

NANOTECHNOLOGY: HOPE OF TOMORROW

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I. Introduction

Nanotechnology is now identified as an area of related to research and technology development at the atomic, molecular and macromolecular levels. In relation to biological structures the nanoparticles are of comparative size and hence their possible mutual interaction is self evident. The particles in the nano range display physical, chemical and biological properties which can be manipulated for the desired objectives. It is predicted that the behavior of the particles at the macro and nano range may be very different and the same material in bulk. Nanostructures and nanomaterials possess a large fraction of surface atoms per unit volume. The ratio of surface atoms to interior atoms changes dramatically if one successively divides a macroscopic object into smaller parts. The total surface energy increases with the overall surface area, which is in turn strongly dependent on the dimension of the material.

Particles of controlled size with at least one dimension of less than 100 nm are considered nanoparticles. Depending on their chemical composition, their optical and electronic properties have generated much attention in studies of properties of particles approaching molecular dimensions. At nanometer length scales, the line between colloids and molecules becomes blurred.

It should be noted that the specific surface area and thus, the total surface energy are negligible when cubes are large, but become significant for very small particles. When the particles change from centimeter size to nanometer size, the surface area and the surface energy increase seven orders of magnitude. Nanoparticles to be discussed here are single crystal, polycrystalline and amorphous particles with all possible morphologies, such as spheres, cubes and platelets. In general, the characteristic dimension of the particles is not larger than several hundred nanometers. If the nanoparticles are single crystalline, they are often referred to as nanocrystals. When the characteristic dimension of the nanoparticles is sufficiently small and quantum effects are observed, quantum dots are the common term used to describe such nanoparticles.

Due to the vast surface area, all nanostructured materials possess a huge surface energy and thus, become thermodynamically unstable or metastable. One of the great challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the nanostructures or nanomaterials from growth in size, driven by the reduction of overall surface energy. In order to produce and stabilize nanostructures and

nanomaterials, it is essential to have a good understanding of surface energy and surface physical chemistry of solid surfaces.

What makes the nano biotechnology field so interesting and revolutionary is the convergence of the angstrom, nano and micro scale worlds with the exploitation of physical principles, chemical synthesis capabilities and functional properties of biological nanostructures. Nature has made highly precise and functional nanostructures for billions of years: DNA, proteins, membranes, filaments and cellular components. These biological nanostructures typically consist of simple molecular building blocks of limited chemical diversity arranged into vast numbers of complex three dimensional architectures and dynamic interaction patterns. A major goal of nanotechnology is to use existing industrial techniques to manipulate atoms and molecules in bulk to make a large, anatomically perfect, usable structure and tangled knots of stuff do not always produce the most usable structures (figure 1).

