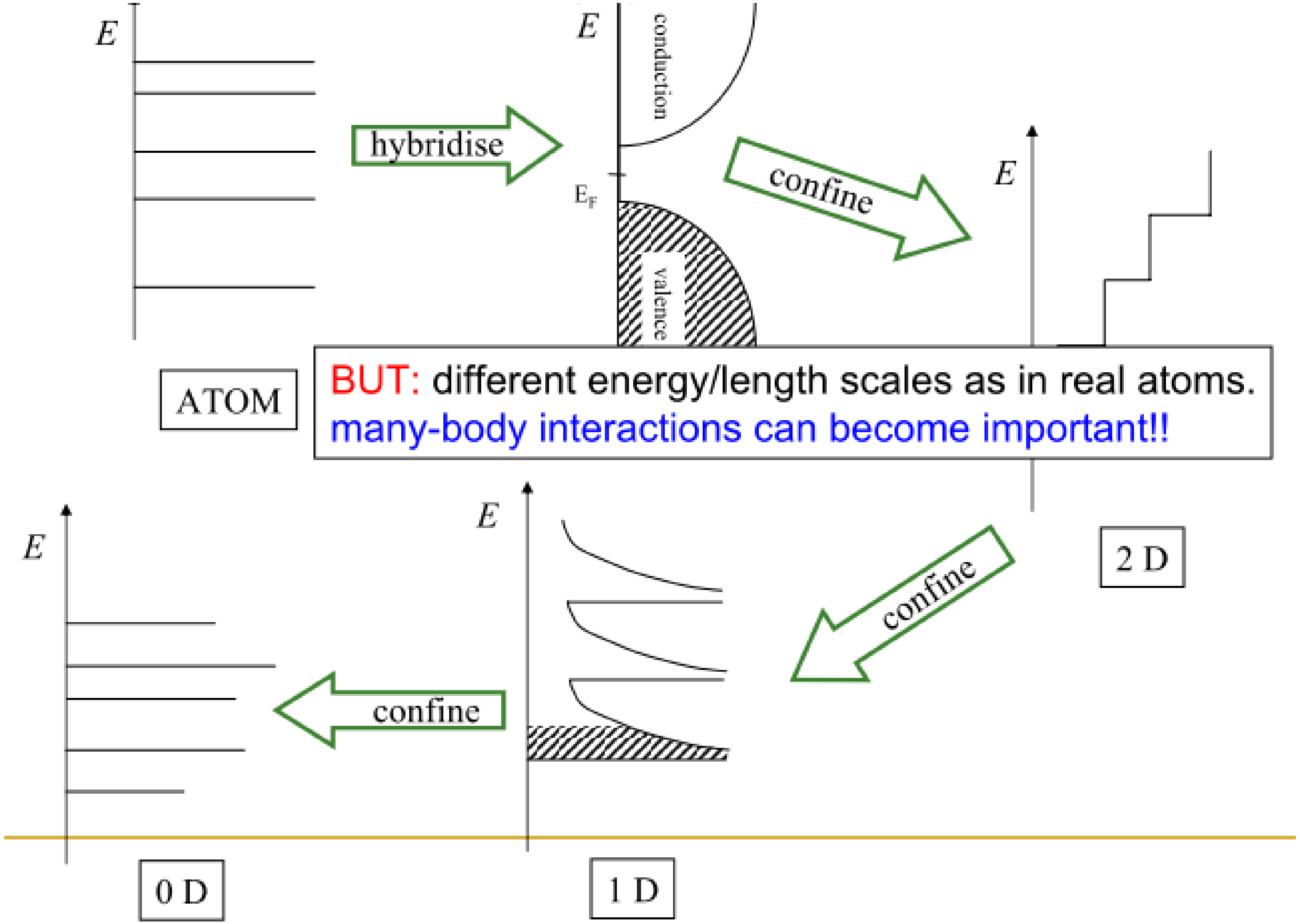
Quantum Dots as Artificial Atoms



Semiconductor nanocrystals are called *artificial atoms* due to their atom-like discrete electronic structure resulting from quantum confinement. *Artificial atoms can also be assembled into artificial molecules or solids, thus, extending the toolbox for material design.*

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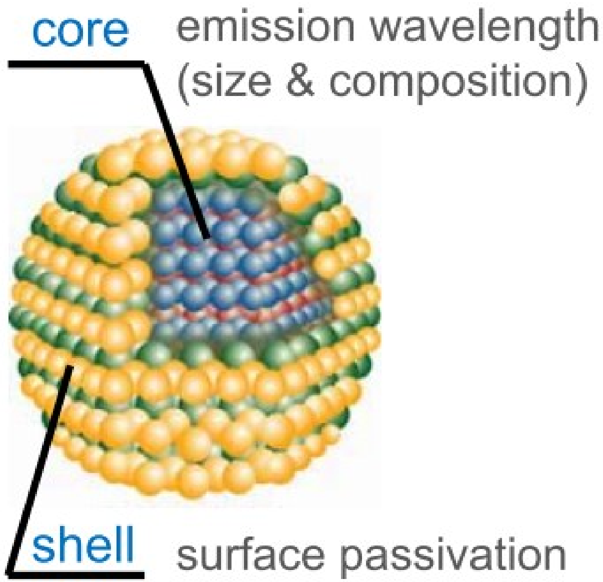
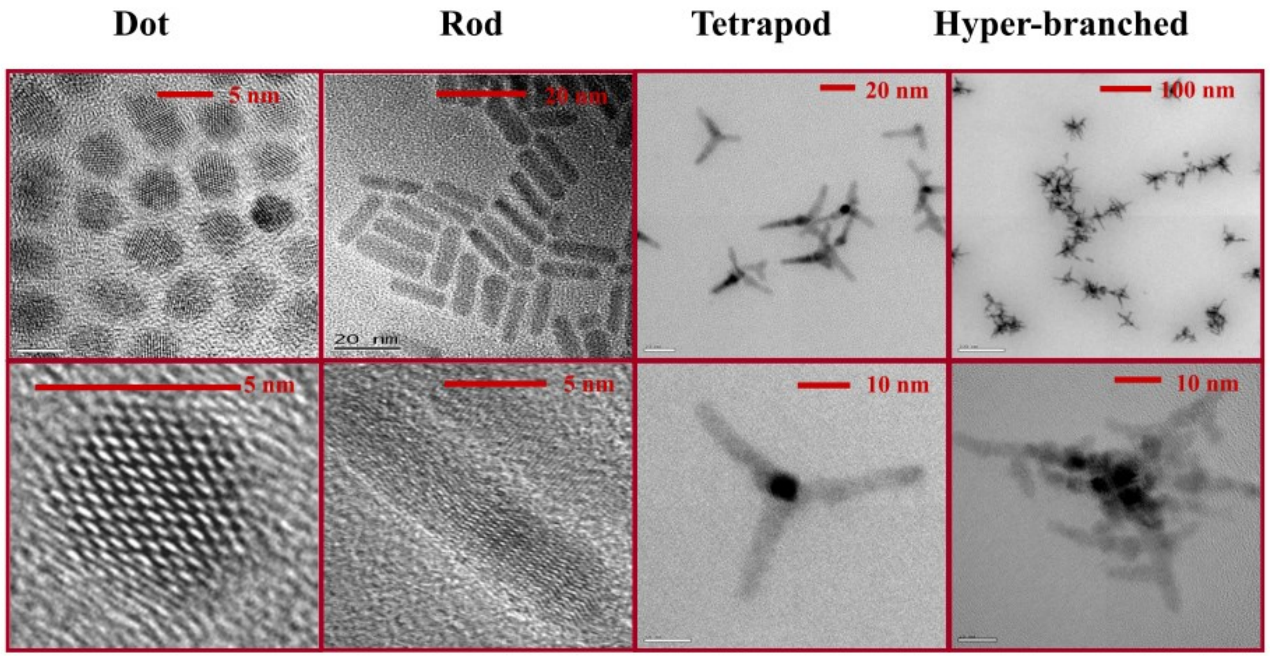
Quantum Dots

Quantum dots are fragments of a semiconductor with a bulk bond geometry and with surface states eliminated by enclosure in a material that has a larger band gap

QDs contain from 100 to 1000 electrons and are 2 to 10 nanometers in diameter or 10 to 50 atoms. Changing the band gap of semiconductors is the most attractive due to its fundamental and technological importance. Widely tunable bandgap semiconductors are considered materials for new generation flat panel displays, photovoltaic, optoelectronic devices, lasers, sensors, photonic bandgap devices, etc.





Properties of quantum dots

- High extinction coefficient
- High electron mobility
- Bandwidth and position adjustment
- Solution process capabilities

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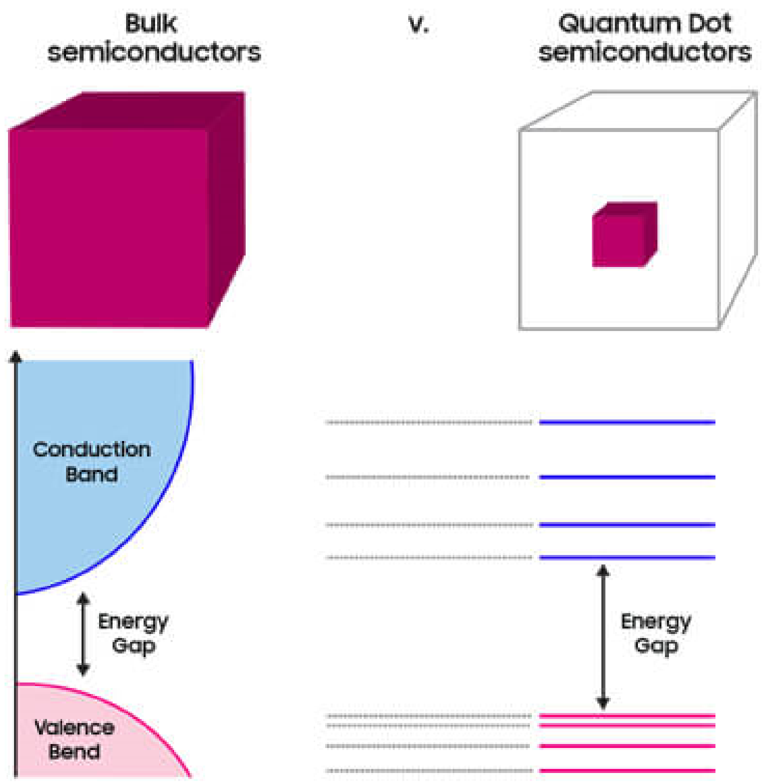
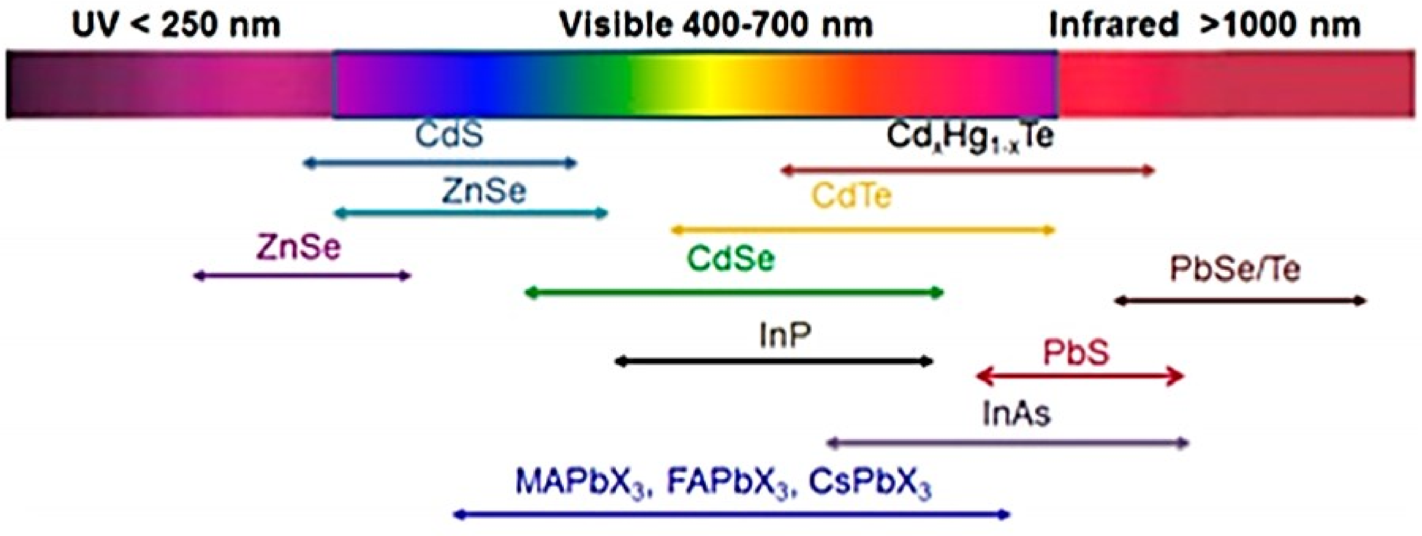
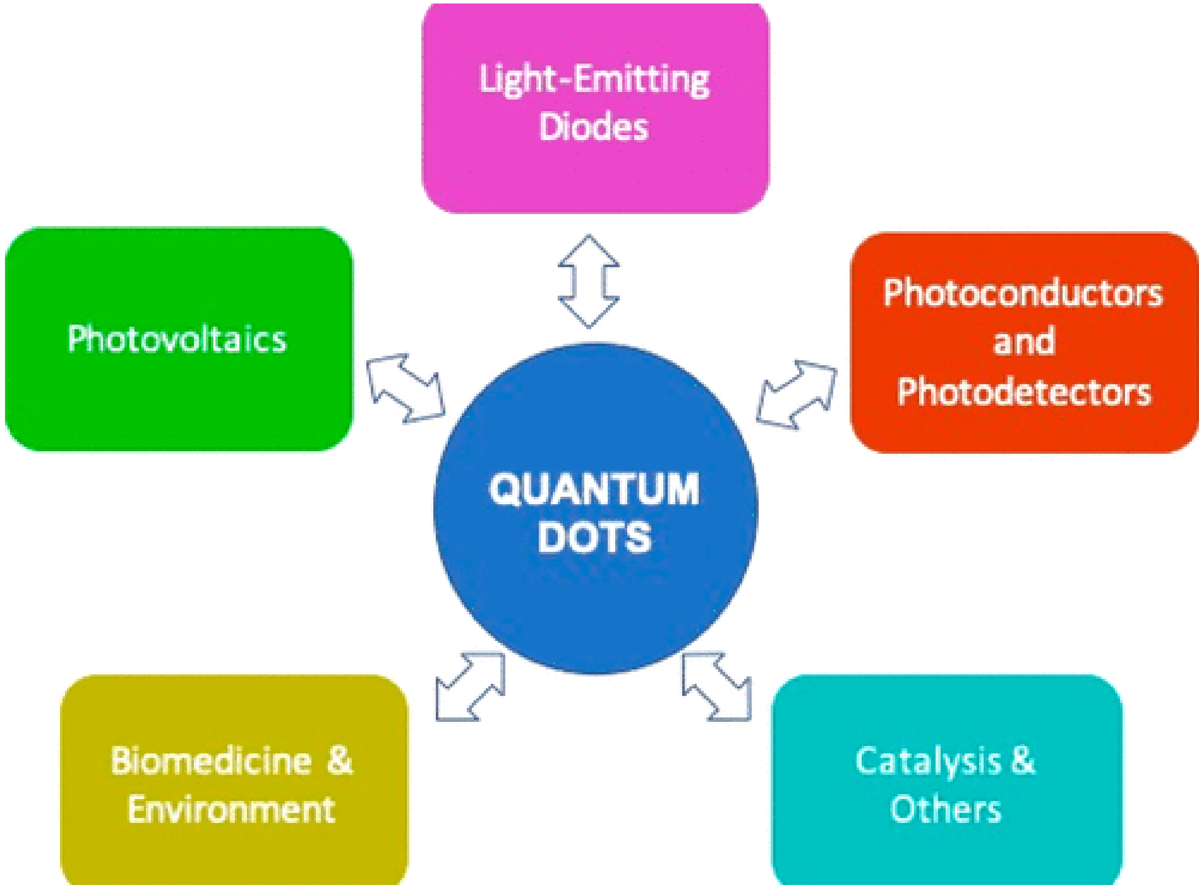
Quantum Dots

