E05 - NANOTECHNOLOGY

Summer of Science 2024

End-Term Report

May - July '24

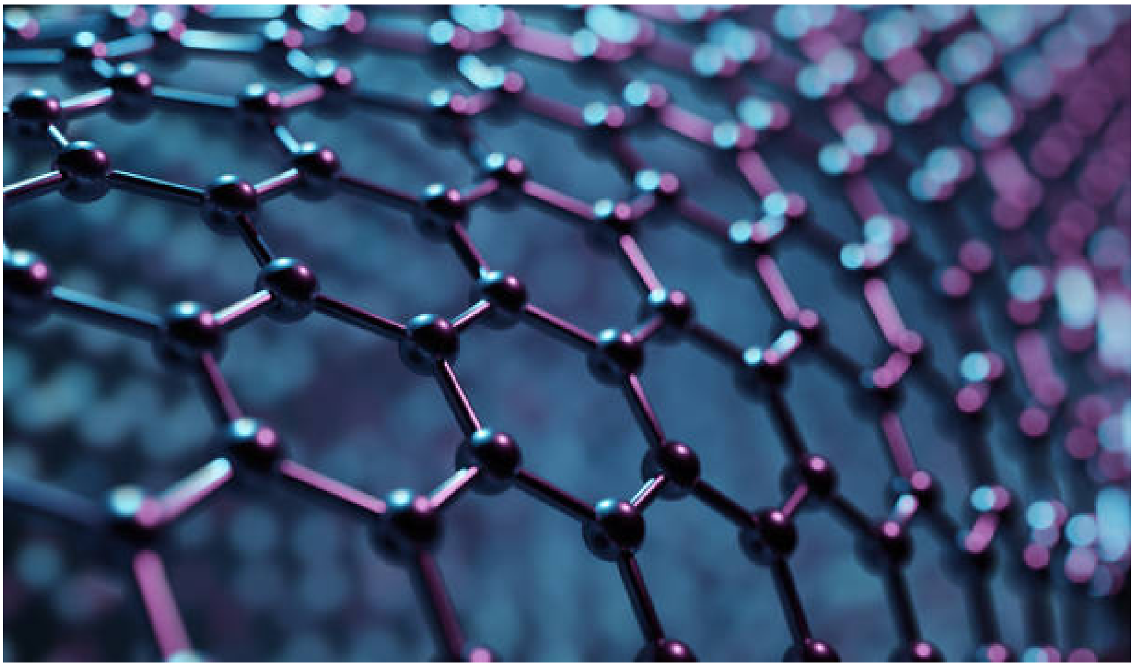

Figure 1: Nanotechnology

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This report seeks to dwell on the evolution of ***Nanotechnology*** and look at its current scope and usage in the scientific world.

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	SUBMISSION OF ENDTERM REPORT

I'm up to date with my POA!

§1. History, Introduction and Applications of Nanotechnology

Merging the area of the atom and the solid is the materialization of the nanoworld. The concept of nanoworld is based on a mix of scientific and technological domains that once were separate. Nanotechnology is a mindset about the world that is rooted in atomically precise perception. The concrete use of nanotechnology lies in arranging and reconfiguring atoms and molecules to make new materials and devices capable of better qualities.

1.1 How small (or big) the nanoscale really is?

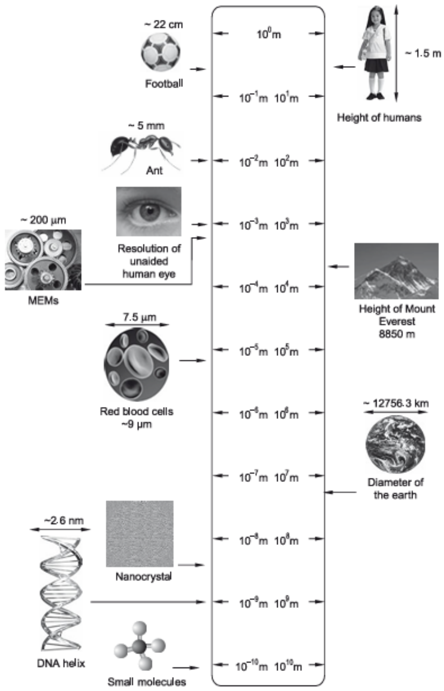

Figure 2: Nanoscale
[6]

The word 'nano' is a Greek prefix meaning dwarf or something very small and depicts one billionth (10^{-9}) of a unit. Nanomaterials have been produced and used by humans for hundreds of years.

But..*How small is a nanocrystal*? For comparison, a nanometer represents a dimension about a few tens of thousand times thinner than a human hair. Figure 2 gives an idea of the scale of different objects, from macroscale to nanoscale. In the case of polycrystalline materials, the grain size is typically of the order of 1-100 microns (1 micron=10^{-6} m). Nanocrystalline materials have a grain size of the order of 1-100 nm and are therefore 100-1000 times smaller than conventional grain dimensions. However, compared to the size of an atom (0.2-0.4 nm in diameter), nanocrystalline grains are still significantly big.

We cannot define an exact dimension for the grain size to classify materials in the nanoscale. This is because it is subjective and depends on the application or end property of interest. But broadly, *nanomaterials may be classified as materials with at least one of their dimensions in the nanometric range, below which there is significant variation in the property of interest compared to microcrystalline materials.*

1.2 What makes the nanoscale so special?

There are various reasons why nanoscience and nanotechnologies are so promising in materials, engineering and related sciences.

First, at the nanometer scale, the properties of matter, such as energy, change. The second exceptional property of nanomaterials is that they can be fabricated atom by atom by a process called ***bottom-up***. The information for this fabrication process is embedded in the material building blocks so that these can self-assemble in the final product.

1.3 Applications in today's world

Given their size, nano-objects have specific qualities which prove useful in a number of different applications. Structures with new properties possessing the properties similar to those of both a molecule and a solid are being discovered. Hence, the scope of nanotechnology is vast and the potential includes *medical and healthcare, electronics and computing, energy, environmental protection, materials science, agriculture and food, consumer products, automotive industries etc.*

§2. Forces at the nanoscale

Interfacial forces are particularly important in the nanorealm, governing the behavior of nano-objects and determining the performance of nanostructured materials and nanodevices. There are intermolecular forces of electrostatic origin that are very important. The capillary force is a manifestation of the wetting phenomenon originating in the interfacial forces. There is also the van-der-Waals or Casimir force which is unique to the nanoscale.