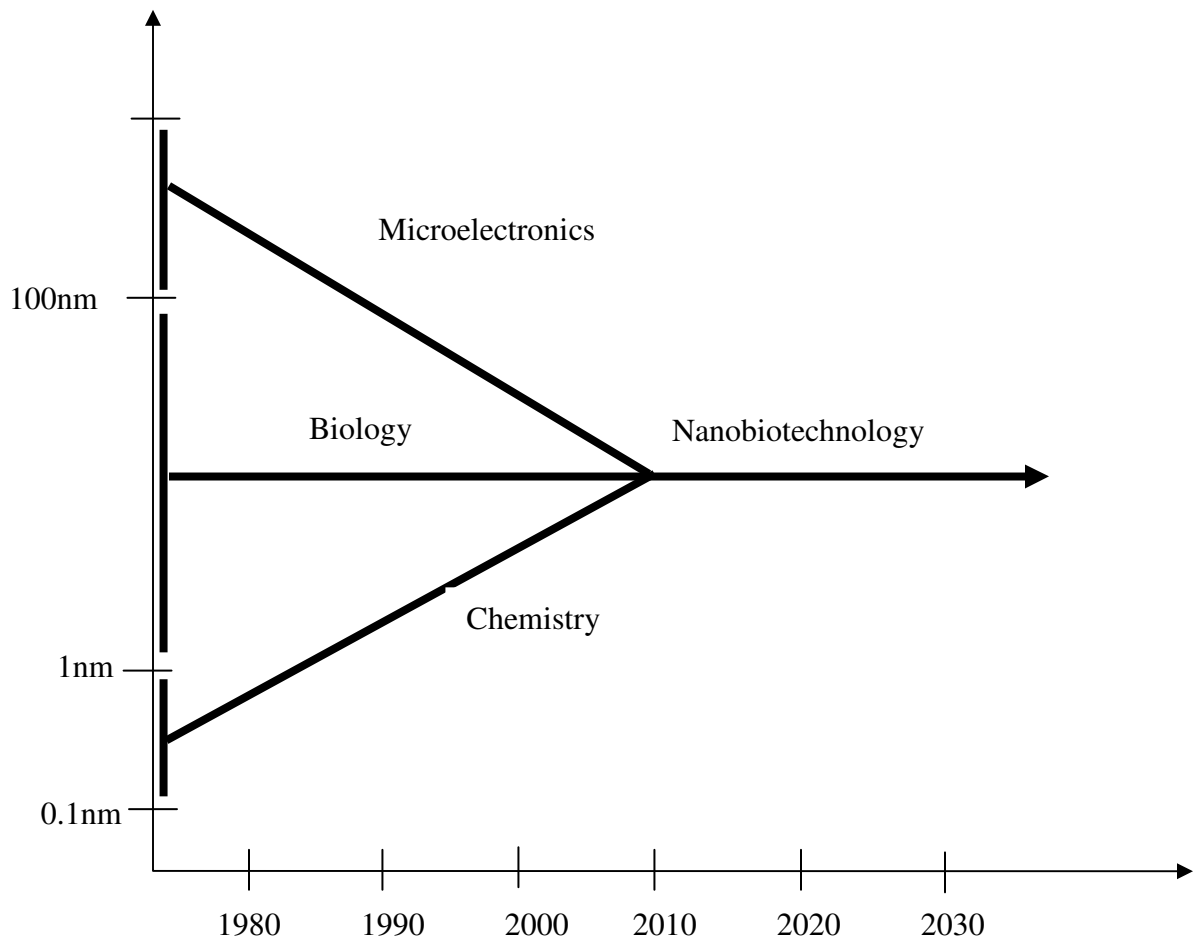


Figure 1: The convergence of angstrom-, nano- and micro-scale.

Surface Energy:

Atoms or molecules on a solid surface possess fewer nearest neighbors or coordination numbers and thus have unsatisfied bonds exposed to the surface. Because of the presence of these bonds on the surface, surface atoms or molecules are under an inwardly directed force and the bond distance between the surface atoms or molecules and the sub-surface atoms or molecules, is smaller than that between interior atoms or molecules. When solid particles are very small, such a decrease in bond length between the surface atoms and interior atoms becomes significant and the lattice constants of the entire solid particles show an appreciable reduction. The extra energy possessed by the surface atoms is described as surface energy, surface free energy or surface tension. Surface energy (T) by definition, is the energy required to create a unit area of surface:

$$T = \left(\frac{\partial G}{\partial A} \right)_{n_i, T, P}$$

where A is the surface area. Let us consider separating a rectangular solid material into two pieces as illustrated. On the newly created surfaces, each atom is located in an asymmetric environment and will move towards the interior due to breaking of bonds at the surface. An extra force is required to pull the surface atoms back to its original position.

It can be estimated that low index facets have low surface energy. Any material or system is stable only when it is in a state with the lowest Gibbs free energy. Therefore, there is a strong tendency for a solid or a liquid to minimize the total surface energy. There are a variety of mechanisms to reduce the overall surface energy. The various mechanisms can be grouped into atomic or surface level, individual structure and the overall system.

For a given surface with a fixed surface area, the surface energy can be reduced through (i) surface relaxation, the surface atoms or ions shift inwardly which occur more readily in liquid phase than in solid surface, (ii) surface restructuring through combining surface dangling bonds into strained new chemical bonds, (iii) surface absorption through chemical or physical absorption of terminal chemical species onto the surface by forming chemical bonds or weak attraction forces such as electrostatic or van der Waals forces, and (iv) composition segregation or impurity enrichment on the surface through solid state diffusion.

II. Physical Properties of Nanoparticles

Some known physical properties of nanomaterials are related to different origins: for example, (1) large fraction of surface atoms, (2) large surface energy, (3) spatial confinement, and (4) reduced imperfections. Examples are:

1. Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants, due to a huge fraction of

