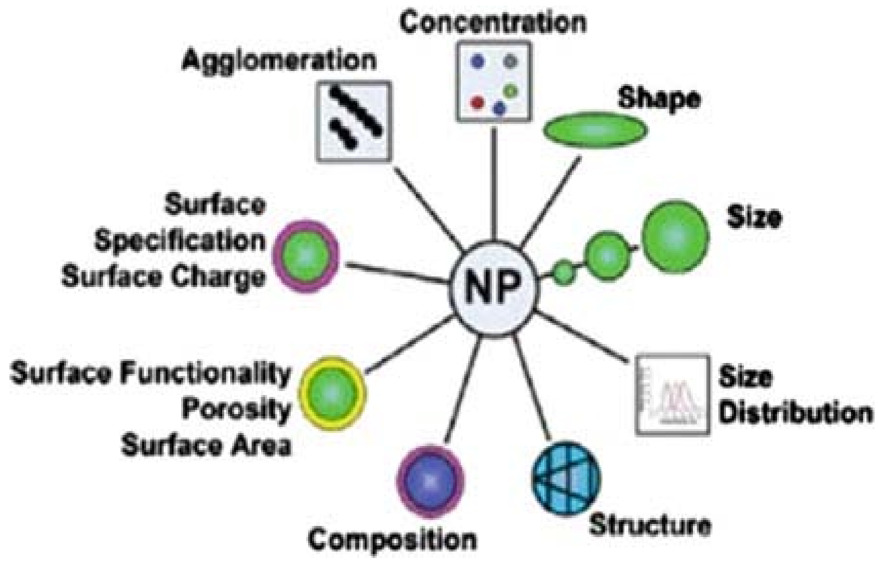
Unique Properties of Nanoparticles

- The macroscopic physical properties of a substance (melting point, boiling point, conductivity, etc.) are determined by studying a pure sample in quantities big enough to be measured under normal laboratory conditions.
- The value which is obtained represents an average value based on the behavior of billions and billions of molecules of water.
- This is not correct for many materials:
- as the size of the material is reduced, and the nanoscale level is reached, it is possible that the same material will display totally different properties (different melting point, conductivity, etc.).
- This is because matter at the nanoscale no longer follows Newtonian physics but rather quantum mechanics.
- In other words, the properties of materials can be size-dependent.
- This might be a rather new concept, conventionally, the properties of a substance (solid, liquid or gas) are related to the atoms and molecules that make up the substance, and the way they are connected to one another (chemical bonds).
- A piece of gold to be golden in color however big or small it is.
- This is correct at the macro and micro-scale level: but at the nanoscale, things start to change dramatically due to quantum effects.
- In fact, gold can be used as a prime example: a colloid of gold nanoparticles is no longer ‘golden’ but ruby-red in color.
- Nanomaterials are closer in size to single atoms and molecules than to bulk materials, and to explain their behavior, it is necessary to use quantum mechanics.
- Quantum mechanics is a scientific model that was developed for describing the motion and energy of atoms and electrons.



- Due to the smallness of nanomaterials, their mass is extremely small and gravitational forces become negligible.
- Instead, **electromagnetic forces are dominant in determining the behavior of atoms and molecules.**
- Tunnelling is a fundamental quantum effect and it is the basis of a very important instrument for imaging nanostructured surfaces called the **Scanning Tunnelling Microscope (STM).**
- **The same instrument can be used as a nanofabrication tool (movement of single atoms).**
- **Increased surface-to-volume ratio:**
- one of the distinguishing properties of nanomaterials is that they have an increased surface area.
- It has already been stated that a nanomaterial is formed of at least a cluster of atoms, often a cluster of molecules.
- It follows that **all types of bonding that are important in chemistry are also important in nanoscience.**
- **They are generally classified as:**
- **Intramolecular bonding (chemical interactions):**
- **these are bonding that involve changes in the chemical structure of the molecules and include ionic, covalent and metallic bonds;**

- **Intermolecular bonding (physical interaction):**
- **these are bonding that do not involve changes in the chemical structure of the molecules and include ion-ion and ion-dipole interactions; van der Waals interactions; hydrogen bonds; hydrophobic interactions.**
- **Surface properties**
- Regardless of whether we consider a bulk material or a nanoscale material, its physical and chemical properties depend on many of its surface properties.
- **The branch of science that deals with the chemical, physical and biological properties of surfaces is called surface science.**
- **The importance of surface atoms**
- In surface science, the chemical groups that are at the material interface determine its properties.
- Properties like catalytic reactivity, electrical resistivity, adhesion, gas storage and chemical reactivity **depend on the nature of the interface.**
- Nanomaterials have a significant proportion of atoms existing at the surface.