One of the other fundamental forces like gravitational can be neglected because it is very weak at the nanoscale. The strong nuclear force can also be neglected since its range is much smaller than the nanoscale.

2.1 Intermolecular forces of electrostatic origin

These forces are responsible for the relatively weak interactions between two objects, typically in the presence of an intervening medium. They are all electrostatic in origin and are quite likely to be seen at surfaces.

Surface Tension

Surface tension γ is formally defined as the free energy G required to create and extend an interface of area A:

$$\gamma = (\delta G/\delta A)_{T,P} \tag{1}$$

where the practically encountered constant temperature and pressure makes the Gibbs free energy the appropriate choice for G.

Generally, work needs to be done to create an interface because it has a higher free energy than bulk. γ_1 and γ_2 are the surface tensions of the old layers lost and γ_{12} is that of the new interface formed. The nanoscopic viewpoint is that the "microscopic" surface tension γ_{12} depends on specific chemical interactions between the surfaces of the two substances involved.

The work of cohesion of a solid is:

$$W^{coh} = 2A\gamma_1 = -\Delta G^{(coh)} \tag{2}$$

On the other hand, the work of adhesion (needed to separate two dissimilar substances 1 and 2) is given by:

$$W_{12}^{adh} = (\gamma_1 + \gamma_2 + \gamma_{12})A = -\Delta G^{(adh)} \tag{3}$$

A major practical difficulty in experimentally determining surface tensions of solutes is that under nearly all real conditions, surfaces are contaminated in a highly non-uniform fashion.

Adsorbed impurity molecules experience different interfacial energies at different locations on the surface due to the different curvatures.

Wetting and Dewetting

Wetting means the spreading of a liquid over a solid surface while dewetting refers to the withdrawal of liquid from a surface. These are both vital processes in natural and industrial processes. Wetting is mostly considered from a mesoscopic viewpoint and therefore fits well into the framework of nanotechnology.

The spreading of a liquid on a soild surrounded by vapours is expected to depend on γ_{SV}, the surface tension between solid and vapour. Young's equation (4) correctly depicts the relation between γ_{SV},γ_{SL}, γ_{LV}:

$$\gamma_{LV} cos\theta = \gamma_{SV} - \gamma_{SL} \tag{4}$$

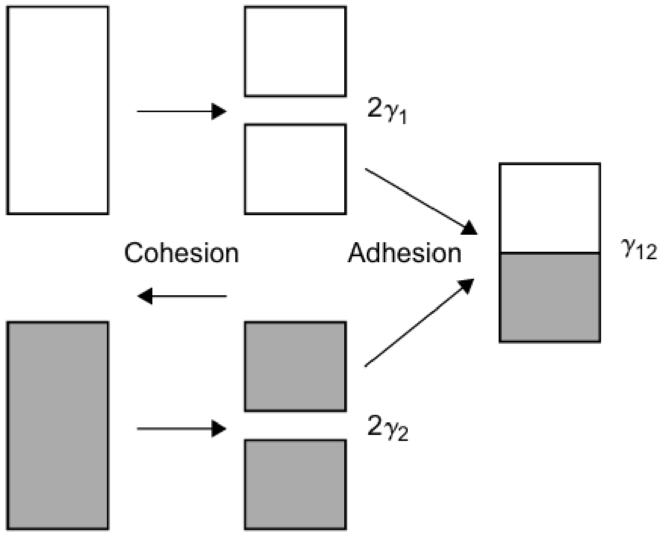

Figure 3: Adhesion and Cohesion of substances
[2]

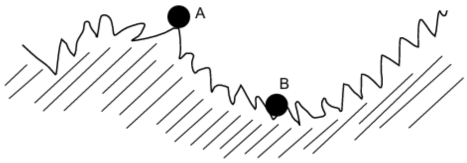

Figure 4: Adsorbed impurity molecules on a possibly real-machined surface
[2]

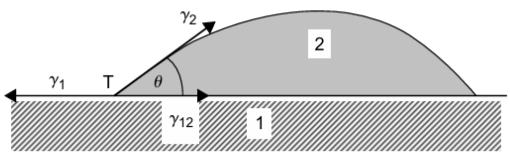

Figure 5: Solid-liquid boundary, neglecting vapor, ie. $\gamma_1 = \gamma_{SV}$
[2]

Degree of wetting is inversely proportional to θ, with $\theta = 0$, corresponding to maximum wetting.

2.2 Capillary force

An attractive force between a solid and a liquid causes the liquid in a capillary of radius r, to rise to a height h, given by:

$$h = \frac{\rho g r}{2\gamma_{LV} cos\theta_{SL}} \tag{5}$$

where, g is the acceleration due to gravity.

Water, being a strong hydrogen bond donor as well as acceptor, attracts a variety of substances, including minerals, which tend to get oxidised.

Impact at the nanoscale

After bath, humans carry with them a thin film of water of the order of 100 μm, which weighs about a few hundred grams. This is much lesser compared to the bearer, the human. In contrast, animals like mice have to carry water of approximately their own weight and a wet fly would weigh many times its own mass. The inadvertent introduction of water into microsystems may completely degrade their performance; nanosystems are even more vulnerable.

Force environment at the nanoscale

For objects wholly immersed in water, it is not the inertia which plays the important role, instead it is the viscosity.

§3. Types of Nanomaterials

To systematically study, understand and appreciate the diversity of nanomaterials, it is important to classify them. The most typical classification is based on dimensions. Nanomaterials are thus classified as 0D, 1D, 2D, and 3D. This classification is based on the number of dimensions of the nanomaterial which are *not in the nanoscale*.

3.1 Zero Dimensional Nanomaterials

Zero dimensional nanomaterials, *usually nanoparticles*, have all their dimensions in the nanoscale.