- surface atoms in the total amount of atom. Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in the mechanical strength is simply due to the reduced probability of defects.
2. Optical properties of nanomaterials can be significantly different from bulk crystals. For example, the optical absorption peak of a semiconductor nanoparticle shifts to a short wavelength, due to an increased band gap. The color of metallic nanoparticles may change with their sizes due to surface plasmon resonance. Electrical conductivity decreases with a reduced dimension due to increased surface scattering, while electrical conductivity of nanomaterial could also be enhanced appreciably, due to the better ordering of microstructure.
 3. Physical properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetism of bulk materials disappears and transfers to super magnetism in the nanometer scale due to the huge surface energy. Self purification is an intrinsic thermodynamic property of nanostructures and nanomaterials. Any heat treatment increases the diffusion of impurities, intrinsic structural defects and dislocations, and these can be transferred to the surface. Increased imperfection has appreciable impact on the chemical and physical properties.
 4. At the nanoscale, inertia and gravity would make no difference. The bacterium swimming through the water comes to a stop in a distance less than the diameter of the hydrogen atom. The motion of things in and around a cell is governed not as much by momentum as by physical interactions with other things. Attractive forces, such as van der Waals forces, and viscous forces between small objects are much stronger than the forces of gravity and inertia at that scale. As a result, all of these molecules and machines and cell parts are in constant motion, being pushed and pulled around in quick, random trajectories determined by their diffusion coefficient; Brownian's motion.

III. Methods in Nanoparticles fabrication

There are two methods involved in nanomaterial synthesis and fabrication of nanostructures (1) top down, and (2) bottom up approach.

Top down Approach

Milling is a typical top-down method in making nanoparticles. Both these approaches play an important role in modern industry and most likely in nanotechnology as well. However there are advantages and disadvantages in both type of approach. Biggest problem with top down approach is the imperfection of the surface structure. It is estimated that conventional top-down technique such as lithography can cause significant crystallographic damage. For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on surface. The surface

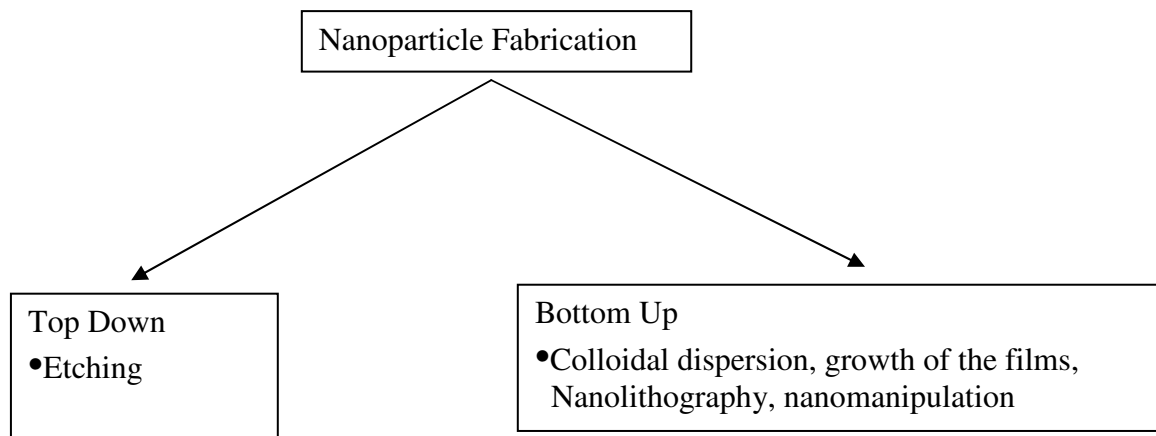
imperfections would result in a reduced conductivity due to inelastic surface scattering, which in turn would lead to the generation of excessive heat and thus impose extra challenges to the device design and fabrication. Another problem with top down approach is that the particles it produces have fairly broad size distribution, and varied particle shape. In addition they may contain a significant amount of impurities from the milling medium and the defects therein. Despite the limitations in the process the method is widely used for its simplicity and relative ease.

Bottom up Approach

Bottom up approach is to build material lowest below atom by atom, molecule by molecule, or cluster by cluster. This approach is used in the fabrication and processing of nanostructures and nanomaterials on a very large scale, and has been in laboratory use and in industry, as use of sodium and nitrate in industry

The characteristic of bottom up approach is to obtain nanostructures with less defects, more homogenous chemical composition, and better short and long range ordering. This is because the into bottom up approach is driven mainly by the reduction of Gibbs free energy, so that nanostructures and nanomaterials so produced are in a state closer to one of thermodynamic equilibrium.

Bottom up approaches are far more popular in synthesis of nanoparticles and are synthesized by homogenous nucleation from liquid or vapor, or by heterogeneous nucleation on substances. The two approaches can be summarized thus:



For the fabrication of nanoparticles, a small size is not the only requirement. For any practical application, the processing condition need to be controlled in such a way that resulting nanoparticles have the following characteristics (1) identical size of all the particles (uniform size distribution), (2) identical shape or morphology, (3) identical chemical composition and crystal structure that are desired among different particles and within individual particles, such as core and surface composition must be same, and (4) individually dispersed or non dispersed, i.e. no agglomeration. If agglomeration does occur, nanoparticles should be readily re-dispersible.