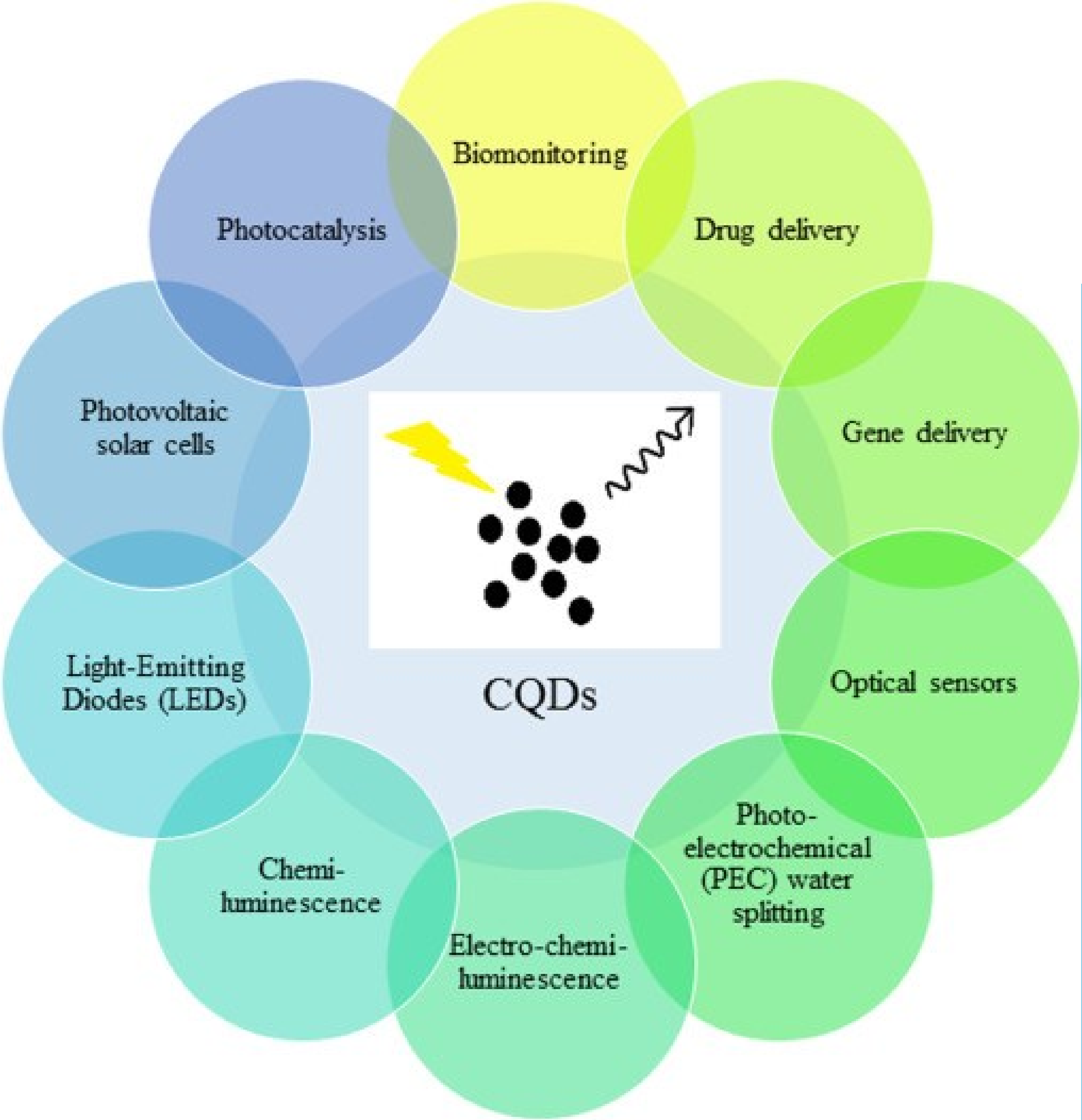




Different type QDs and their emission spectrum range that can be adjusted by their size/shape

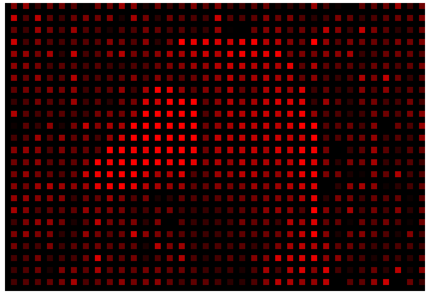
Quantum Dots

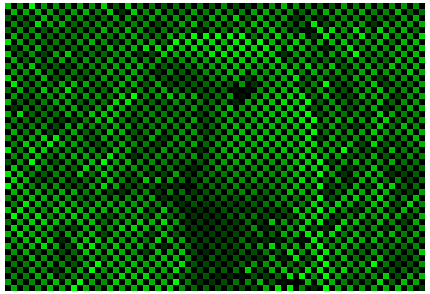


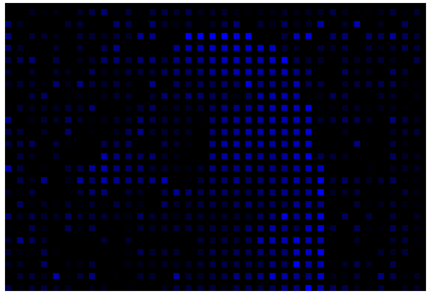


Quantum Dots

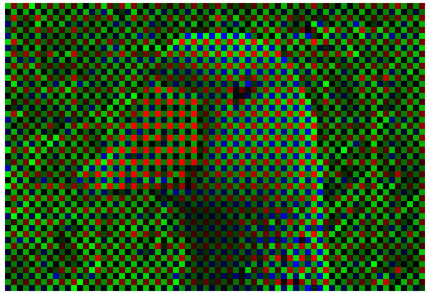
RGB (red, green and blue) refers to a system representing the colors used on a digital display screen. Red, green and blue can be combined in various proportions to obtain any color in the visible spectrum. The RGB model uses 8 bits each - from 0 to 23 - for red, green and blue colors.

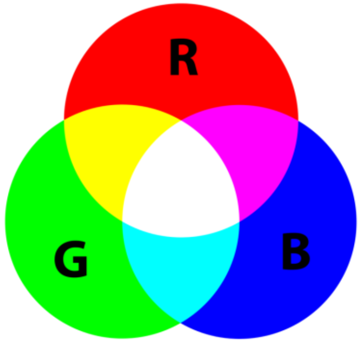


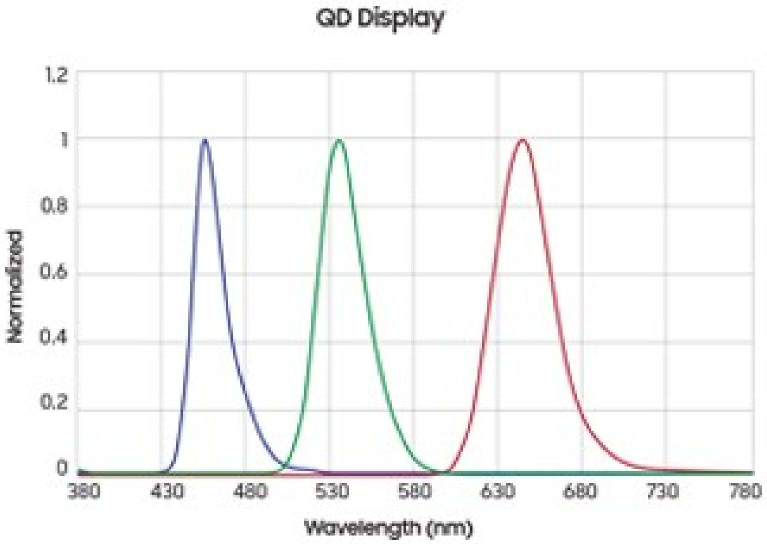


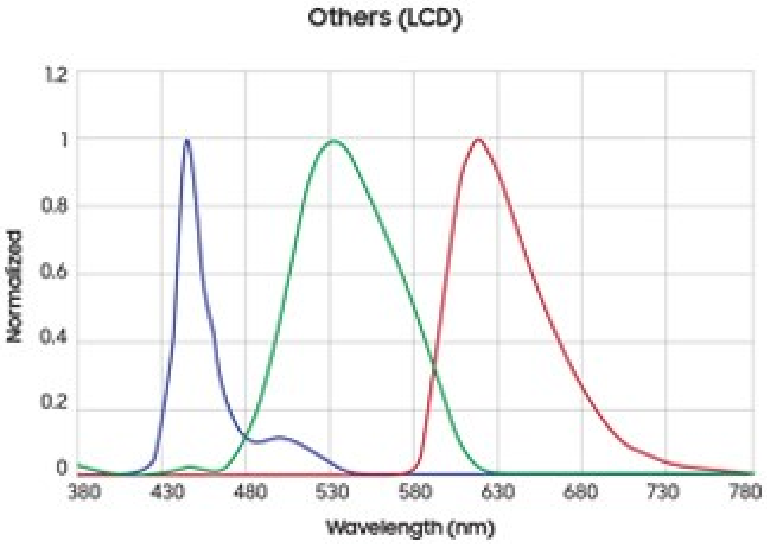


A new goal of improving the three primary colors of the display is to minimize the problem of color mixing. QDs allow the production of light sources with a narrow spectrum without overlap.