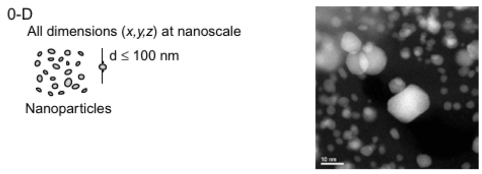

Figure 6: 0D nanomaterials or nanoparticles
[2]

0D nanomaterials can be classified as follows:

- Amorphous / Crystalline
- Single crystalline / Poly Crystalline
- Composed of single / multi-chemical elements
- Metallic / Ceramic / Polymeric
- Various shapes and forms
- Existing individually / incorporated in a matrix

3.2 One Dimensional Nanomaterials

One dimensional nanomaterials, unlike nanoparticles, have one dimension which is *out of the nanoscale.* This gives them a needle-like shape. Examples of one-dimensional nanomaterials are *nanotubes, nanorods, and nanowires.*

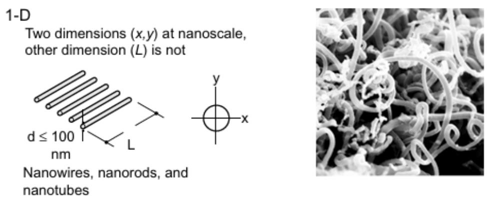

Figure 7: 1D nanomaterials
[2]

Similar to 0D nanomaterials, they can be classified as follows:

- Amorphous / Crystalline
- Single crystalline / Poly Crystalline
- Chemically Pure / Impure
- Metallic / Ceramic / Polymeric
- Standalone materials / Embedded within another medium

3.3 Two Dimensional Nanomaterials

2D nanomaterials have two of their dimensions that are not confined to thenanoscale. This results in a plate-like structure. Examples of 2D nanomaterials are *nanofilms, nanolayers, and nanocoatings.*

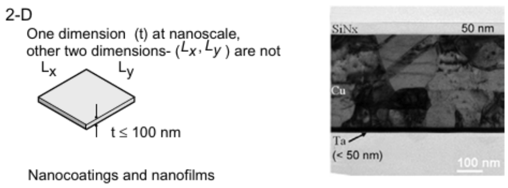

Figure 8: 2D nanomaterials
[2]

They can be classified as follows:

- Amorphous / Crystalline
- Metallic / Ceramic / Polymeric
- Various chemical compositions
- Used as Single Layer / Multi Layer structures
- Deposited on a substrate
- Integrated in a surrounding matrix material

3.4 Three Dimensional Nanomaterials

3D nanomaterials, also known as *bulknanomaterials*, have all three dimensions out of the nanoscale! This makes it questionable and comparatively difficult to reason as to *why these materials are classified as nanoparticles at the first place?* The reason for it is that they possess a nanocrystalline structure or involve the presence of features at the nanoscale. They might consist of multiple arrangements of nanosize crystals in different orientations.

This presence of features means that they could be composed of dispersions of nanoparticles, bundles of nanowires/nanotubes as well as nanolayers.

They can be classified as follows:

- Amorphous / Crystalline
- Chemically Pure / Impure
- Metallic / Ceramic / Polymeric

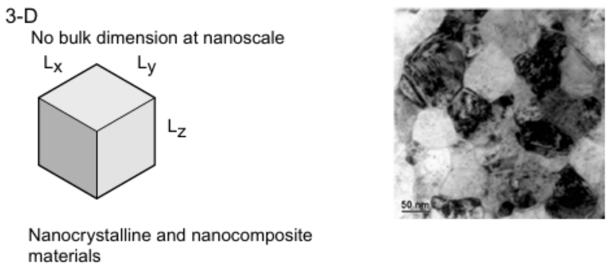

Figure 9: 3D nanomaterials or Bulk nanomaterials
[2]

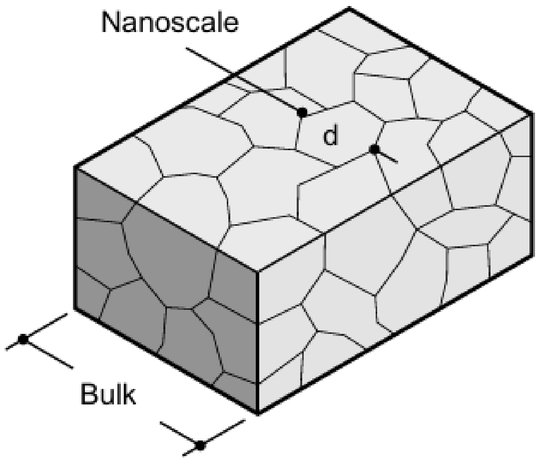

Figure 10: 3D nanocrystalline nanomaterial in bulk form
[2]

- Composite materials
- Composed of multi nanolayers

§4. Properties of Nanomaterials

4.1 Scale and Size

1. Nanomaterials are famously known to have a *very high surface area to volume ratio*. Because of this, a nanomaterial's shape is of great interest since various shapes produce distinct surface-to-volume ratios and therefore different properties. This increases their reactivity and makes them very useful.

2. It can be shown that one single particle with 10 microns can generate 1 billion nanosized particles with a diameter of 10 nm, whereas the total volume remains the same.

3. The bulk properties of materials (density, modulus, yield strength, thermal and electrical conductivity) are intrinsic. It is a basic assumption of continuum mechanics that materials behave in this way - their mechanical properties are scale-independent. It has been a useful and fairly accurate assumption, greatly simplifying the analysis of structures.

4.2 Mechanical Properties

1. The smaller the crystals that make up the nanocrystalline material, the greater the fraction of disordered material, which now becomes large enough to influence mechanical and other properties.

2. If this crystal becomes of atomic dimensions, the material is now completely distorted and is called *amorphous*.

3. Nanomaterials can exhibit very high strength and hardness compared to bulk materials.

4. They also have very high elasticity, making them useful in several applications.

4.3 Electrical Properties

1. At the nanoscale, two effects are important:
   - **Quantum effect** - In this, due to electron confinement the energy bands are replaced by discrete energy states, leading to cases where conducting materials can behave as semiconductors or insulators
   - **Classical effect** - Here, the mean-free path for inelastic scattering becomes comparable with the size of the system, leading to a reduction in scattering events.

2. Because of the above effects, bulk nanomaterials or 3D nanomaterials are good conductors of electricity. In contrast, nanosize grains tend to reduce electrical conductivity.

3. Nanocrystalline materials, like TiO_2 have high dielectric constants due to *interface polarization*.

4.4 Optical Properties

Blue shift

For small-sized semiconductor crystals, the band gap increases. Thus, absorption and emission spectra shift towards lower wavelengths. This is know as the *blue shift*.

Red shift

When agglomeration of metallic nanoparticles takes place, another optical plasmon effect takes place. This is known as the *red shift* and results from a shift towards lower plasmon frequencies.

Fluroscence and Luminescence

Quantum dots have bright and tunable fluorescence. This means that their brightness ie. emission wavelength can be finely adjusted as per requirement, making them very useful for biological imaging and light-emitting devices.