Nanoparticles through Homogenous Nucleation

Following the simple laws of crystal formation of nanoparticles by homogenous nucleation, a super saturation of growth species need to be created. An obvious choice would be to lower the temperature of an equilibrium mixture, such as saturated saturation leading to super saturation. One such method is to generate a super saturation through in situ chemical reactions.

For the fabrication and processing of nanomaterials and nanostructures, following challenges need to overcome:

1. Overcome the huge surface energy, a result of large surface to volume ratio.
2. Ensure all nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure that altogether result in desired physical properties.
3. Prevent nanomaterials and nanostructures from coarsening through either Oswald ripening or agglomeration as time evolves.

IV. Carbon Nanotubes

Carbon nanotubes were discovered by Iijima (1991) using an electron microscope while studying cathodic material deposition through vaporizing carbon graphite in an electric arc evaporation under an inert atmosphere. The nanotubes produced by Iijima (1991) appeared to be made up of a perfect network of hexagonal graphite, rolled up to form a hollow tube. The nanotube diameter range is from one to several nanometers which is much smaller than its length (which is from one to few micrometers).

Working with carbon nanotube is a matter one of its alignment. Strength of carbon nanotubes stems from the fact that aligned tubes are stronger along their length. Carbon nanotubes hold great promise in the making of materials with superior mechanical, electrical, and thermal properties. The relationship between the use of carbon fiber and its cost is showing an inverse relationship. Strength has been the major benefit of carbon nanotube fibers, but along with this the light weight conductive wires would greatly impact energy distribution. Finding a light weight, durable, energy efficient alternative to traditional wires not only would help space endeavors, but also could boost the creation of more fuel-efficient cars and other everyday items.

Carbon nanotubes and fullerenes are shown to exhibit unusual photochemical, electronic, thermal and mechanical properties. It is also shown that single-walled carbon nanotubes (SWCNTs) could behave metallic, semi-metallic, or semi-conductive one-dimensional objects. Very high tensile strength (~100 times that of steel) of ropes made of SWCNTs has been determined experimentally (Yu et al 2000).When dispersed in another medium, it is demonstrated that SWCNTs could retain their intrinsic mechanical attributes or even augment the structural properties of medium host. SWCNTs have similar electrical conductivity as copper and similar thermal conductivity as diamond.

V. Nanophotonics

The optical properties do not depend entirely on the material; they also depend upon the size of the material. If we take a gleaming, the yellow brick of gold and make it very thin, it turns blue. Or if we take nanometer scale particles from the same block of gold, they can be orange, or purple, or red. Nanophotonics are the nanoscale interaction of photons and materials. Nanophotonics is helping to rewrite the rules governing what can be done with photons. For example, near field microscope can be used to see things smaller than the wavelength of light (figure 2).

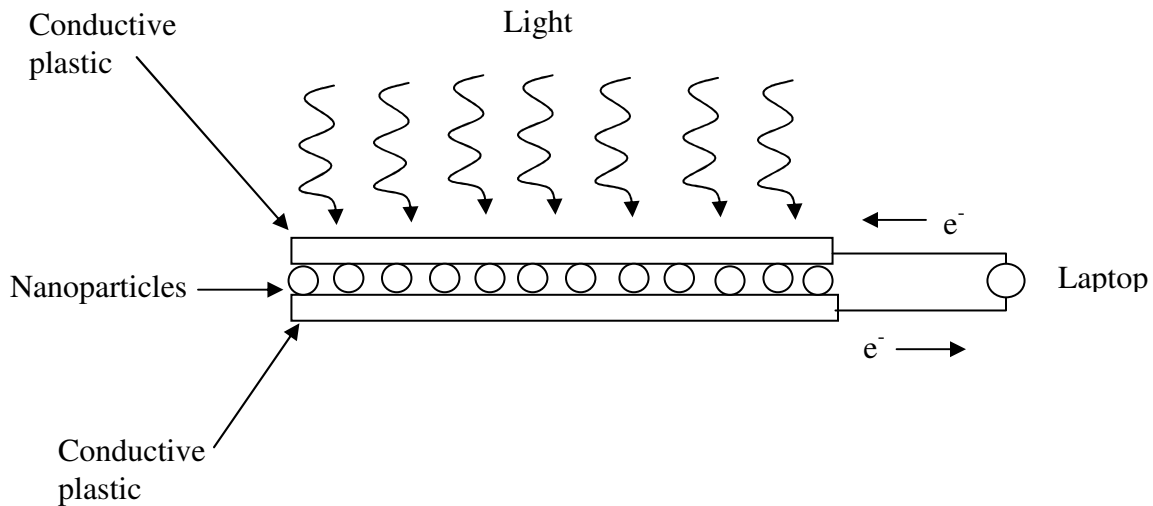


Figure 2: Solar cell using nano-technology.