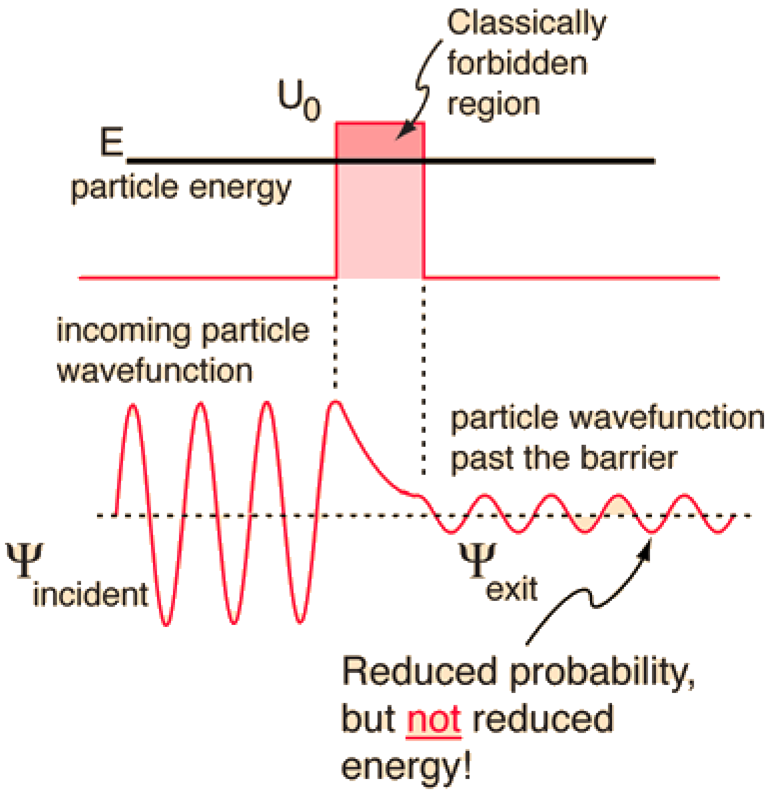


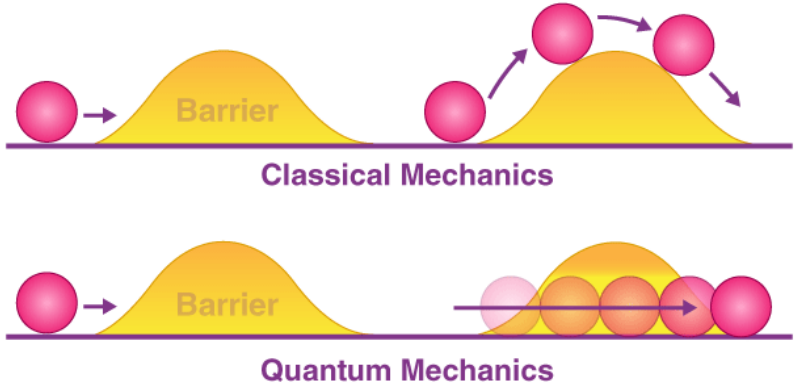


Quantum Tunneling

According to classical physics, a particle with energy E less than the barrier height U_0 cannot penetrate — the region inside the barrier is classically forbidden. However, the wave function associated with the free particle must be continuous at the barrier and will exhibit an exponential decay inside the barrier.

The wave function must also be continuous on the far side of the barrier, so there is a finite probability that the particle will tunnel through the barrier.





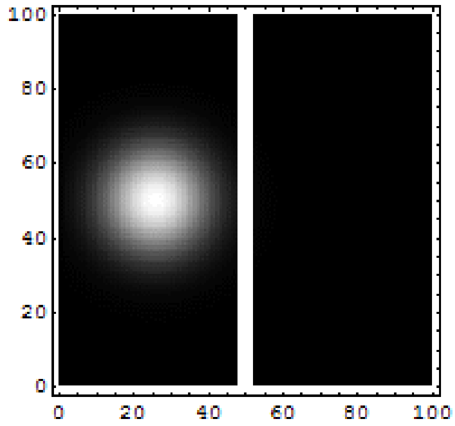
Wave functions have a probability of disappearing on one side and reappearing on the other side.

The first derivative of the wave functions is continuous.

Neither the wave nor the particle disappears.

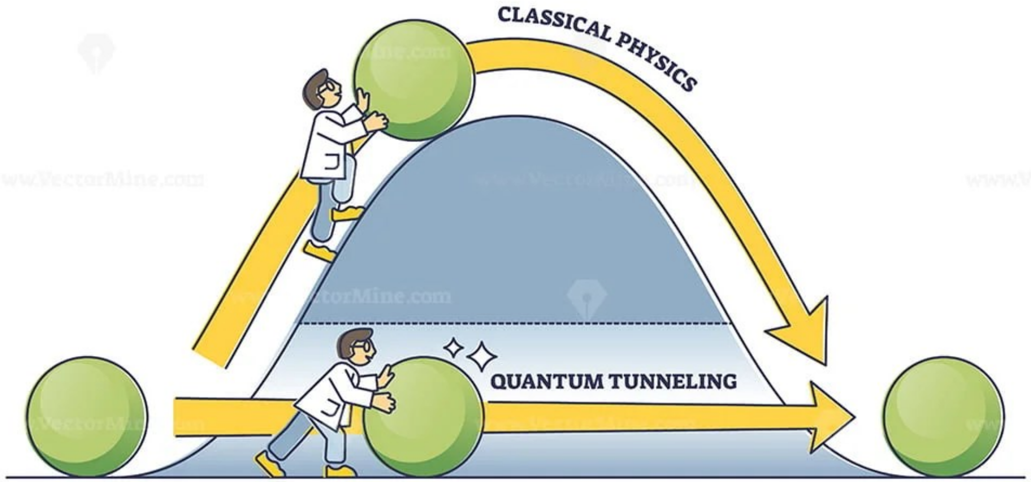
Tunneling occurs at a barrier thickness of about 1–3 nm.

Quantum Tunneling



Quantum tunneling cannot be explained using the laws of classical mechanics, where a dense potential barrier needs potential energy.
This phenomenon is extremely important for the development of new nanoelectronic devices.

Its principle of operation is used in modern devices such as the tunneling diode, scanning tunneling microscope, and quantum computing.
It is predicted that quantum tunneling will create physical limits on how small transistors can be, due to the fact that electrons will be able to tunnel past them if they are too small.
This is seen as one of the new consequences of quantum mechanics and is fundamental to nanotechnology.



Global Challenges

Climate Change: The warming of the planet due to human activities such as burning fossil fuels and deforestation is leading to severe consequences such as extreme weather events, rising sea levels, and disruptions to ecosystems.

Nuclear Weapons, Global War Risk: The presence of nuclear weapons poses a threat to global security, with the potential for catastrophic consequences

Pandemics: The emergence of new infectious diseases, as evidenced by events like the COVID-19 pandemic, highlights the vulnerability of human populations to pandemics and the need for robust global health systems.

Biodiversity Loss: The loss of biodiversity due to habitat destruction, pollution, climate change, and other factors threatens ecosystems and the services they provide, such as clean air, water, and food.

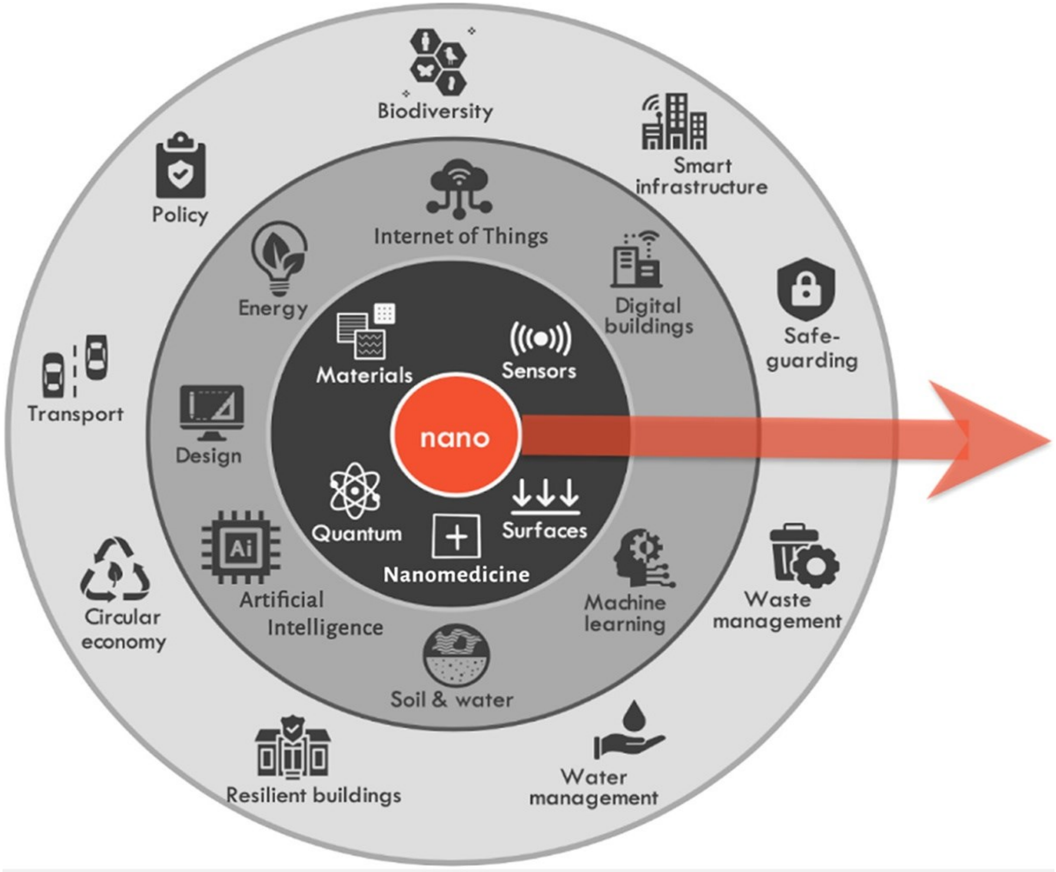
Technological Risks: Advances in technology, including artificial intelligence and biotechnology, bring both benefits and risks such as job displacement, privacy concerns, and the potential for misuse or unintended consequences.

Resource Depletion: The unsustainable consumption of natural resources, including water, arable land, and minerals, is leading to depletion and environmental degradation.

Social Inequality: Persistent social inequalities based on factors such as income, race, gender, and access to education and healthcare contribute to social unrest and undermine global stability.

Global Challenges

Nanomaterials represent a prosperous field with huge potential across various industries. Their unique properties at the nanoscale offer groundbreaking advancements in medicine, electronics, energy, and environmental sustainability. Through precise manipulation and engineering, nanomaterials exhibit extraordinary characteristics, such as increased strength, conductivity, and reactivity. However, their safety, ethical implications, and mass production remain subjects of ongoing research and debate. Overall, nanomaterials promise transformative applications but require careful consideration for their responsible development and deployment.

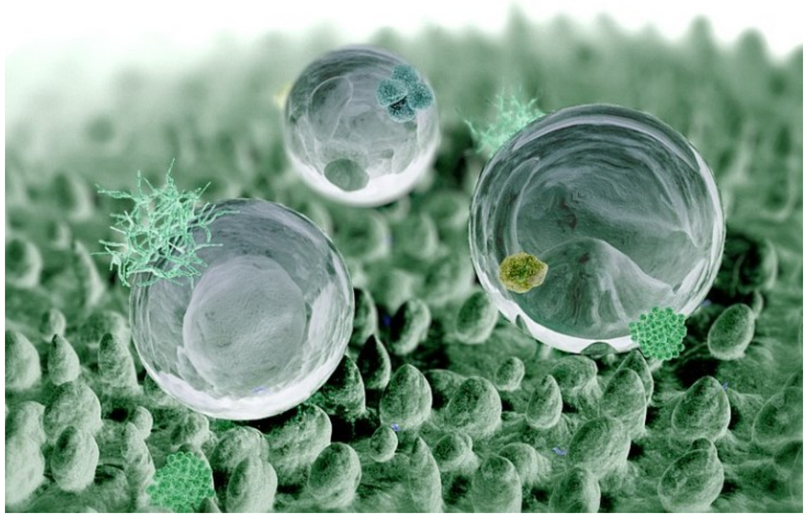


Nanotechnologies in Nature

Nilufer (lotus) leaf effect

The lotus grows in small lakes and ponds, ponds and puddles, and the surfaces of its leaves are always bright, clean and smooth, as if untouched by polluted water. It symbolizes pure cleanliness, as there is no bacteria and pathogen formation on the lotus leaves, which do not usually accumulate water on them. The water drops act like a drop of "mercury" on the lotus leaf and slide slowly over the surface, thus sweeping away any dirt and dust accumulated on the surface, leaving a clean surface behind.

Dirt particles are picked up by water droplets due to the micro- and nanoscopic architecture on the surface, which minimizes the droplet's adhesion to that surface.