4.5 Thermal Properties

Melting Point

Due to nanoscale effects, it can be shown that the melting point of nanomaterials can either be increased or decreased with respect to the bulk material.

Thermal Transport

Thermal transport here refers to the transfer or conduction of heat in nanomaterials. There are widely two mechanisms of thermal transport in nanomaterials. These are as follows:

1. **Phonon Transport -** *Phonon*, a type of quasiparticle, refers to a discrete quantum of vibrational mechanical energy. Hence, it is a *quantized lattice vibration.* In non-metallic nanomaterials, heat transfer mainly happens through phonon transfer.

   However, phonon scattering at boundaries and interfaces reduces the thermal conductivity to some extent. Phonon scattering happens due to reduced sizes and high surface area-to-volume ratio in nanomaterials.

2. **Electron Transport -** Thermal transfer in metallic nanomaterials occurs mainly by electron transfer and partly by phonon transfer. But, scattering at surface and grain boundaries can still reduce the overall conductivity.

4.6 Chemical Properties

As mentioned above, nanomaterials effectively react due to high surface area. High surface area also provides them with more active sites for catalysis, hence offering much higher catalytic activity than the usual bulk catalysts. Their surfaces can be modified using functional groups for various purposes like enhancing stability.

Nanomaterials like TiO_2 are very good photocatalysts due to increased surface area allowing more absorption of light and resulting in higher efficiency.

4.7 Magnetic Properties

Superparamagnetism

When particle or grain size in nanomaterials becomes significantly small than a certain *critical diameter* (usually in the range of a few nm), these materials are likely to lose magnetism due to thermal fluctuations. This means that even ferromagnetic or ferrimagnetic materials tend to behave like paramagnetic materials.

The reason for this lies in the fact that in these very small grains, the thermal energy is sufficient to randomly flip the directions of magnetic moments. The phenonmenon de scribed above is called *supermagentism.*

Remanant magnetisation and coercive field

The figure above shows the usual magnetic hysteresis in ferromagentic materials. On removal of external field, the magnetic domains do not revert to their original configuration, thus resulting in *remnant magnetisation.* Also, the *coercive field* is the applied magnetic field that needs to be

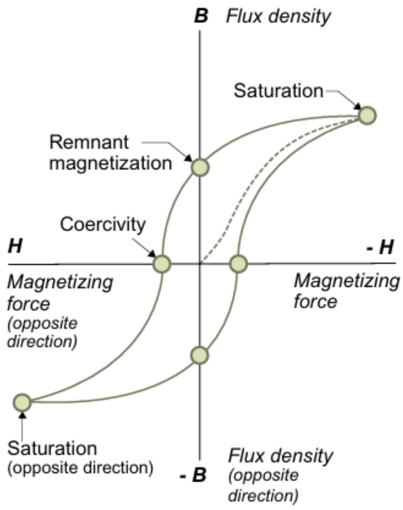

Figure 11: Hysteresis in ferromagnetic materials
[2]

applied in the direction opposite the initial magnetic field, to bring the magnetisation back to zero.

The magnetisation or hysteresis curve can be changed by reducing particle/grain size. With decreasing grain size, coercive field of ferromagnetic materials increases and reaches its peak somewhere near the critical diameter, after which it drastically reduces until the magnetisation becomes unstable and superparamagnetism is reached.

4.8 Acoustic Properties

Acoustic waves have wavelengths ranging from microns to kilometers. Thus, they tend to have negligible direct effects on nanomaterials. However, acoustic waves can have indirect effects (as in the case of seismic waves) on nanomaterials.

Also, sound waves are used to create nanomaterials!

§5. Functional MRI and Techniques used in Observation and Imagery

Observation of nanomaterials with precision is crucial for their study. The progress made in the field of observational techniques has made significant contributions to the nanoworld.

5.1 Observation using electrons - TEM, SEM

Electron microscopy uses the *wave nature of electrons.* As particles, electrons require vacuum to travel. So, electron microscopes are in the form of metal vacuum enclosures, consisting of:

- Electron guns such as cathode ray tubes
- Electromagnetic lenses to control the path of electrons

Following are the two kinds of electron microscopes:

1. **TEM (Transmission Electron Microscope) -** In TEM, the electron beam interacts with the crystalline sample to create a *diffraction figure or hologram.* The diffraction figure is then studied to analyse the atomic structure of the sample. Then, depending upon the associated wavelength or energy of the electrons, the final resolution of the image takes place.

2. **SEM (Scanning Electron Microscope) -** An electron beam scans the surface under consideration, resulting in a variety of different signals, which when gathered and analysed produce the image of the observed sample.

   Electrical charges pass from the surface of an object to the point of the microscope without any contact. This current varies strongly with distance. The movement of the point of the microscope is controlled with a specific current value in order to follow exactly the surface of the sample.

   However, SEMs offer a certain restriction, in that, they need vacuum to function and the surface to be observed needs to be very carefully plated, cooled and cut into sections. There are new kinds of SEMs (called environmental SEMs) which overcome this restriction of conventional SEMs. Using these, scientists can view surfaces in their natural state.

5.2 Functional MRI

Functional MRI or fMRI is a powerful tool to enable scientists to study how the brain works. The excitation of groups of neurons is observed by the amplification of the resonance signal and the rise in blood flow caused by the increase in the metabolism of the neurons.

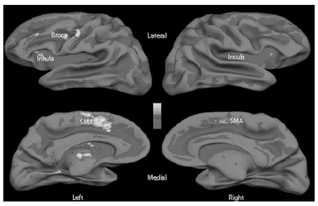

Figure 12: Images obtained though fMRI
[3]

One of the important applications of fMRI is in the study and research of nanomedicines, covered in the next section.

§6. Nanomedicines, Quantum Tunneling and their implications

6.1 Nanomedicines

A very recent and important application of nanotechnology is *nanomedicine*. All biological creatures, ranging from the most complex organisms to the simplest unicellular organisms, are made up of cell(s). And these cells are made up of the building blocks of the nanoscale - proteins, nucleic acids, and lipids. Nanotechnology is thus evolving under the domain of biology.

Nanomedicine is a very recent field of study, The ongoing research and study in this field will help us realise its importance in day-to-day life and maximise the potential of nanotechnology.

Described below are some of the important applications of nanomedicine.

Detection of biological species

Magnetic nanoparticles are used to detect some biological species, like microorganisms that cause disease. Magnetic nanoparticles together with antibodies bind to their target.