Photonic Properties of Nanomaterials

In a way the photonic properties of materials are a reflection of their properties. Particles of titanium dioxide and zinc oxide-both metal oxide semiconductors have found use in sunscreens because they absorb ultraviolet radiation that damages the skin.

Particles of both of these materials also scatter visible radiation, making them very good white pigments in paint, but this same property also turns skin white. Because titanium dioxide nanoparticles are having 50 nanometer in diameter are now available, they are having larger band gap, so they are transparent to visible light. This makes the sunscreen clear, but they still absorb the ultraviolet radiation.

One way to get better efficiency is to make a solar cell with multiple band gaps. This may be possible with using multiple materials. The high band gap material can grab the high energy photons with minimal heat loss, while the low band gap material soaks up the remaining low energy photons. However, the crystals with this structure are difficult to fabricate.

Colors and Uses of Gold and Silver Particles

Varying the size of an aluminum particle changes the wavelengths of light that it will absorb and scatter. If the extinction were to have peak in the visible range, we could vary the particle size so as to tailor which color of light the particle absorbed. The particles, roughly 6 to 20 nm in diameter absorbed the shorter wavelengths of blue and yellow light and not the longer wavelengths reds. Metal particles can be coated with a specific type of a molecule that is known to bind another specific target molecule. Then when these “functionalized” particles are introduced to an environment where the target molecules may be present, we can monitor color changes or just keep track of where the colored particles end up detecting, identifying, and tracking all sort of molecules. If we chemically quote gold particles with a snippet of DNA, and then add the particles to a solution containing an unknown stand of DNA, the solution will turn from red to blue if the sequence match and the dot aggregate. Otherwise, the solution remains red. Detecting specific DNA sequences is critical to diagnosing genetic and pathogenic diseases.

VI. Quantum Dot and Quantum Structures

To reduce the volume of a box, we can shorten its length, its width or its height. The same is true of the region occupied by the electrons in a solid. There are three dimensions to confine, and achieving quantum confinement typically necessitates confining at least one of these dimensions to less than 100 nanometers, or even to just a few nanometers. The more we confine the dimensions, the more the density of states functions looks like that of an atom.

When all three dimensions are minimized, we are left with a “quantum dot”. The dot can be a particle located inside a larger structure or on its surface. It can be a part of a colloid or entirely isolated .It can also be a place where electrons have been trapped using electric fields. Because quantum wells and quantum wires each have at least one dimension in which the electrons are free to move, these structures are said to exhibit “partial confinement”. Quantum dots exhibit “total confinement” with quantum dots ,the number of electrons per unit volume remains level until the next higher allowed energy state –at which point the number jumps up. The electron density increases with energy because high energy orbital usually holds more electrons .The quantum dot is unique because the density of states function ceases to be continuous. There are specific numbers of states for the electrons to occupy at a given energy, and there are no more states available until the next energy. Consequently, the number of free electrons in a given volume stays constant between one allowed energy and next.

Coulomb forces are electrostatic. If we have two or more charges near one another, they exert coulomb forces upon each other. In the case of quantum dot, the charges are all negative electrons. The isolated droplet of electrons repels another electron. This is the coulomb blockade and it helps prevent constant tunneling to and from a quantum dot

A quantum dot has a capacitance, C_{dot} , a measure of

$$C_{dot} = G\epsilon d,$$

Where ϵ is the permittivity of the material surrounding the dot, d is the diameter of the dot, and G is a geometrical term (if the quantum dot is a disk, $G=4$, if it is a spherical particle, $G=2$). It may be pointed out that this capacitance is that of an object isolated in space and can store charge on its own and therefore can have a capacitance.

The energy needed to add one negatively charged electron to the dot is known as the charging energy E_c :

$$E_c = e^2/2C_{\text{dot}}$$

E_c is inversely proportional to the dot's capacitance: a large capacitor can quite easily accommodate another electron without too much energy required. However, in case of extremely small capacitors (as in quantum dots) the charging energy can be substantial. It can be large enough to "block" tunneling electrons.