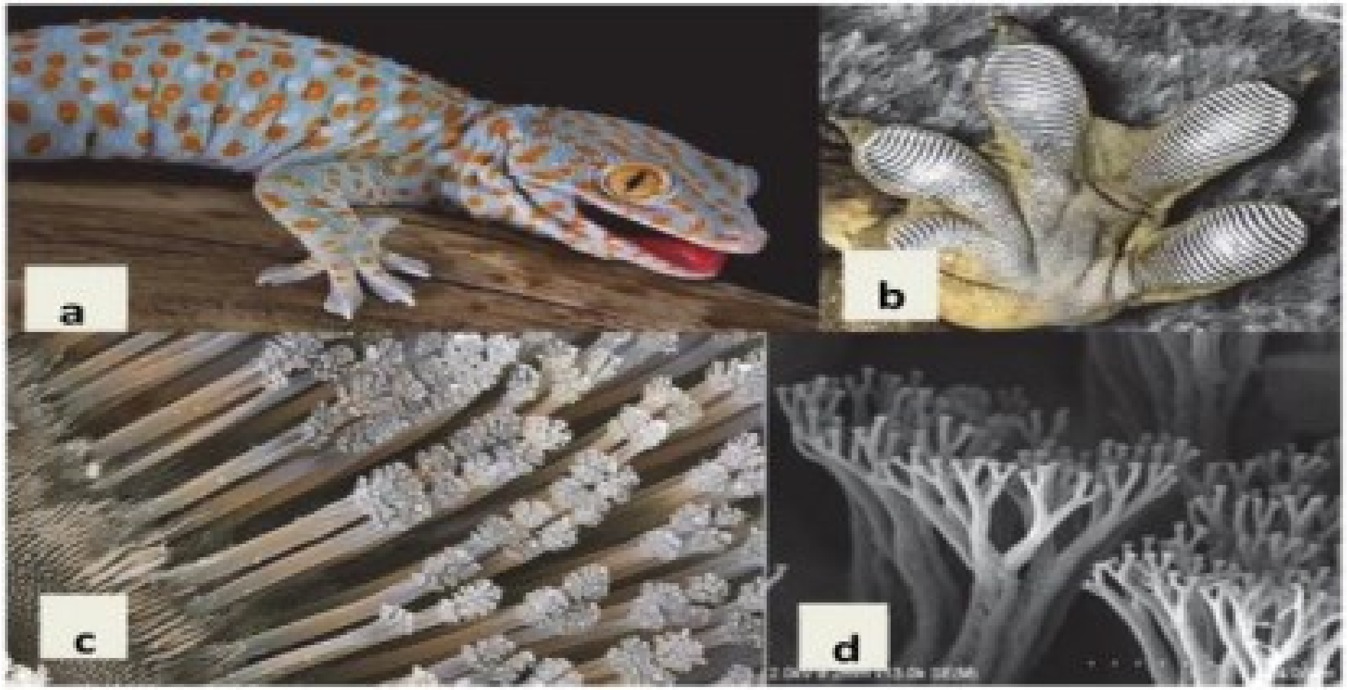


Based on the concept of the lotus effect, nanotechnology uses examples for industrial and everyday life

Nanotechnologies in Nature

Gecko effect

As a result of billions of years, we are able to examine in detail the most developed form and structure examples that are most suitable for living conditions with modern electron microscopy techniques. One of these is the ability of lizards, known as the "Gecko Effect", to move rapidly in all conditions (humid, dusty, rainy, and other) vertically and inverted on any surface, defying gravity

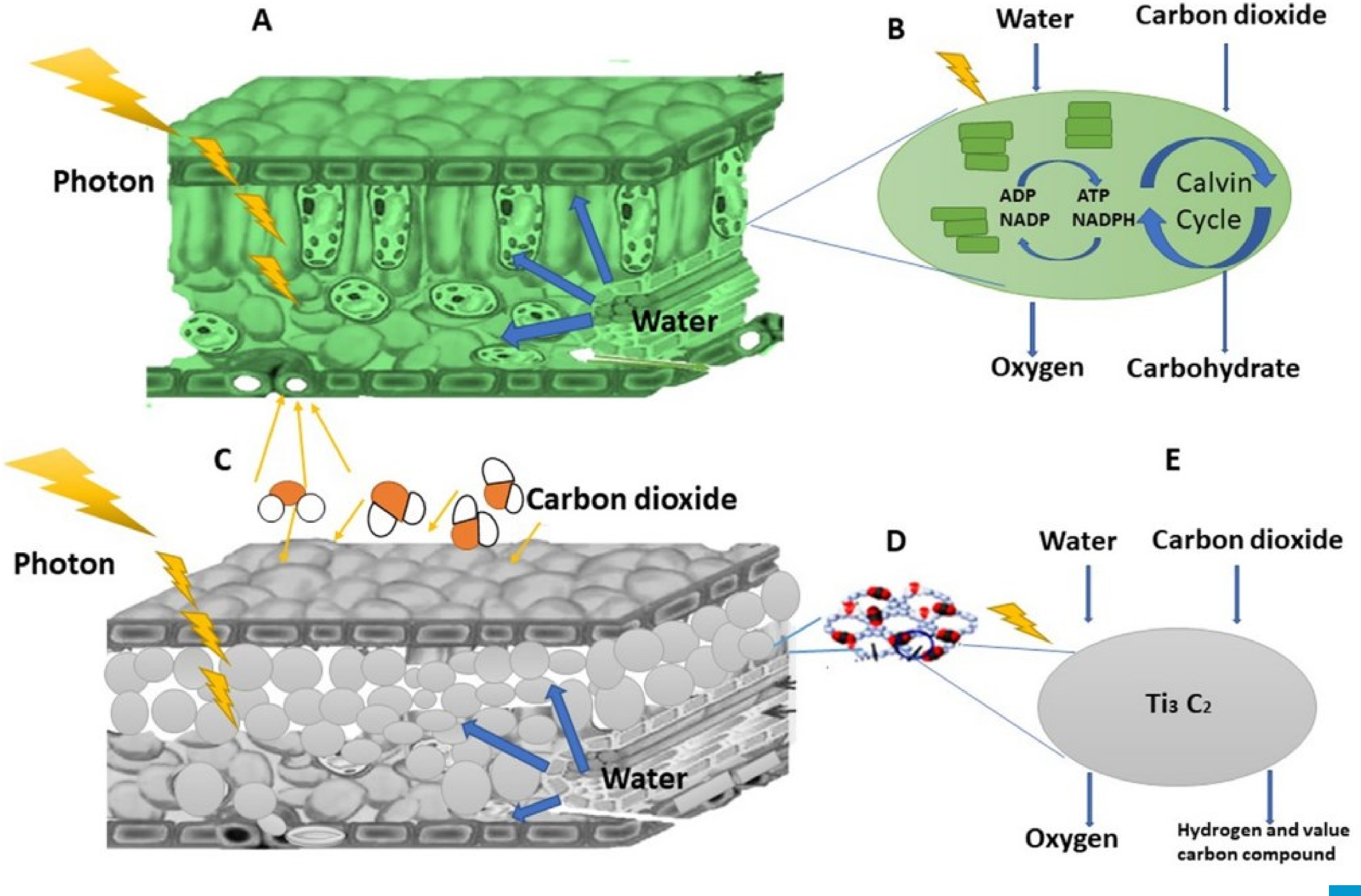


a) Gecko, b) bottom of the foot, c) hairy area at the bottom of the foot, d) SEM image of the hairs on the lower part of the gecko foot

Nanotechnologies in Nature

Photosynthesis

Diagram showing natural photosynthesis and artificial photosynthesis at micro and nanoscale; It shows light being absorbed and diffusion of gas in the natural leaf (A) and artificial leaf (C). Fixation of carbon dioxide at nanoscale in chloroplast (B) and adsorption of carbon dioxide at nanoscale (D) and conversion into fuel (E) only in the artificial photosynthesis.



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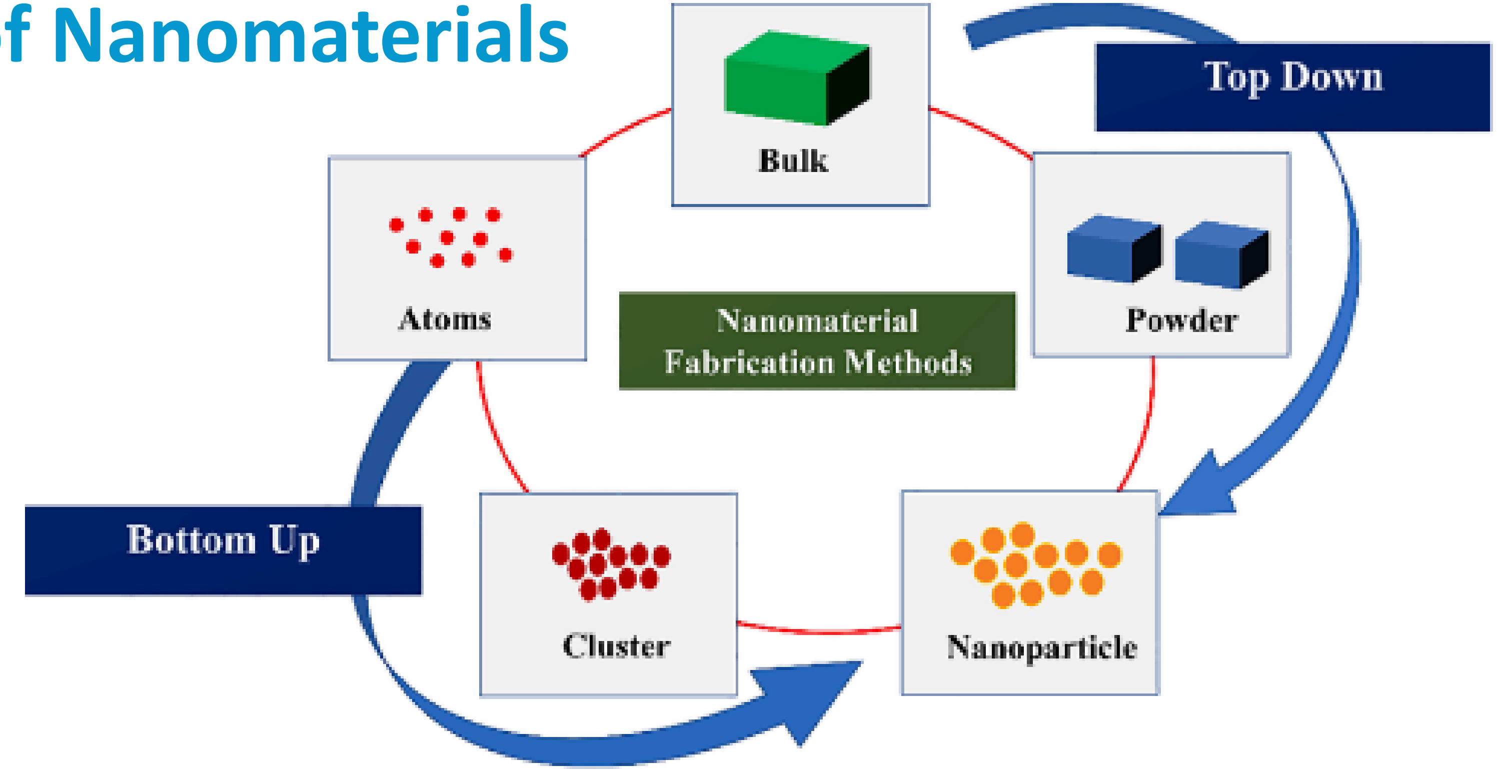
Manufacturing of Nanomaterials



The two basic approaches to creating nanomaterials in a controlled and repeatable manner are the "top-down" and "bottom-up" techniques, either for atoms to assemble (break) or disassemble (dissociate) bulk solids into small pieces or to get on a few atoms from them.