In this case, the magnetization vector of all nanoparticles becomes parallel resulting in a strong magnetic signal. And if illness is not present, the antibodies do not recognize the target and do not bind. Thus, all magnetization vectors will remain randomly oriented, leading to a weak magnetic signal.

Bio-identification

Recently, gold particles have been used for bio-identification. One set of gold particles carries DNA which binds to one half of the target sequence. The other set carries DNA which binds to the other half. The DNA with the complete target sequence couples to both sets of particles, binding them together. As these gold nanoparticles aggregate, there is a shift in the wavelength of light from red to blue. Thus, the red and blue lights can be used to check whether a certain DNA corresponds to a particular individual.

Targeted drug delivery

Nanoparticles can be used for delivering drugs specifically to the infected cells, without affecting the undamaged cells much, hence reducing their side effects. They can be designed to release the drugs in a controlled manner to ensure sustainable effect.

This has applications in cancer therapy, where chemotherapeutic agents directly deliver drugs to the tumor cells, reducing systemic toxicity.

6.2 Quantum Tunneling

Quantum tunneling is a phenomenon in quantum mechanics wherein a particle has some probability to pass through a potential barrier, even if its energy is less than that of the barrier. This is in sharp contrast to classical mechanics, where a particle would need enough energy (greater than that of the barrier) to overcome it.

Application in STMs (Scanning Tunneling Microscopes)

STMs use the quantum tunneling phenomenon to image surfaces at the atomic level. They measure the tunneling current between a sharp metallic tip and the sample surface and provide high-resolution images, allowing for manipulation of individual atoms.

§7. Lithography or Printing Techniques and Self-assembly

7.1 Lithography or Printing Techniques

Lithography techniques involve printing and patterning to transfer geometric patterns on substrates. *Substratum* refers to the base material on which the patterns are created. These techniques have applications in nanotechnology.

Dip Pen Nanolithography (DPN) was developed by Chad Mirkin to place finely resolved molecules of a substratum. In DPN, a weak adherent molecular ink is coated onto the tip of scanning probe microscopes. When we need to print, the tip is lowered in the vicinity of the substratum. As the affinity of the ink to the substratum is very high, the ink molecules are transferred to it through a water meniscus by capillary action.

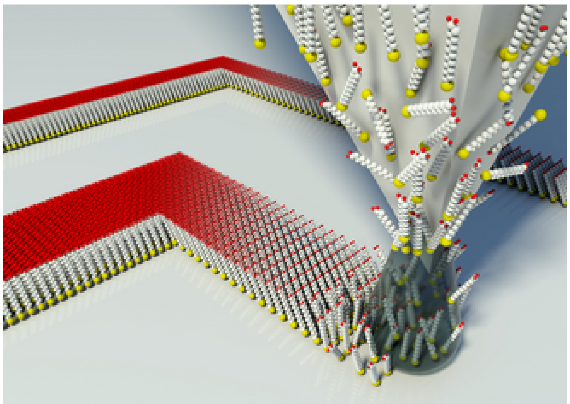

Figure 13: Classical mechanism of DPN

DPN, being strongly dependent on ambient relative humidity, is not a very accurate printing method.

7.2 Self-Assembly

Assembly refers to organizing and gathering things together to produce an organized structure, leading to a decrease in entropy. For the components to fit together, they are subject to specific constraints and their entropy must decrease, meaning, ΔS is negative. Hence, according to the equation $\Delta G = \Delta H - T\Delta S$, the free energy G must increase. This means that, in general, the process won't occur by itself. Instead, a segregated system will tend to become homogeneous. Hence if $|\Delta H| > |T\Delta S|$, we would have atleast the possibility of self-assembly, since the process would be spontaneous.

The final goal of a self-assembly technique, which can be used for manufacturing devices, is that the same structure is formed every time the constituent components are mixed. In order for this to happen, energy must be supplied to the system. *Ideally*, self-assembly should utilise random that is, thermal energy, but sometimes the supplied energy might be in the form of electric or magnetic fields.

§8. Carbon-based nanodevices - nanotubes and nanodiamonds

8.1 Introduction to Nanodevices

A nanodevice is a device with at least one overall dimension in the nanoscale, or comprising one or more nanoscale components essential to its operation. The figure below summarizes the main functional categories of these devices.

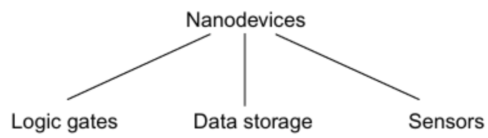

Figure 14: Functional categories of nano-devices
[1]

Two different types of nano-objects exist which are made up of carbon - *nanodiamonds* and *carbon nanotubes.*

8.2 Nanodiamonds

Nanodiamonds are made by *plasma spraying techniques.* They are made of thousands of atoms and their enhanced hardness is used to create specific coatings. After the nanodiamonds are treated with luminescent properties, they are used as a single photon source for the study of quantum cryptography. These nanocrystals are coated with active molecules from the natural world. They will make excellent biological markers for analysis in the field of confocal microscopy.

8.3 Carbon Nanotubes

Carbon Nanotubes are a major area of research and innovation currently. These tubes are single or multi-walled rolls in the form of tubes with a few nanometers' diameter. They have remarkable physical and chemical characteristics of the atomic grids which enable scientists to use them in numerous fields of scientific study.

Mechanical Properties

- They are ten times harder than iron.
- When inserted as *adjuvants*, they enhance the resistance of textiles and composite plastic materials.

Eletcrical Properties

- Their electrical qualities as insulators, semi-conductors or even as conductors make them very attractive for creating electronic components at a miniaturization level that silicon technology has never achieved. Thus, the smallest transistor in the world was made on a nanometric level.
- The creation of complex circuits, however, poses significant difficulties. Nanotubes do not really provide a reliable solution with regard to these difficulties. Also, the reproducibility of these electrical characteristics is not perfect.

Uses of nanotubes

- Nanosensors are likely to be used in the field of biosensors.
- Chemists can transplant certain molecules to the biosensors which have the ability to bond with other molecules in a particular environment, allowing them to be analyzed.
- Consequently, high-quality detectors are created. These machines are used for the transportation of medicine inside the human body.

§9. Nanosystems and their design

The essence of systems lies in the fact that they cannot be usefully decomposed into parts. The behaviour of each part affects the system as a whole.