When we constrain electrons inside a region of minimal width, we create a "quantum well". Quantum wells can be made from alternating layers of different semiconductors, or by deposition of very thin metal films. By further constraining the depth of the electron's domain, we create a "quantum wire". Nanotubes and other nanoscale wires can be quantum wires.

Use of Quantum Dots

We change their size and their band gap changes. So, if we were able to make a solar cell using layers containing different sizes of quantum dots, covering the whole spectrum of photon energies, we might truly drive up the efficiency. Another possibility has been suggested in which a single high energy photon is made to excite multiple electrons. This phenomenon is called impact ionization may be quantum dots be used to fix energy from the sun.

VII. Biomedical Applications

Semiconductor quantum dots are rapidly emerging as luminescence probes for many biological and biomedical applications owing to their extremely small size (10 nm in diameter), high photo stability, tunable optical properties, and multimodality. Such inorganic-organic composite nanomaterials have shown extreme efficiency in cancer diagnosis in vivo, with their small size which facilitates, unimpeded systematic circulation and attached targeting molecules, allowing for specific 'homing in neoplastic sites'. Similar to other nanoparticles, QD's can be modified via conjugation of various surface molecules for targeted delivery. QD's provide sufficient surface area to attach therapeutic agents for simulating drug delivery and in vivo imaging as well as for tissue engineering. QD-apatamer (Apt)-doxorubicin (Dox) conjugates for target cancer therapy, imaging and sensing. It was shown that this multifunctional nanoparticle system can deliver doxorubicin by activating the fluorescence of QD, while allowing for simultaneous imaging of cancer cells and sense the delivery of doxonrubicin by

activating the fluorescence of QD, while allowing for simultaneous imaging of cancer cells.

Under some conditions QDs can become cytotoxic. It was discovered that Cd Se particles may leak cytotoxic cadmium ions after long term exposure to UV light, while CdTe particles produce reactive oxygen species due to the loss of their protective coating after long term circulation. QD also found application in the near infrared (NIR) imaging (700-1000 nm) .The use of NIR-QD can maximize the depth of tissue penetration, allowing for more accurate and sensitive detection of photons in vivo. NIR-QD may be a superior alternative because they can circumvent the problem of auto-fluorescence which is often associated with optical imaging of naturally occurring compound in animal tissue. Thus QDs have tremendous potential in vivo imaging and have been accordingly used, lymphatic mapping in animal model.

VIII. Biological Shapes at the Nanoscale: Carbon and Water are the Essential Tools

Water ensures that biomolecular machines are interacting with each other. Almost all the molecules in a cell contain carbon, water being the primary exception. However, the carbon rich area of a molecule tends to be hydrophobic and will not easily form hydrogen bonds with water. Molecules containing carbon-rich areas therefore contort so as to pull these areas inwards, thus causing biological molecular machines to fold into their unique shapes-shapes that endow such molecules with very specific chemical functionalities. The forms assumed by DNA, RNA, and most proteins are such that hydrophilic regions on the outside .In contact with water, while hydrophobic regions bunch into the core.

The bio molecular machines inside a cell take on various shapes. The shape of machine determines their interaction with each other, which in turn what fundamental biological processes will occur, such as energy conversion, reproduction, or movement. One of the most important things involved is water.

First, all things are made up of at least 70% water, which means everything is always wet, the major driving force for molecular interaction exploit water. Water ensures that biomolecular machines are interacting with each other. Water is a polar molecule, and electrically charged molecules, as well as other polar molecules such as alcohols, sugars, and molecules with oxygen-rich regions, are all attracted to water's polar regions. Molecules that are attracted to water are called hydrophilic. They participate in hydrogen bonding interactions with the water molecules and therefore dissolve easily into aqueous solutions.

Almost all the molecules in a cell contain carbon, water being the primary exception. Carbon atoms have four vacancies in their outer shells and thus form four covalent bonds. This, and the fact that carbon can bond to itself to form the chains ,branched trees, and rings, causes complex and gigantic organic molecules. However, the carbon-rich area of a molecule tends to be hydrophobic and will not readily form hydrogen bonds with water. Molecules containing carbon-rich areas therefore contort so as to pull these areas inward, thus causing biological molecular machines to fold into their unique shapes-shapes that endow such molecules with very specific chemical functionalities. The forms assumed by

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IX. DNA Nanotechnology:

1. The formation of three dimensional structures built from DNA building blocks,
2. The rapid, single-molecule analysis of nucleic acids using nanopores. In this approach, single stranded DNA or RNA is translocated through a voltage biased nanopore in a linear manner, thereby blocking the open pore ionic current. A prerequisite for this method to work is that the diameter of the nanopore must accommodate the single stranded DNA or RNA only.
3. DNA chemically linked to inorganic matter for the construction of nanoelectronic devices.