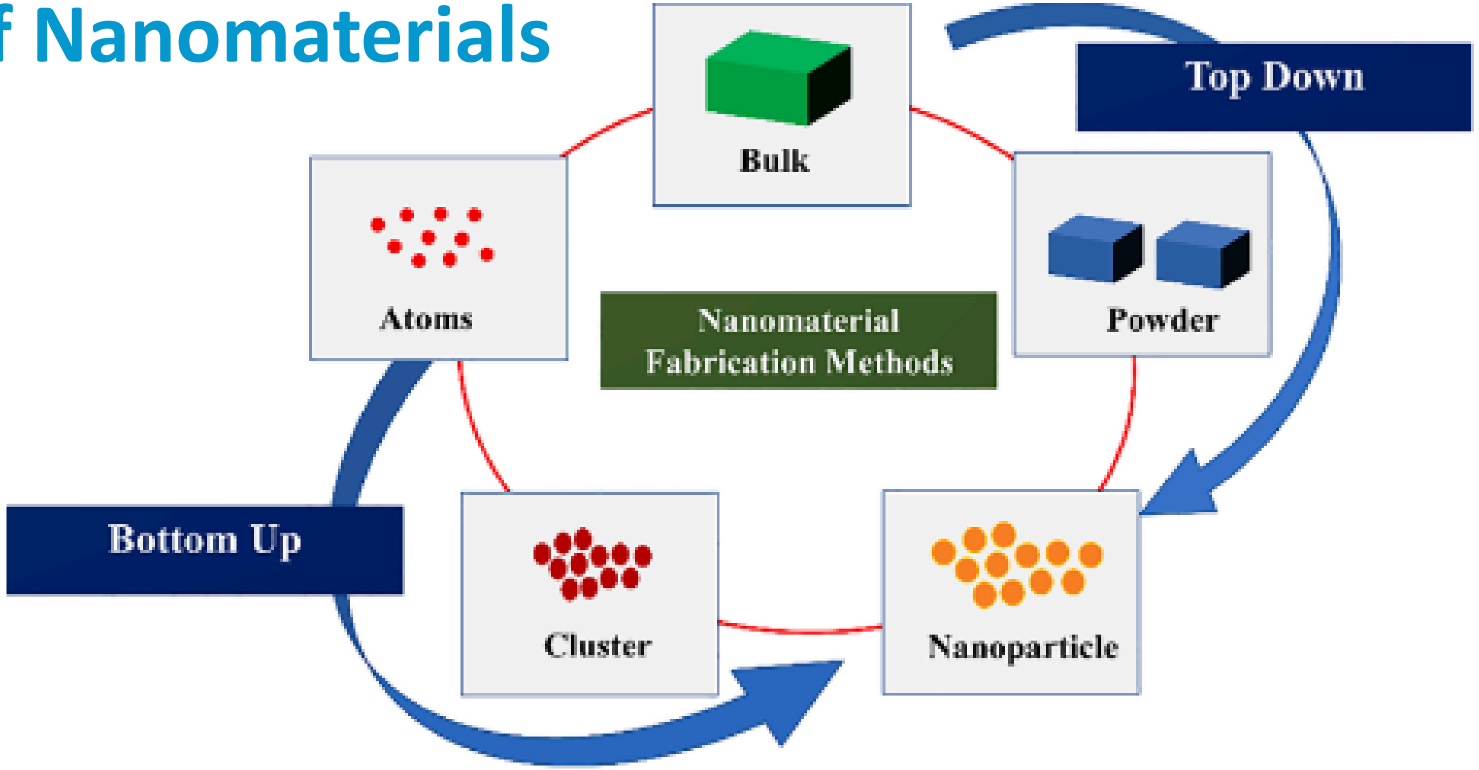
In the physical methods, mechanical methods offer the least expensive ways to produce nanomaterials in bulk (break the particles into nanostructures). But chemical fabrication methods are always easy to upscale and many, such as anodizing, are widespread industrial processes.

Top-down approach is the process of making nanostructures that start with larger structures and break away to nanosize to form nanomaterials. Methods of deposition and nanopatterning of thin films are more advanced, and this approach has been pushed further into the nanofabrication. Also, applying the top-down assembly process of nanocomponents over large areas is difficult and expensive.

Manufacturing of Nanomaterials

The building of nanostructures starting with small components such as atoms or molecules is called **bottom-up approach**.

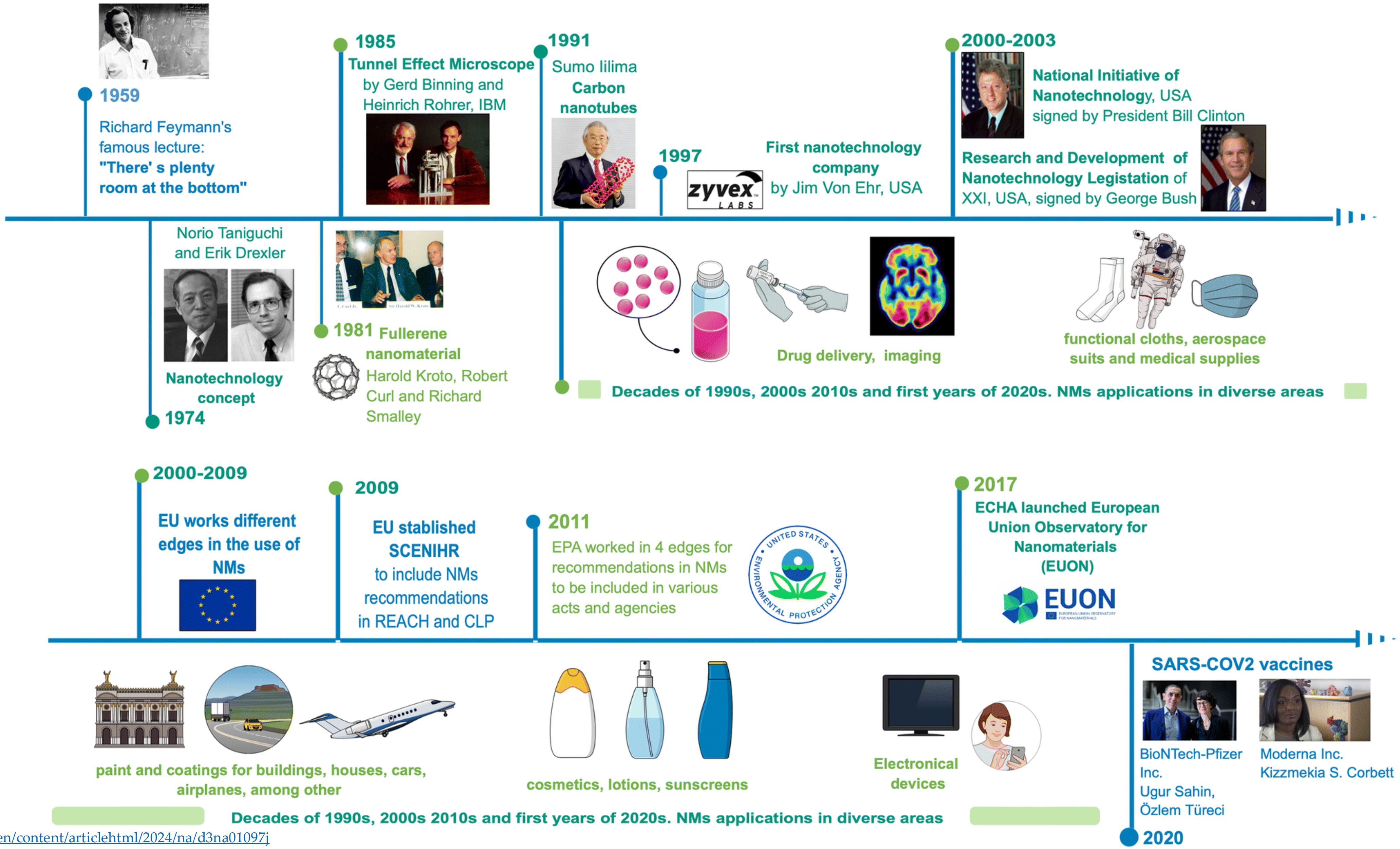
The bottom-up techniques make use of self-processes for ordering of supramolecular or solid-state architectures from the atomic to the mesoscopic scale. The methods of bottom-up include gas-phase and liquid-phase methods.



Chemical vapor deposition (CVD) and plasma arcing are called gas-phase methods, whereas liquid-phase represented by the most established method is sol-gel synthesis.

The choice between bottom-up and top-down approaches depends on the specific requirements of the desired nanomaterial and the intended application. Bottom-up approaches excel in providing atomic-level control and the ability to synthesize complex nanostructures, while top-down approaches offer scalability and compatibility with existing manufacturing processes. Researchers often employ a combination of these approaches, leveraging their respective strengths to achieve desired material properties and structures.

History and Development of Nanotechnology



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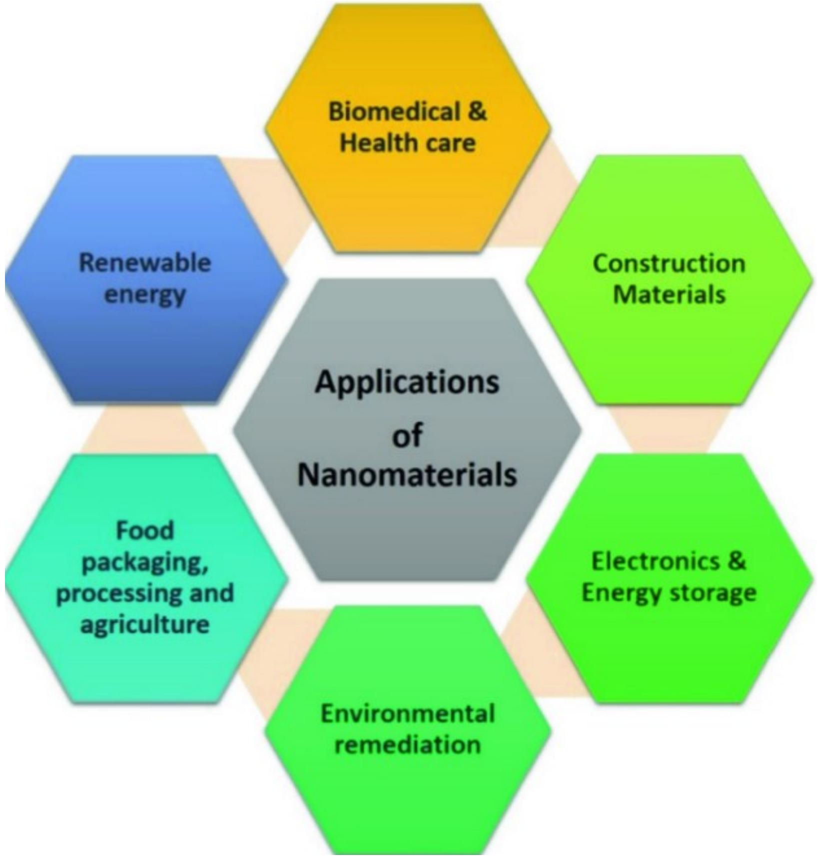
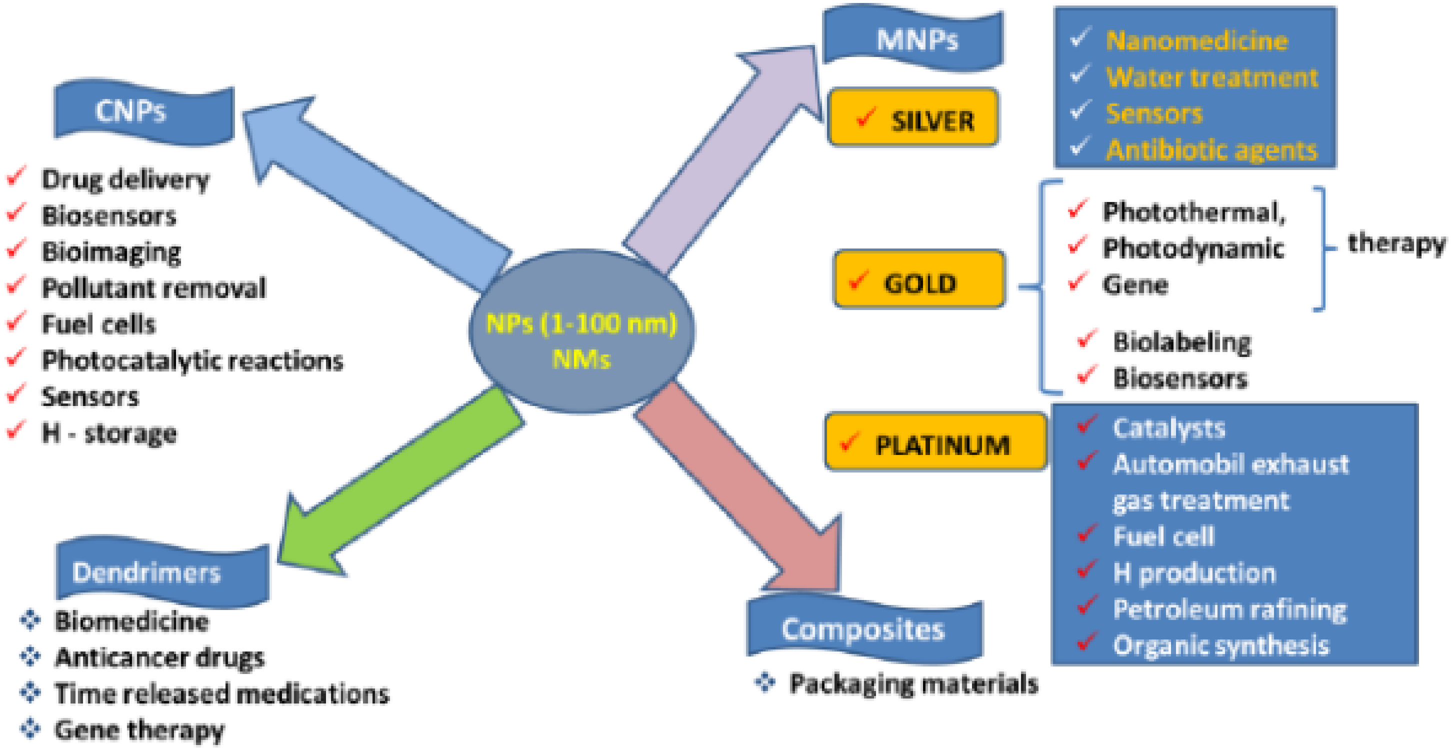
Nanomaterials. Modern Applications





The fields of application of NPs are extremely wide and continue to expand every day. A very good analogy is spheres with an increasing diameter because it exhibits non-linear changes in applications. Thus, the most notable areas of application of new materials are medicine and biotechnology, obtaining materials with special properties, and new materials for the production and storage of energy.