Nanosystems are classified as those systems which have dimensions in the nanoscale. Examples of nanosystems are liposomes, silica, carbon nanotubes, etc. Examples of living nanosystems are the feet of gecko, a reptile. Their feet are hierarchically divided into tens of thousands of minute pads which allow for a large area of conformal contact with irregular surfaces. The adhesive forces are provided by the Lifshitz–van der Waals interaction. These van-der Waals interactions are normally considered to be weak and short-range, but they are additive and hence sufficiently strong if there are enough points of contact. Design at the nanoscale requires the consideration of the sections described below.

9.1 Material Selection

Nanoscale engineering offers greater possibilities in terms of expanded material options, enhanced performance, precision control, and multifunctionality compared to the macrosystems, especially with bottom-up nanofabrication, including nanocomposites. However, nanoscale processes reveal the statistical nature of current methods and highlight the need for eutactic environments for ultimate precision, particularly in fields like semiconductor processing.

9.2 Computational Modelling

A nanodevice is small enough for it to be possible to explicitly simulate its operation with atomic resolution (molecular dynamics), using present-day computing resources. To realize potential nanodevices, Feynman–Drexler diamondoid devices have been used. The main atomistic simulation technique is molecular dynamics: the physical system of N atoms is represented by their atomic coordinates, whose trajectories $x_i(t)$ are computed by numerically integrating Newton's second law of motion:

$$m_i \frac{d^2 x_i}{dt^2} = \frac{\delta V}{\delta x_i} \tag{6}$$

where m_i is the mass of the ith atom and V is the interatomic potential.

However, such atomic simulations use predefined empirical potentials, with parameters adjusted by comparing predictions of the model with available experimental data. It is not possible to give a general guarantee of the validity of this approach. Also, since no complete diamondoid nanodevices have as yet been constructed, the output of the simulations cannot be verified by comparison with the experiment.

9.3 Need for evolutionary design

An immediate corollary of the creation of useful devices of nanotechnology is that there must be a large number of these, that is their *vastification*. If r is the relative device size, and R the number of devices, then usefulness may require that $rR \sim 1$, implying the need for 10^9 devices.

If this number of components increases further by one or two magnitudes, it won't really be practical to have such systems, so alternative routes to the design and fabrication of such vast numbers are being explored. In this spirit, evolutionary design principles become essential for designing nanodevices.

The figure below shows an evolutionary design algorithm. It might be initialized by a collection of existing designs or guesses at possible new designs.

One should, however, bear in mind that even deterministically designed complex systems like a motor car, ship, or airplane, at current levels of technological sophistication, have a vast behavior in space and every possible combination of control parameters cannot be explicitly tested. Given that therefore we already in practice sacrifice complete knowledge of the system, even though it

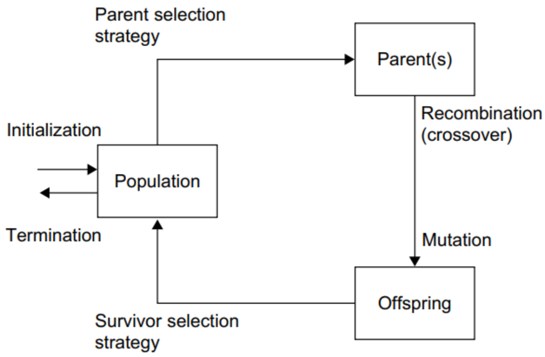

Figure 15: An algorithm for evolutionary design
[1]

is attainable, in principle, and yet still have a high degree of confidence in its ability to function safely, it may be unreasonable to object to using an evolutionarily designed artifact.

§10. Bionanotechnology

Bionanotechnology is defined as the application of biology to nanotechnology. It is the directed use of organisms to make useful products and is typically achieved by genetically modifying organisms; that is, bionanotechnology is the use of biological molecules in nanomaterials, nanoscale devices, or nanoscale systems. It is the incorporation of biological molecules into nanoartifacts.

Described below are the three major applications of bionanotechnology - DNA as a self-assembling construction material, biosensors, and biophotonic devices.

10.1 DNA as construction material

As *Nadrian Seeman* first pointed out, the specific base-pairing of DNA, together with the ease of nucleotide polymerization and the relative robustness of the molecule have collectively aroused interest in the design and construction of artificial nanoscale artifacts of arbitrary shape made from DNA. In principle both DNA and RNA could become universal construction materials, however, a drawback is that the design of the required DNA strands is a laborious, empirical process.

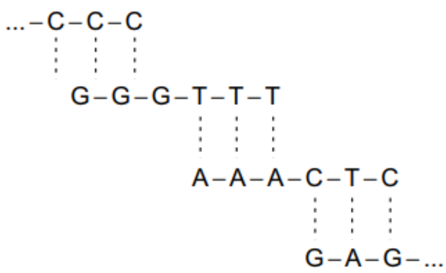

Figure 16: Four oligonucleotides in DNA, which can only assemble in the manner shown [1]

Once synthesized, it suffices to randomly stir a solution of the components together at an appropriate temperature. Their assembly then proceeds uniquely, as shown in the figure. This field has recently grown enormously to encompass very elaborate constructions. The process is connected with tile assembly and computation.

10.2 Biosensors

By definition, a *biosensor* is a device that uses a living organism or biological molecules (especially enzymes or antibodies), to detect the presence of chemicals. The classic biosensor is the amperometric glucose sensor, comprising glucose oxidase coating an electrode.

The ongoing research in the field is about coupling the enzyme directly to the electrode such that it can be regenerated by passing electrons to it. This is not nanoscale technology, but if the enzyme could indeed be coupled directly to the electrode, it would typically require the active site of the enzyme to be within $\sim$1 nm of the electrode. Hence it enters the realm of nanoengineering, in which a carbon nanotube might be used as the electrode. This allows to reduce the size of the device, such that ultimately it might incorporate a single enzyme that can detect single glucose molecules.

10.3 Biophotonice Devices

Molecules based on the chromophore rhodopsin are robust enough to be incorporated into artificial devices that convert light into chemical energy. Bacteriorhodopsin, a photoactive protein, which constitutes about a third of the outer membranes of the archaeon *Halobium salinarum*, living in salt lakes has been studied for use in biophotonic devices.

When the optically active site of the protein absorbs a photon of red light, there is a conformational change, generating strain between it and the rest of the protein. This translocates a proton across the membrane.