Nanoparticles for Biological Assays

Nanoparticles have found widespread use for biological assays:

Nanoparticles have substantial advantages over classical organic dyes because of their superior photophysical properties, which overcome many of the spectral limitations as molecular fluorophores. Semiconductor quantum dots, for example, have tunable, narrow emission spectra with very high photostability. They have the advantage of a single exciting wavelength providing for multiple emission wavelengths. Quantum dots also appear to be valuable reagents for nucleic acid bioassays including single nucleotide polymorphism analysis.

Metallic nanoparticles such as colloidal gold (1-5 nm in diameter) are popular staining agents in biological electron microscopy, appearing dark in transmission electron microscope images (due to high Au density) and bright in scanning electron microscopy images (due to high back scatter coefficient).

In addition, colloidal gold has been successfully used for biological assays such as DNA hybridization. For example, gold nanoparticles show a characteristic plasmon resonance absorption which is useful for detection purposes. A conductivity based method is adopted, which utilizes oligonucleotide electrodes functionalized gold particles that provide conductivity between microelectrodes upon the binding of the nanoparticles to the electrodes. Super magnetic nanoparticles such as iron oxide particles (Fe_3O_4) have enormous potential, for separation and biomolecular assay applications. They can be magnetized in a magnetic field, but than re-dispersed after removal of the field.

Nanoparticles as Drug Delivery Vehicles:

New type of drug delivery vehicles are in high demand. Top-down melling processes can be used to reformulate highly insoluble drugs as nanoparticles, thereby providing more

efficient uptake. Liposomes inside pharmaceutical encapsulated have also been in use. Although liposomes exhibit outstanding biocompatibility and low toxicity, problems such as uncontrolled drug leakage and low delivery efficiency remains major obstacles.

Magnetically guided drug targeting makes use of microparticles composed of elemental iron particles and activated carbon with drug absorbance and release properties in order to direct the drug agents directly to the target tissue.

Another class of important nanoparticles is dendrimers. These are spherical nanoscale, polymeric, polyvalent molecules of well defined chemical structure. These are now being used for early treatment of cancer.

Cyclodextrins, Liposome and Monoclonal Antibody:

While physical scientists have been toying with the concept of experimenting with structures like nanotubes and buckyballs and diamondoids, in the arena of biology there are other nanostructures like cyclodextrins (Alexander et al 2002), liposomes (Feng et al 2004) and monoclonal antibodies (Thompson et al 2004). These nanostructures of biological origin have many applications including drug delivery and drug targeting.

Cyclodextrins, are cyclic Oligosaccharides. Their shape is like a truncated cone and they have a relatively hydrophobic interior. They have the ability to form inclusion complexes with a wide range of substrates in aqueous solutions. This property is responsible for encapsulation of drugs in drug delivery.

Liposome is a spherical synthetic lipid bilayer vesicle, created in the laboratory by dispersion of a phospholipid in aqueous salt solutions. Liposome is quite similar to micelle with an internal aqueous compartment. Liposomes, which are nanoscale size range, self assemble based on hydrophilic and hydrophobic properties and they encapsulate materials inside. Liposome vesicles can be used as carriers for a great variety of particles, such as small drug molecules, proteins, nucleotides and even plasmids to tissues and into cells. For example, a recent commercially available anticancer drug is a liposome, loaded with doxorubicin, and is approximately 100 nanometer in diameter.

A monoclonal antibody protein molecule consists of four protein chain, two heavies and two lights, which are folded to form a Y shaped structure. It is about ten nanometers in diameter. This size (small) is important, to ensure that intravenously administered particles can penetrate small capillaries and reach cells in tissues where they are needed for treatment. Nanostructures smaller than 20nm can transit out of blood vessels.