Areas	Applications
Automotive	Lightweight construction; Catalysts; Painting; Tires; Sensors; Windshield and body coatings
Construction	Materials; Insulation; Flame retardants; Surface coatings; Mortar
Electronics	Displays; Data memory; Laser diodes; Fiber optics; Optical switches; Filters; Conductive coatings; Antistatic coatings; Transistors
Engineering	Protective coatings for tools, machines; Lubricant-free bearings
Food and Drink	Packaging; Storage life sensors; Additives; Juice clarifiers
Medicine	Drug delivery systems; Contrast medium; Rapid testing systems; Prostheses and implants; Antimicrobial agents; In-body diagnostic systems
Textiles	Surface coatings; “Smart” clothes (anti-wrinkle, stain resistant, temperature controlled)
Chemical	Fillers for paints; Composite materials; Impregnation of papers; Adhesives; Magnetic fluids
Cosmetics	Sunscreen; Lipsticks; Skin creams; Toothpaste
Energy	Lighting; Fuel cells; Solar cells; Batteries; Capacitors
Environmental	Environmental monitoring; Soil and groundwater remediation; Toxic exposure sensors; Fuel changing catalysts; Green chemistry
Household	Ceramic coatings for irons; Odor removers; Cleaners for glass, ceramics, metals
Sports	Ski wax; Tennis rackets; Golf clubs; Tennis balls; Antifouling coatings for boats; Antifogging coatings for glasses, goggles
Military	Neutralization materials for chemical weapons, bullet-proof protection

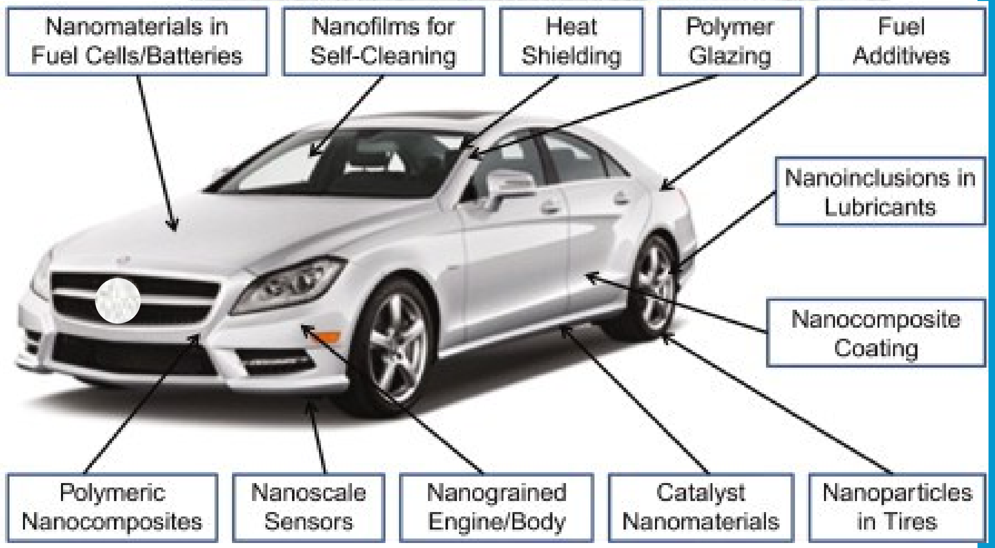
Nanomaterials. Applications

Automotive

Nanostructured materials are of great importance for the automotive industry. Above all, nanomaterials play a critical role in efforts to reduce vehicle weight, increase structural strength and flexibility, and improve vehicle safety and reliability.

Automobiles commonly use nanomaterials such as aluminum-carbon nanotube composites, carbon nanotubes, aluminum-silicon-carbide composites, and graphene.

Nanomaterials are used to fabricate thermoelectric materials that convert waste heat into electricity. Nanoscale engineering improves the Seebeck coefficient and reduces thermal conductivity, enhancing the efficiency of thermoelectric generators for applications in waste heat recovery, automotive exhaust systems, and other energy harvesting applications.



Nanomaterials. Applications

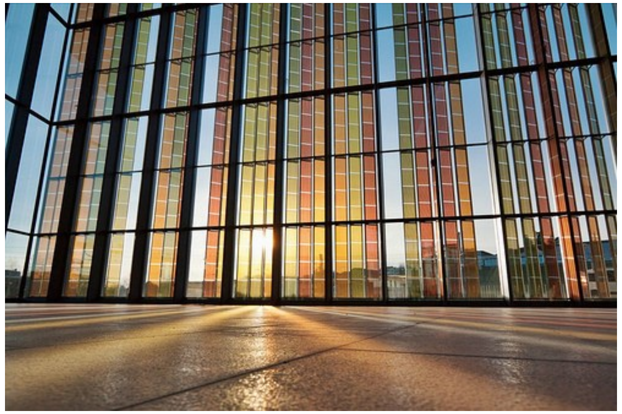
Energy

Nanotechnologies have great potential for cleaner, more efficient, and environmentally friendly energy generation. Energy-related technologies where nanotechnologies can play important roles are as follows: lighting, heating, transport, renewable energy, energy storage, fuel cells, hydrogen production, and storage.

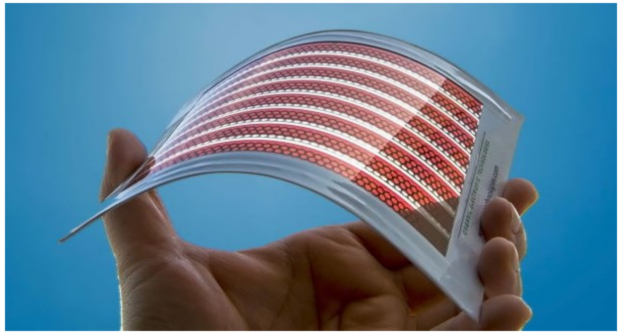
Pyroelectric ZnO nanowires can convert time-dependent temperature differences into electricity by spontaneous polarization in the conversion based on the temperature difference. The developed nanogenerator will be able to meet the energy requirements of nanodevices by converting balanced and waste energy.

Nanotechnologies are used in lithium-ion batteries, which are emphasized for hybrid and electric vehicles, and significant improvements have been made in efficiency and effectiveness

Nanotechnology has revolutionized solar cell technology by introducing nanostructured materials that enhance light absorption, charge separation, and electron transport. These advancements lead to higher conversion efficiencies and lower production costs in photovoltaic systems.



SwissTech Convention Center to the EPFL campus | Student house (2012)



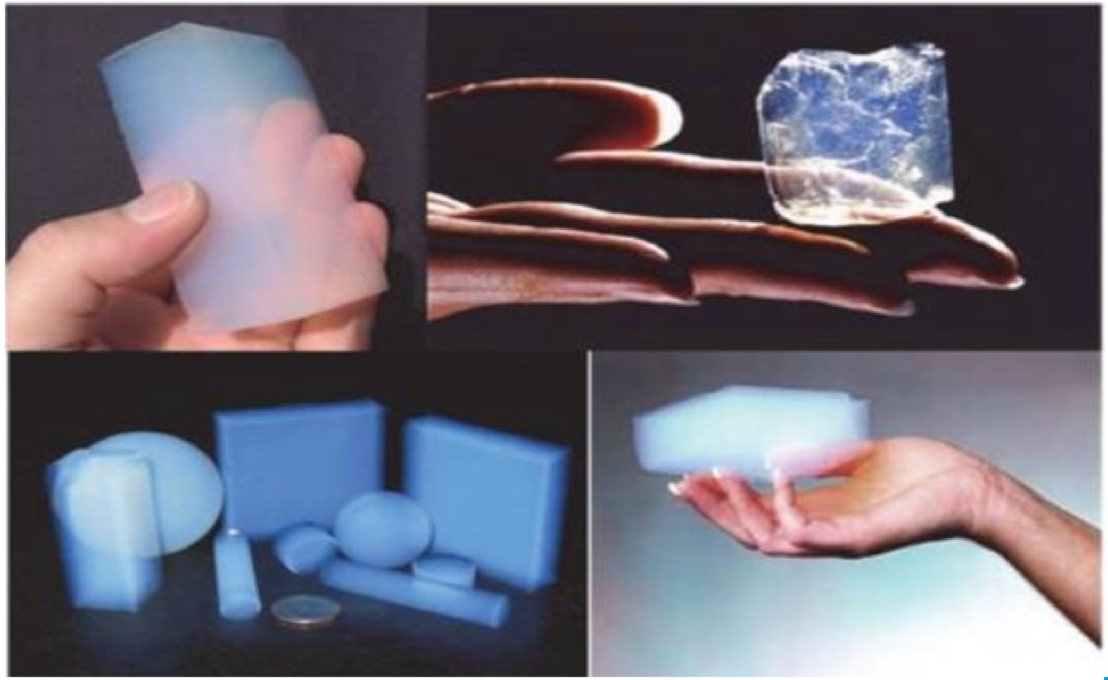
Nanomaterials. Applications

Environment

Nanosensor applications that can continuously measure and give warnings and alarms in case of deviation from the given threshold values are becoming widespread in order to monitor air, water and environment pollution. Environmental cleaning (remediation) consists of works that are free from chemical and radiological contaminants and do not endanger human health, together with separation and other processes. Faster and cost-effective cleaning-purification is possible with nanomaterial applications. The most appropriate approach in nanotechnological methods is selectivity and cleaning and elimination of organic / inorganic pollutants

Aerogels are a class of synthetic porous ultralight material derived from a gel, in which the liquid component for the gel has been replaced with a gas, without significant collapse of the gel structure.

The result is a solid with extremely low density and extremely low thermal conductivity. Aerogels can be made from a variety of chemical compounds



Examples of aerogels that can effectively clean water, sea-ocean, soil against oil spills, various aerogels and silica aerogels samples

Nanomaterials. Applications

Defense technologies

Nanotechnological developments have led to the emergence of textile products that have important functions in textile science and technologies. Many innovations in nanoscience and nanotechnologies have started to be applied in land, air, sea and space vehicles, which are the most strategic areas in defense fields.

For defense technologies, war uniforms with the following characteristics and qualities, with nanotechnological developments that can meet the requirements expected from uniforms and combat clothing, clothes, camouflage nets, camouflage covers have been developed.

Defense tools are becoming areas where nanotechnologies are used in every aspect as advanced technology platforms all over the world in an extremely diverse and wide range. Defense tools in which different nanotechnologies are applied and especially stand out with their "stealth" features.

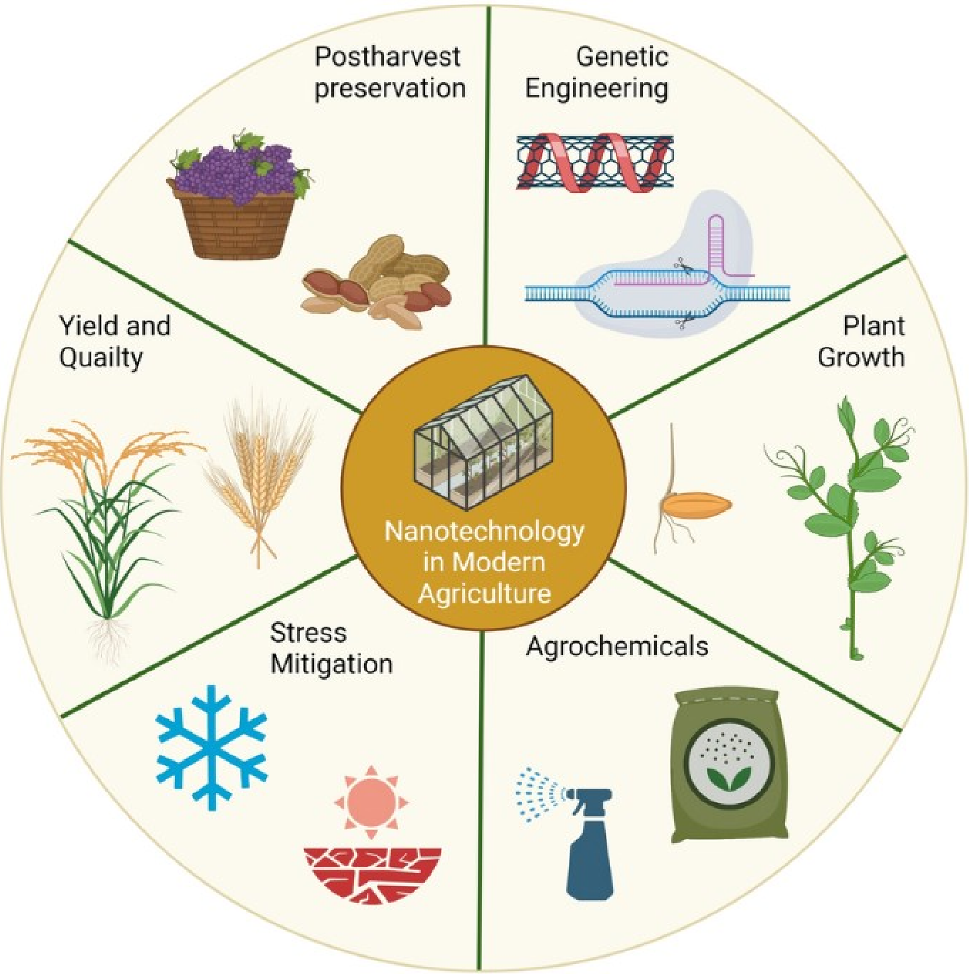
The defense tools in which different nanotechnologies are applied and especially stand out with their "stealth" features

Nanomaterials. Applications

Modern agriculture

Thus, to ensure safer and sustainable crop production, the use of advanced nanotechnological approaches in plants (phytonanotechnology) is of great significance.