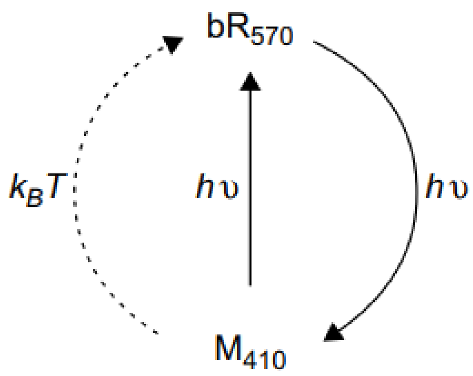

Figure 17: Bacteriorhodopsin Photocycle
[1]

This process is called *bacteriorhodopsin photocycle*, and has applications in bionanotechnology. Bacteriorhodopsin can be used to create long-lasting optical memories and optical switches that operate at high speeds with minimal light, useful for developing optical computers.

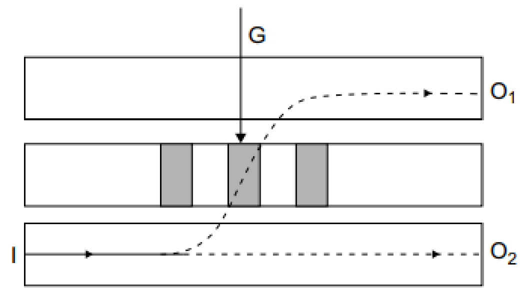

Figure 18: An optical switch
[1]

Not only can the switch operate extremely rapidly, but only weak light is needed. The remarkable optical nonlinearity of the protein is manifested by exposing it to a single photon! These switches can be used to construct all-optical logic gates and, hence, optical computers.

§11. Advanced applications, uses and impact of Nanotechnology in our lives

Applications of nanotechnology in the world are vast. These applications can be divided into the categories - Medicine and Healthcare, Energy, Environment, and Information and Communication Technologies.

11.1 Medicine and Healthcare

The applications of nanotechnology in medicine and healthcare are studied under the field of Nanomedicine, which has already been covered in the section 6.1 of this report.

11.2 Environment

Pollution Detection and Control

- Nanotechnologies offer the ability to control matter at the nanoscale level by creating materials with specific properties that can serve specific functions.
- Environmental issues like pollution often arise from the presence of a specific contaminant within a mixture of materials, in solid, liquid, or gaseous forms.
- The small size of nanomaterials, along with their high surface-to-volume ratio, help in the very sensitive detection of these pollutants and allow the development of highly miniaturized, accurate, and sensitive pollution-monitoring devices (nano-sensors).
- Nanomaterials can also actively interact with a pollutant and decompose it into less toxic species.

Remediation and Mitigation

- Soil and groundwater contamination from manufacturing processes involves heavy metals and organic compounds at industrial sites, landfills, and abandoned mines.
- Traditional remediation methods are laborious, expensive, and disruptive to ecosystems.
- Nanotechnology offers cost-effective, in situ remediation techniques that can access hard-to-reach areas and target specific pollutants, enhancing efficiency and sensitivity.
- This technology also addresses water contamination, such as mercury and arsenic, providing fast and effective treatment solutions.
- Key nanomaterials for remediation include:
  1. iron and bimetallic nanoparticles
  2. semiconductor nanoparticles
  3. dendrimers
  4. magnetic nanoparticles

Nanomembranes and Nanofilters

- Nanotechnology can also be used for the fabrication of nanofilters, nano-adsorbents, and nanomembranes with specific properties, which are used for decontaminating water and air.

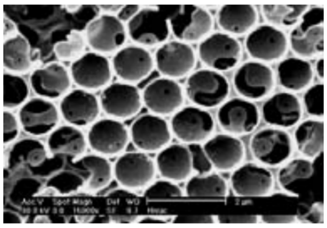

Figure 19: Ceramic Nanomembrane
[7]

- It is the ability of nanotechnology to manipulate matter at molecular level, which makes it a promising solution in this field.
- Nanotraps designed for a certain contaminant with a specific pore size and surface reactivity can be produced.

Recovery of Catalytic Material

- Most of the catalysis reactions make use of rare-earths like Palladium (Pd).
- Because palladium resources are limited, there is a need to recycle palladium. Thiss involves its reduction from Pd(II) to $Pd(0)$.
- For environment-friendly alternatives to chemical recycling processes, there is ongoing research about the use of bacteria to mediate the reduction of Pd reduction.
- The enzyme hydrogenase found in the membrane of many bacteria has the potential to transfer electrons from an organic substrate to Pd(II).

11.3 Energy

The combustion of fossil fuels mainly fulfills the world's energy demands. However, this approach has several disadvantages – limited availability of fossil fuels coupled with growing energy demands and the environmental degradation caused by fossil fuels.

To resolve this energy shortage problem. Solar energy and hydrogen fuel cell technologies have been seen as potential alternatives. However, solar projects have their disadvantage in terms of low efficiency of photovoltaics, energy storage issues, etc. Nanotechnology offers to provide solutions to many of these issues. This report describes in detail the use of nanotechnology for the same.

Problems with Solar Energy

The development of devices for the efficient and cost-effective conversion of solar energy to electricity is a major problem. Another problem is the storage and transport of the produced electricity since the regions where solar has the most potential is deserts, so transporting this energy becomes a concern.

Photovoltaics (PVs)

Conventional photovoltaics (PVs) consist of p and n-type semiconductors. All semiconductors absorb only a fraction of the total solar energy available – some absorb visible light only, while some absorb UV. For example, Titanium Dioxide (TiO_2), a non-toxic semiconductor can only absorb the UV portion of the solar energy. This is just 5% of the total. So, TiO_2 solar PVs, though cheap, have very low conversion efficiencies. Currently, a maximum efficiency of 15–20%

in a PV cell is obtained using crystalline silicon (Si). But, these PV cells have the disadvantage of being expensive, thus limiting their application. To meet energy demands we need at least about 45% efficiency of solar cells. Various nanomaterials are being investigated to achieve this. The devices must be made of materials that absorb visible light, which constitutes a 46% portion of the solar spectrum. There are two approaches employed for the same:

1. **Development of silicon nanocrystals which are designed to absorb more solar energy:**

   The lower efficiency of silicon PVs can be linked to the indirect bandgap of silicon crystals, resulting in weak absorption of light. The use of nanocrystals in these cells can significantly increase their light-absorbing capacities. This is because, in sufficiently small nanocrystals, the band gap is quasi-direct instead of indirect. This enhances the optical properties of the silicon PVs.