X. Nanoparticles and Toxicity

Though there has been a rapid progress in the use of nanoparticles for a variety of purposes, their toxicological fallout is not yet explored. It was reported that titanium oxide/zinc oxide nanoparticles used in sunscreen can catalyze oxidative damage to DNA in vitro and in cultured human fibroblasts. It has been suggested that the probable dermal

toxicity and morphological changes seen were due to accelerated oxidative stress in the skin after having been exposed to the single walled carbon nanotubes. In a separate study it has been demonstrated that exposure to unrefined single-walled carbon nano tube may lead to increased pulmonary toxicity due to oxidative stress. Other toxicity studies of carbon nanotube describe the cause granulomas in rats and mice after exposure. Crystalline silver nanoparticle related cytotoxicity in lesioned skin, growing human fibroblast, and keratinocytes has also been demonstrated. Nanoscale materials are now used in electronic optoelectronic, catalytics pharmaceutical, biomedical, personal care, energy and material applications. A summary of this is presented in figure 3.

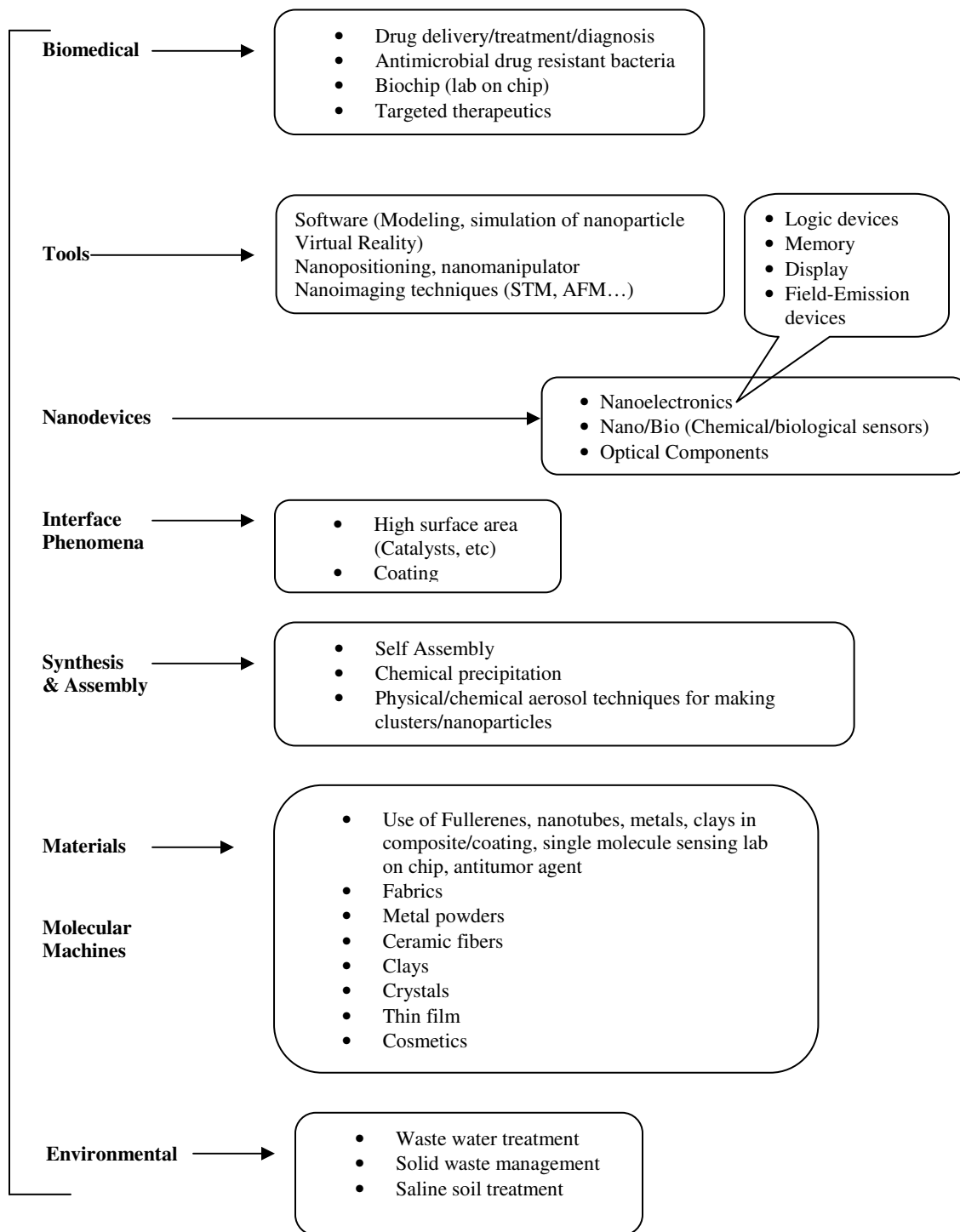


Figure 3: - Possible applications of nanoparticle treatment

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