Phytonanotechnology involves the application of nanotechnology principles and techniques to study and manipulate plants at the nanoscale. It focuses on understanding the interactions between nanoparticles and plants, as well as harnessing these interactions for various purposes. Phytonanotechnology offers a multifaceted approach to addressing key challenges in modern agriculture, including improving crop productivity, resource efficiency, and environmental sustainability. However, it's essential to continue research into the safety, efficacy, and long-term impacts of nanomaterials in agricultural systems to ensure their responsible and sustainable integration into farming practices.



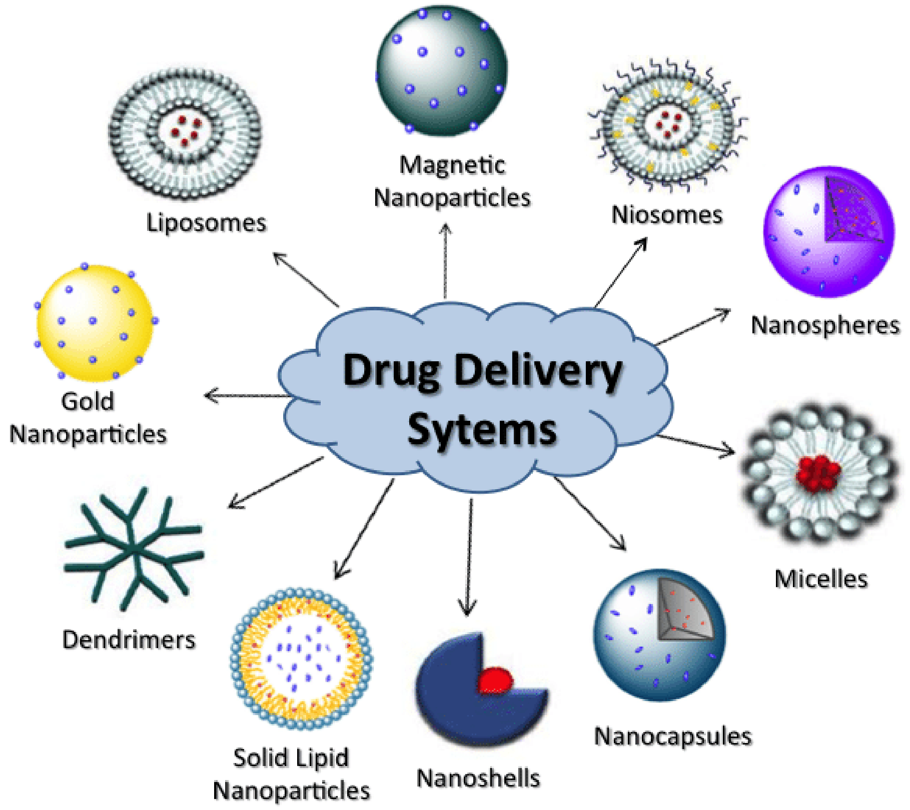
https://doi.org/10.1186/s12951-021-01176-w

Nanomaterials. Applications

Nanomedicine and drug delivery

The drug development process is a complex, cost-effective, time-consuming process and failure of a drug candidate takes place as a result of the number of limitations such as poor pharmacokinetic profile, lack of efficacy, side effect, fluctuations in plasma drug levels.

Nanotechnology plays a vital role for the development of materials by controlling their shape and size at the nanometer scale to improve physicochemical and pharmacological properties to treat various diseases such as obesity, diabetes, malaria, cardiovascular disorders, cancer, leukemia, Alzheimer's disease and Parkinson's diseases.

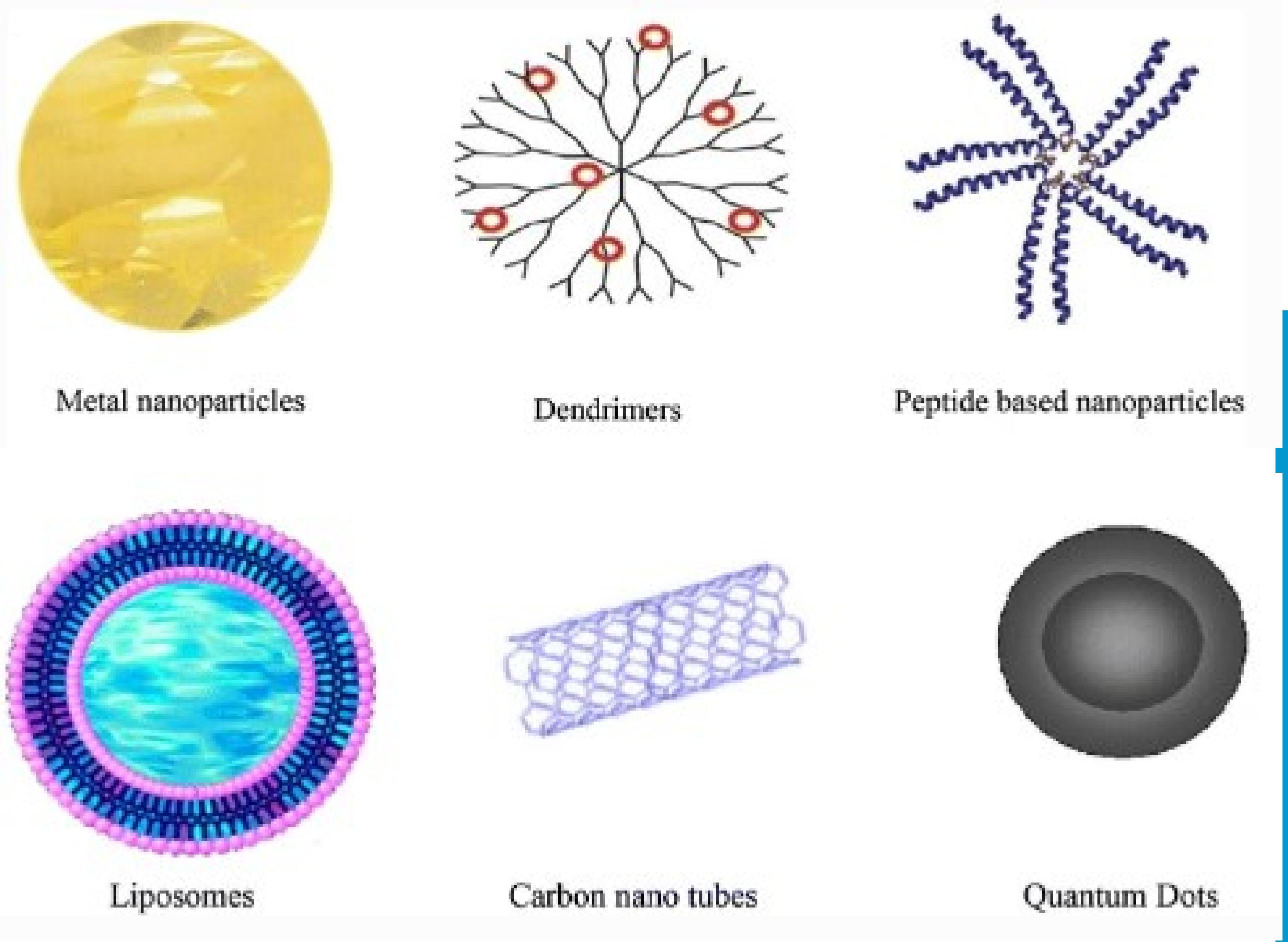


Nanomaterials. Applications

Nanomedicine and drug delivery

The surface properties of nanoparticle, such as surface charge, hydrophobicity, and functional groups are key factors for their biological activity. This technology is potentially applied at the cellular level of disease state in human beings with a high degree of specificity and also to achieve the utmost therapeutic efficacy with fewer side effects.

Nanoparticles are categorized into two types organic nanoparticles and inorganic nanoparticles. Examples of organic nanoparticles are dendrimers, micelles, liposomes, whereas gold NPs, quantum dots, superparamagnetic iron oxide NPs are called inorganic nanoparticles.



Common types of nano-drug carriers

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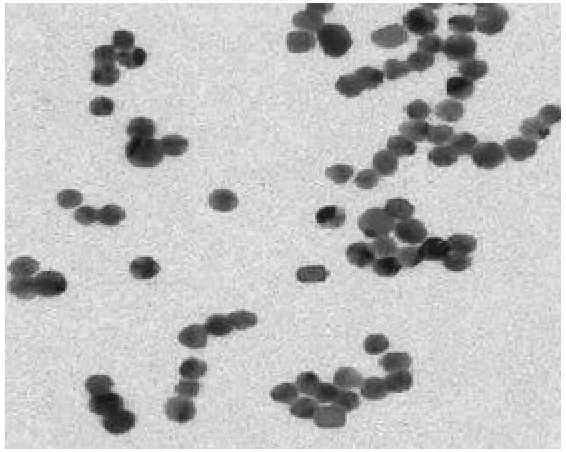
Nanomaterials. Applications

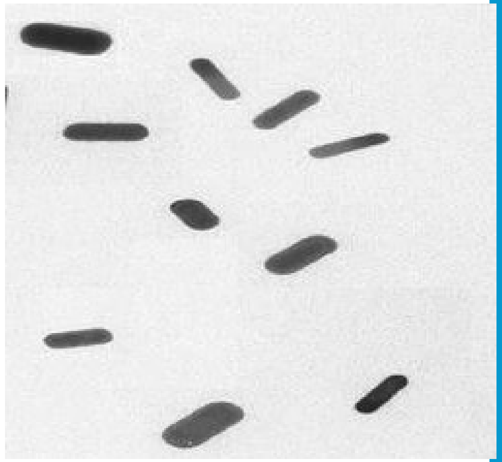
Nanomedicine and drug delivery

Due to their size, shape, and functionality, nanoparticle systems play a vital role in creation of DNA delivery vectors. They can penetrate deep into tissues and are absorbed by the cells efficiently. Nano-sized colloidal carriers of drugs can be regarded as an advanced development in pharmacotherapy. They act as potential carriers for several classes of drugs like anti-cancer, anti-hypertensive and hormones, etc.

Submicron colloidal particles have been used as nanoparticles for the purpose of drug delivery and also used for the diagnosis of diseases. Nanoparticles have widened the scope of pharmacokinetics for insoluble drugs. For example, the trans-retinoic acid nanoparticle coated by $CaCO_3$ was developed as a new drug delivery system.

Gold nanoparticles and nanorods have many unique properties, which have been explored for potential applications in bio-molecular detection. Gold nanoparticles are generally produced by reducing chloroauric acid. Gold nanoparticles are chemically inert.





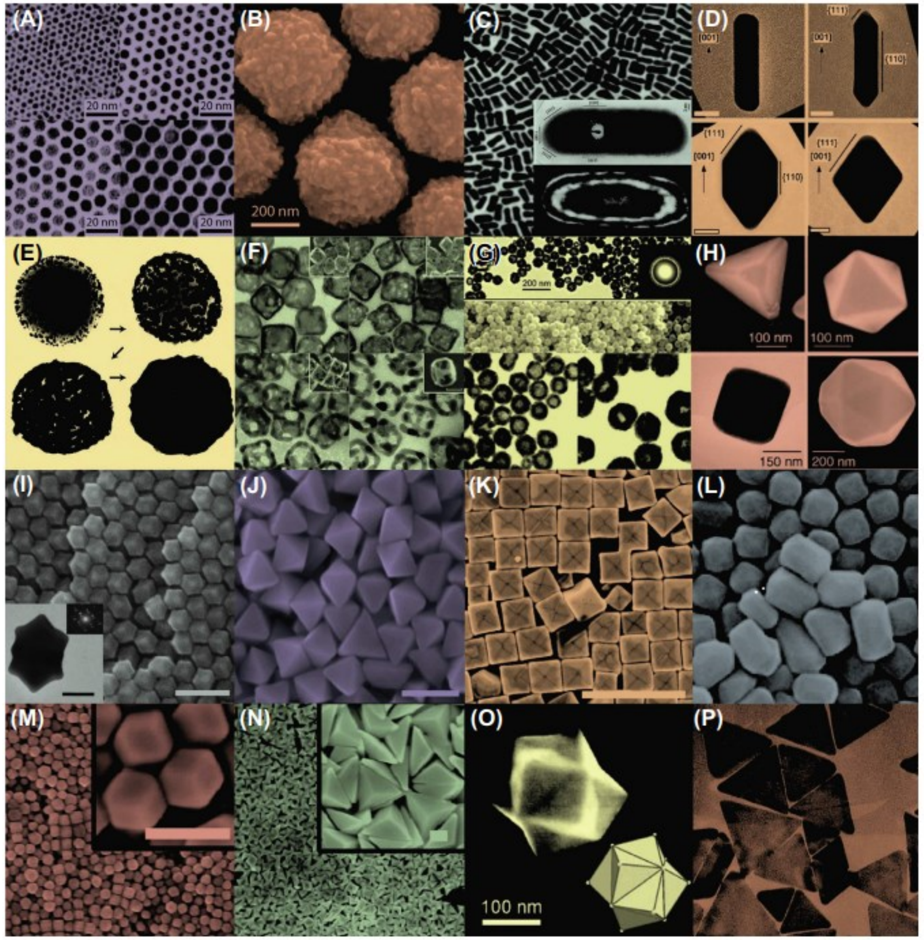
TEM images of gold nanoparticles and nanorods