   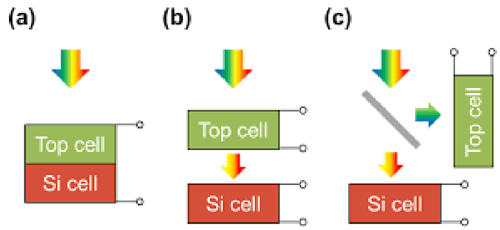

   Figure 20: Various configurations of Tandem Solar Cells

   An example of the use of nanocrystals in solar PVs is in silicon-based tandem solar cells, which have an upper layer based on nanocrystals and the bottom layer of standard silicon cells. Within solar cells, nanocrystals help in increasing the generation of electric current.

2. **Biomimetic approaches where PV devices are made to mimic "photosynthesis", the best-known solar conversion process:**

   QDSSCs use semiconductor nanocrystals, coated to the surface of a mesoporous TiO_2. They are similar to Graztel Cells which use dye coated on TiO_2 surface. However, QDSSCs have many advantages over these Graztel cells. They can match the solar spectrum better because their absorption spectrum can be tuned with particle size. It was found that when PbSe nanocrystals of diameter less than 10nm absorbed a photon, they could produce up to 3 electrons. This is much more compared to the conventional PV solar cells, which just produce 1 electron upon absorption of 1 photon. The production of 3 electrons is called "carrier multiplication".

Solar Heating

Solar heating involves a material that absorbs sunlight and releases that directly as heat into a water source or heat exchange material. Many nanomaterials can be used to enhance this process because of their large surface area and improved absorption properties. Nanotechnologies can be used to engineer complex nano-structured mirrors and lenses to optimize solar thermal collection. Also, aerogels with nanopores are used as transparent and thermally isolating materials to cover solar collectors.

11.4 Information and Communication Technology

Nanotechnology is already a key player in Information and Communication Technologies (ICT) research and development. Computer microprocessors and memory storage devices have been miniaturized over the last few years. This has naturally brought transistors to dimensions of lower than 100 nm. However, as the materials of semiconductors, metals, and insulators are reduced

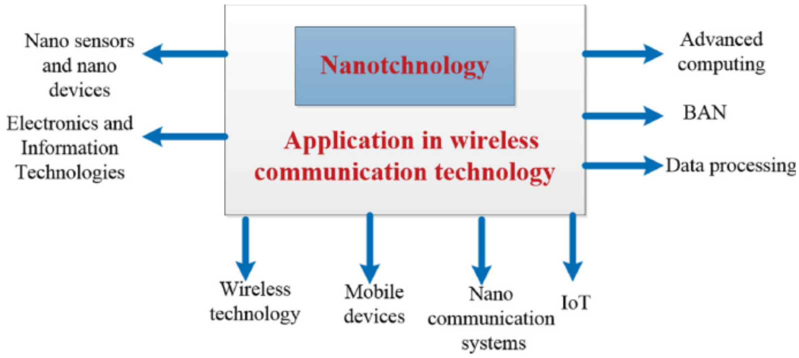

Figure 21: Applications of Nanotechnology in ICT

to nano-size, quantum effects start to predominate and determine their properties, resulting in several issues. Nanotechnology offers the opportunity to exploit, *rather than avoid*, quantum effects in the development of the next generation of integrated circuits (ICs). Nanomaterials, for their quantum properties, and nanotechnology tools allow for the creation of new data storage and processing methods because miniaturisation cannot proceed forever with the methods and tools that have been used so far. The evolution of the ICT sector is likely to go beyond what is considered 'electronics' today. There are visions of electronics being embedded in our clothing and the environment around us in *a network of devices that create 'ambient intelligence'*. There is intense research to bring to fruition the tools required to realize 'ambient intelligence'.

§12. Environmental issues associated with Nanotechnology

Nanosciences and nanotechnology cannot escape the double-edged sword of progress and the inevitable risks. It can be confirmed that nanomaterials and nanotechnologies have made significant contributions in health delivery, but there are also reasonable concerns about how these same materials might have detrimental health effects if not used carefully. Air- or waterborne nanoparticles from natural sources or other materials can cause adverse health effects.

The very characteristics of nanomaterials that are attractive may have significant adverse health and environmental consequences. These are because of the very small sizes and corresponding transport and penetration abilities as well as their high relative surface areas, which naturally increase surface reactivities. Tiny irreducible nanoparticles work their way not only in air but also in water supplies and soils, which eventually make their way to our foods.

Studies on quantum dots for their harmful effect have revealed the following points:

1. The toxic effect of quantum dots depends on multiple factors, like their physicochemical properties and environmental conditions.

2. Exposure of human beings to quantum dots could be from the environment or during therapeutic use.

3. Quantum dots can accumulate within organs and tissues like in lungs posing health risks.

4. Introduction of quantum dots into the environment may occur via waste streams from industries, research, and clinical settings. The persistence of these materials in the environment can be of long duration and the environmental exposure depends on the partition of quantum dots between water, air, and various soil types.

5. The main concern of quantum dots is their content in metals, such as Cd (cadmium) or Se (selenium), which are known to cause adverse effects on the environment and in vertebrates, including humans.

6. So, it is the stability of the metalloid core-coating complexes that make quantum dots potentially harmful. In particular, the oxidative, photolytic, and mechanical stability of the quantum dots coating and metalloid core are the most important parameters governing the bio-reactivity and risk concerns of quantum dots.

All nanoparticles, on exposure to tissues and fluids of the body, have a tendency to be adsorbed to macromolecules at the site of entry. There are several areas of possible human exposure during the production of nanoparticles - respiratory tract, dermal absorption, intestines, bloodstream, and cells. Following are some examples of the environmental impacts because of nanoparticles:

- Water fleas or Daphnia could die at relatively low concentrations of C_{60} molecules (Buckminster fullerenes) and nanoscale titanium dioxide TiO_2 in water. Studies have shown that C_{60} nanoparticles are absorbed through their gills and even at low concentrations, they overcome the blood-brain barrier and cause damage to the brain.

- In zebrafish embryos, carbon nanotubes have been shown to cause a delay in the hatching of offspring.

- The bactericidal activity of some nanomaterials could produce adverse effects in sewage treatment works and cause a change in the composition of the microbial population in water.

- Experiments using aluminium nanoparticles have revealed a reduced growth of the roots of many crops. This effect was not seen for larger aluminium particles.

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