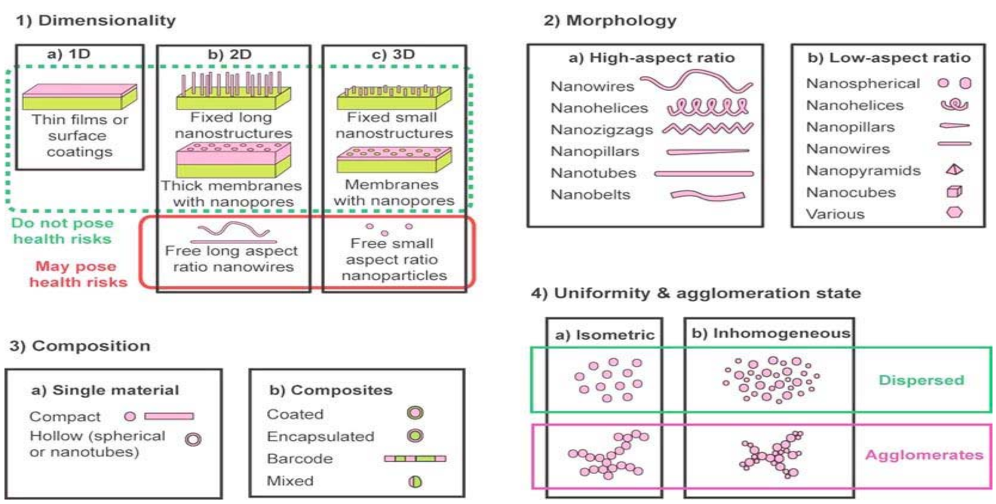
Shape also matters

- **Given the same volume, the extent of the surface area depends on the shape of the material.**
- **A simple example is a sphere and a cube having the same volume.**
- **The cube has a larger surface area than the sphere.**
- **For this reason, in nanoscience, not only the size of a nanomaterial is important, but also its shape.**
- **The fact that in a nanomaterial a larger fraction of the atoms is at the surface influences some physical properties such as the melting point.**
- **Given the same material, its melting point will be lower if it is nano-sized.**
- **Surface atoms are more easily removed than bulk atoms, so the total energy needed to overcome the intermolecular forces that hold the atom 'fixed' is less, thus the melting point is lower.**

Surface energy

- Atoms and molecules that exist at the surface or at an interface are different from the same atoms or molecules that exist in the interior of a material.
- This is true for any material.
- Atoms and molecules at the interface have enhanced reactivity and a greater tendency to agglomerate: surface atoms and molecules are unstable, they have high surface energy.
- Nanomaterials are inherently unstable, therefore there are various methods that nanomaterials adopt to minimize their inherent high surface energy.
- One of the ways of reducing the surface energy in nanoparticles is agglomeration.
- The surface of 10 identical nanoparticles is equal to the sum of the surface energy of each individual nanoparticle.
- If these were to agglomerate, and become one large particle, the overall surface energy would be reduced.
- Nanoparticles have a strong intrinsic tendency to agglomerate.
- To avoid this, surfactants can be used. This also explains why when nanoparticles are used in research and industry they are often immobilised on a solid support or mixed within a matrix.

Even in commercial products that claim to contain nanoparticles (such as sunscreens) microscope images show that they are actually present in the form of agglomerates of > 100 nm dimensions.



- **A catalyst is a substance that increases a chemical reaction rate without being consumed or chemically altered.**
- **Nature's catalysts are called enzymes and are able to assemble specific end products.**
- **Man-made catalysts are not so energy efficient: they are often made of metal particles fixed on an oxide surface.**
- **The 'active surface' increases when the size of the catalysts is decreased:**
- **the smaller the catalyst particles, the greater the surface-to-volume ratio.**
- **nanoscale gold particles can catalyse chemical reactions.**

Electrical properties

- **Some nanomaterials exhibit electrical properties that are absolutely exceptional.**
- **Their electrical properties are related to their unique structure.**
- **Two of these are fullerenes and carbon nanotubes.**
- **For instance, carbon nanotubes can be conductors or semiconductors depending on their nanostructure.**
- **Optical properties**
- **Some nanomaterials display very different optical properties, such as color and transparency, compared to bulk materials.**
- **Nanomaterials in general can have peculiar optical properties as a result of the way light interacts with their fine nanostructure.**
- **Colloids of metal nanoparticles such as gold or silver can show colors which are not found in their bulk form, such as red, purple or orange, depending on the shape, size and surrounding media of the nanoparticles.**
- **An example that a colloid of gold nanoparticles about 15 nm in size is ruby-red! The properties of metal nanoparticles make them useful in sensing.**

Color in semiconducting)nanocrystals (quantum dots

- **Tuning the size of the semiconductor nanocrystal is a means of tuning the band gap and, therefore, the wavelength absorbed/emitted by the crystal.**
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- **QDs are currently used as an alternative to conventional dyes in fluorescence microscopy and in other methods where dyes are used (e.g. dye-sensitised solar cells).**
- **As a result, the same material (e.g.CdSe) emits different colors depending on its size.**
- **Sunscreens contain ZnO and TiO2 clusters of about 200 nm.**
- **Visible light interacts with these clusters and all of its wavelengths are scattered.**
- **The combination of the visible spectrum is white: therefore, the sunscreen appears white.**
- **If the dimensions of the cluster are reduced, for instance from 200 to 100 nm, maximum scattering occurs around 200 nm and the curve is shifted towards shorter wavelengths, which are no longer in the visible spectrum: the effect is that the same material (e.g. ZnO), now in smaller size (100 nm), no longer appears white but transparent.**

Magnetic properties

- **In general, the magnetic behavior of a material depends on the structure of the material and on its temperature.**
- **The typical size of expected magnetic domains is around 1 µm.**
- **When the size of a magnet is reduced, the number of surface atoms becomes an important fraction of the total number of atoms, surface effects become important, and quantum effects start to prevail.**
- **When the size of these domains reaches the nanoscale, these materials show new properties due to quantum confinement,**
- **for example the giant magneto-resistance effect (GMR).**
- **This is a fundamental nano-effect which is now being used in modern data storage devices.**

Mechanical properties

- **Some nanomaterials have inherent exceptional mechanical properties which are connected to their structure.**
- **One such material is carbon nanotubes: these are extremely small tubes having the same honeycomb structure of graphite, but with different properties compared to graphite. They can be single-walled or multi-walled.**
- **Carbon nanotubes are 100 times stronger than steel but six times lighter!!**