Nanomaterials. Applications

Nanomedicine and drug delivery

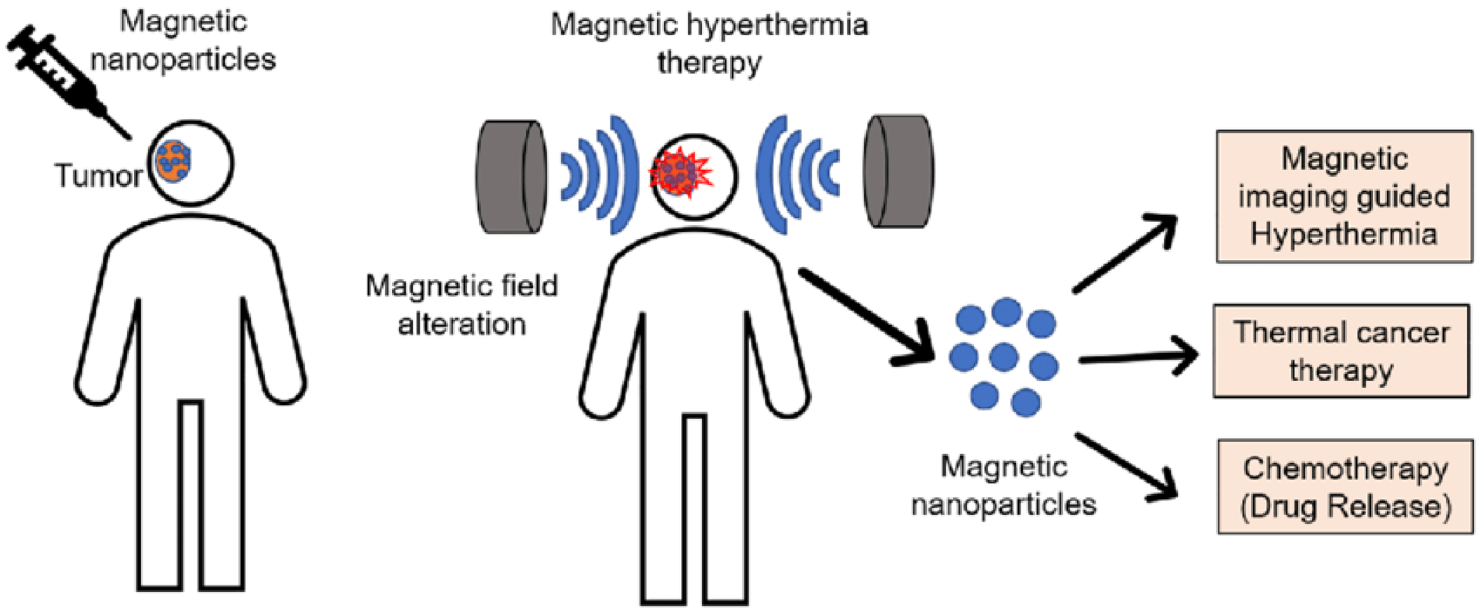
Future cancer treatments might use gold nanoshells to fight tumors. Gold nanoshells are tiny spheres of glass covered with a thin layer of gold. In an experimental treatment, gold nanoshells are injected into the body and collect in the tumor. Near-infrared light is then shined on the tumor. The light passes safely through healthy tissue but heats the gold nanoshells and destroys the tumor. Pilot studies indicate that the treatment is successful, with minimal side effects.

An important issue that needs to be addressed is the engineering of the particle surface for optimizing properties such as bioavailability and nonimmunogenicity for the use of gold nanoparticles in various biomedical applications.



Gold nanoparticles of various sizes and shapes with potential applications in biomedicine.

Nanomaterials. Applications



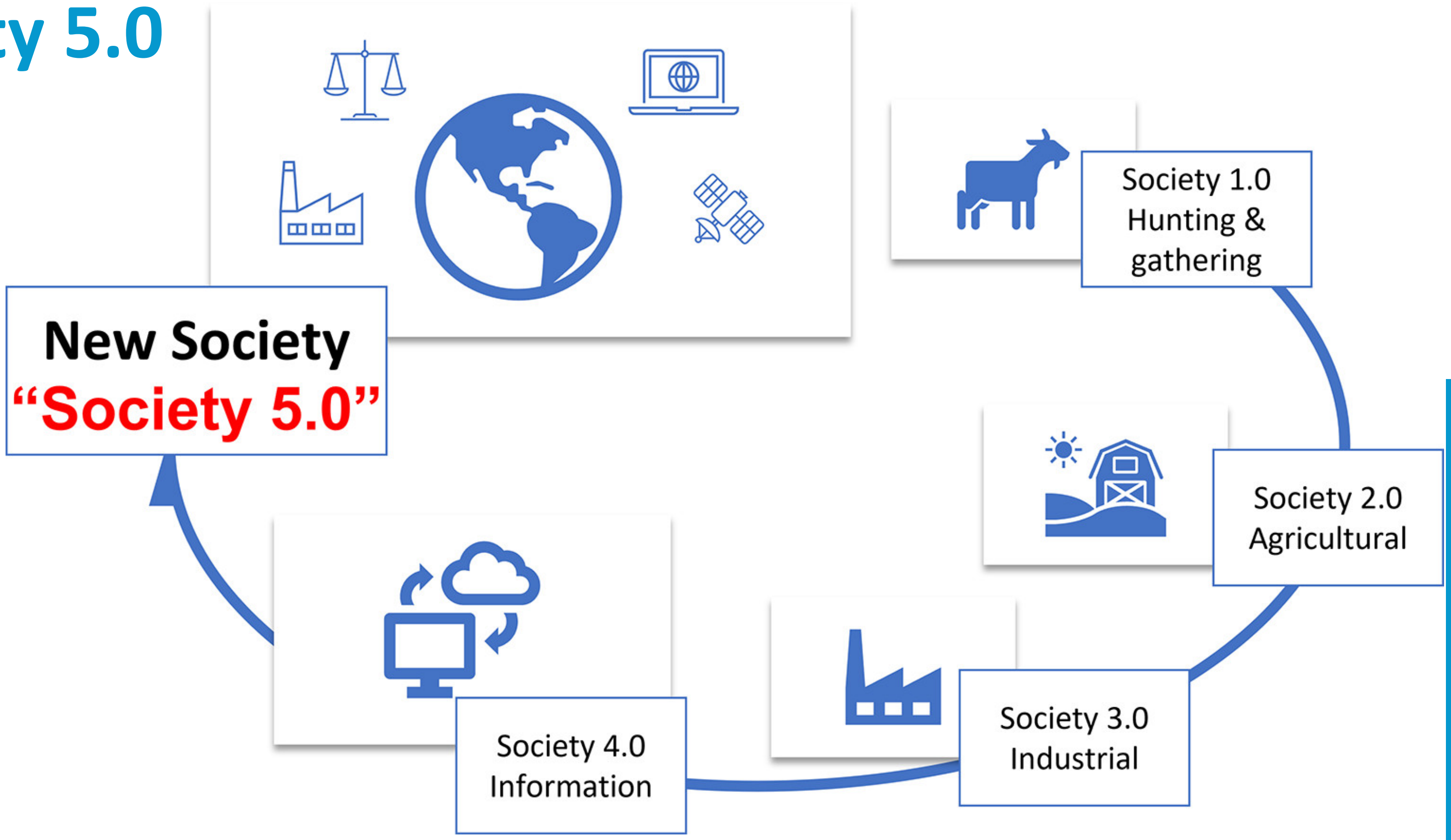
Biomedicine. Hyperthermia

Magnetic hyperthermia is a therapeutic approach that uses magnetic nanoparticles, typically iron oxide nanoparticles (e.g., magnetite or maghemite), to generate heat in response to an alternating magnetic field (AMF) for targeted treatment of diseases, particularly cancer.

An external AMF is applied to induce oscillating magnetic fields around the nanoparticles. The magnetic nanoparticles rapidly reorient themselves with the changing magnetic field, leading to frictional losses and heat generation through relaxation processes.

The heat produced by magnetic nanoparticles in response to the AMF raises the temperature of the target tissue, causing localized hyperthermia. The elevated temperatures can induce cytotoxic effects on cancer cells or other target cells while minimizing damage to surrounding healthy tissues.

Advancing to Society 5.0



In Society 5.0 all people and things are connected with the Internet of Things (IoT), where knowledge and information are shared, necessary information is provided with artificial intelligence (AI)

Nanotechnology and materials will play a main role in the advancement of Society 5.0.

Nanotechnology will be instrumental in driving the digital revolution by offering a wide array of nanodevices for use in Society 5.0 applications such as IoT sensors, autonomous vehicles, smart robots, and more. nanotechnology and materials are expected to contribute significantly to the realization of a sustainable society by facilitating water purification, reducing CO_2 emissions, and promoting material recycling approaches. New technologies will support our health and well-being through the development of wearable biosensors and biomaterials for regenerative medicine.

REGINNA 4.0

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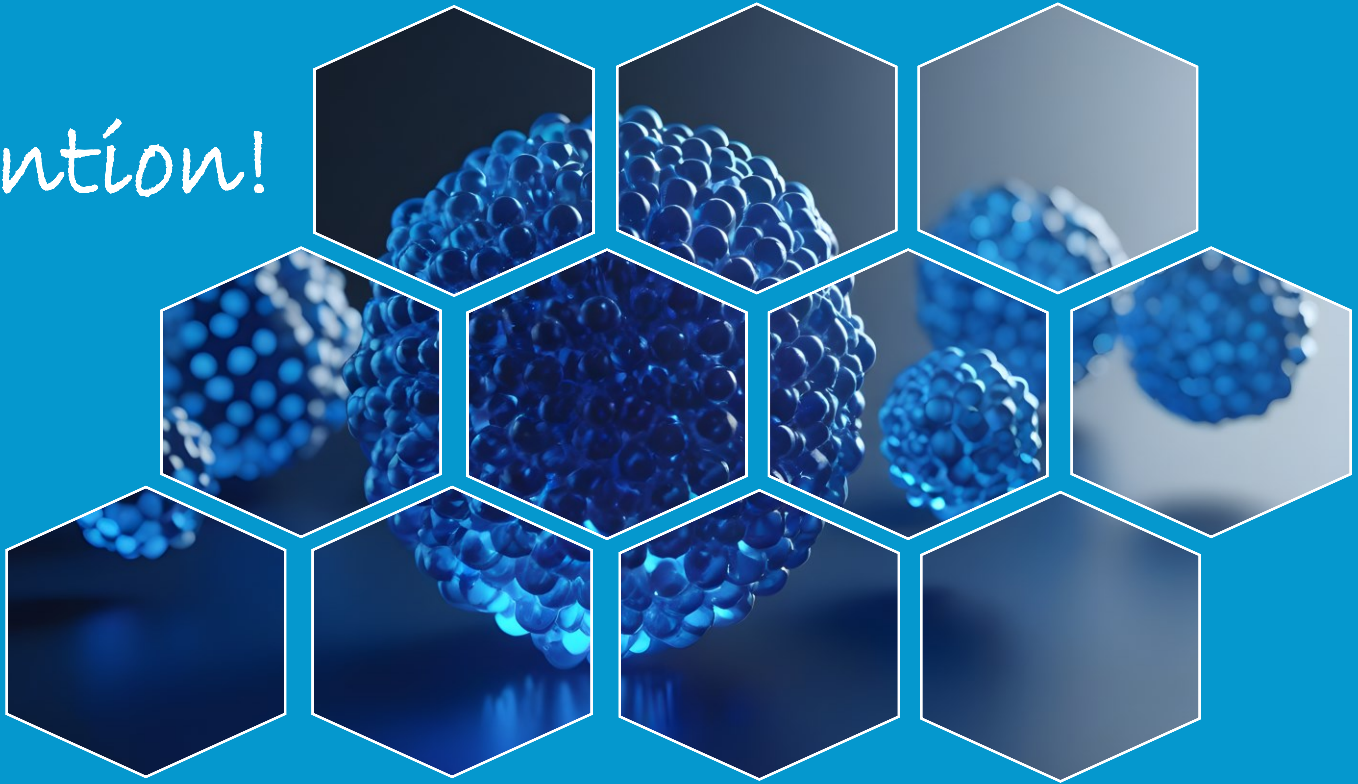
Thank you for your attention!



Liliia Turovska, PhD

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