1. APPLICATIONS OF NANOMATERIALS

Introduction – Photocatalytic applications – Fuel cells applications – Biosensor applications – Information Technology – Next-Generation Computer Chips – Data storage devices – Phosphors for High-Definition TV – Sun-screen lotion – Materials Technology – Gas sensing applications – Pharmaceutical fields – Biomedical applications

Introduction

Though nanoparticles are very small, they are the important materials to build the future world. Nanomaterials exhibit very interesting structural, electrical, electrochemical and magnetic properties due to changes in their structure and bonds. They have applications almost in all Engineering fields as shown in Fig. 5.1.

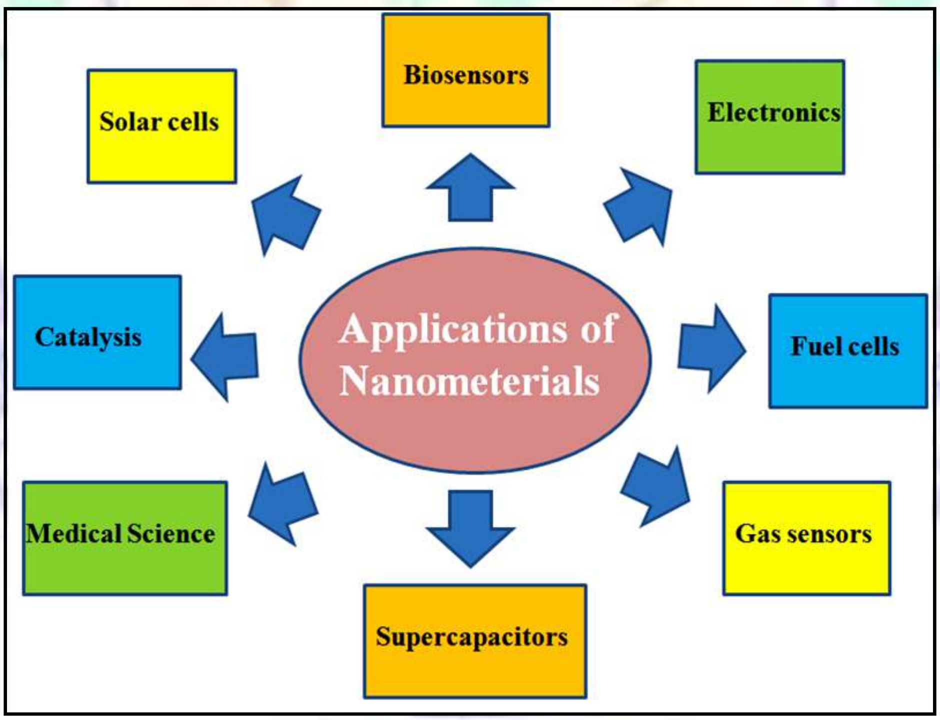

Fig. 5.1 Applications of nanomaterials

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Recently, nanomaterials are used for a wide number of applications, for example in industry, as magnetic links for bank cheques and jet printing ,high density magnetic data storage devices, magnetic information storage, xerography, catalysis, magnetic refrigeration, electronics (recording media) as photocatalyst for organic dye removal, water splitting, gas sensors, electrode in Li-ion batteries, sewage treatment and biomedical applications. Some of the detailed applications of nanomaterials are given below.

5.1 Photocatalytic applications

In recent years, heterogeneous photocatalysis has received increasing attention for environmental applications such as air purification, water disinfection, hazardous remediation and water purification. However, the high photocatalytic degradation of TiO_2, ZnO, CuO, NiO, SnO_2, In_2O_3, ZnO/CuO, and SnO_2/In_2O_3 has been attracted extensive attention of many researchers. Fortunately, utilization of coupled oxide semiconductors could increase the charge separation and extend the energy range of photo-oxidation. By far, many research groups have carried out the photocatalytic activity experiments of various coupled semiconductors. Among them, ZnO/CuO and SnO_2/In_2O_3 nanocomposites as efficient photocatalyst is determined by the photocatalytic degradation of the dyes, under UV light at different irradiation times. The photocatalytic efficiency was calculated using the relation $\eta = (1 - C/C_0)$, where C_0 is the concentration of the dye before illumination and C is the concentration of the dye after a certain irradiation time. It should be observed that by increasing the irradiation time, the maximum absorption peak decreases, which implies that the concentration of the dye decreases in the presence of the coupled metal oxide nanoparticles under UV illumination. In order to find the photocatalytic behavior, the initial and UV irradiated samples are subjected to UV absorption analysis. Further, in the effective coupled metal oxide photocatalyst, the decrease of the absorption peak may be observed in the samples, which can be ascribed to the double bond of the chromophore in the dye structure had been destroyed after UV irradiation. And also, it may be noted that the peak became gradually smoother with increasing irradiation time, which means that a sufficient photocatalytic reaction had been taken place to destroy the chromophore of the dye. In addition, compared to the UV-vis characteristic absorption peak of the initial dye solution, the apparent decrease of the absorption intensity should be indicated that the photocatalytic capability of the catalyst to degrade the dye. Hence, the material is observed to be photocatalytically active.

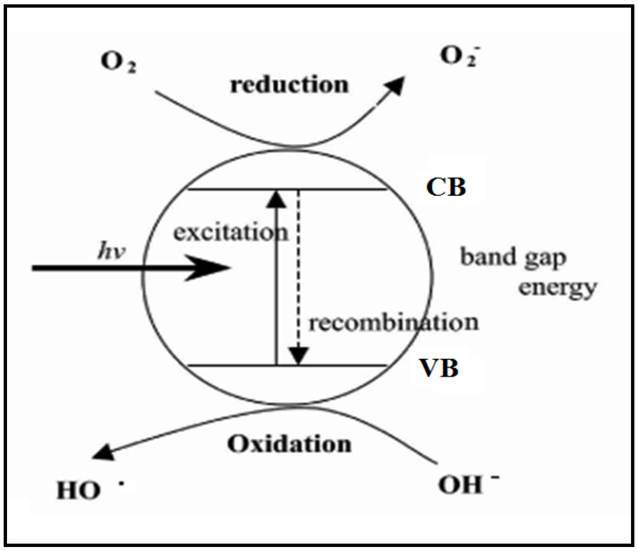

Fig. 5.2 Schematic representation of the photocatalytic mechanism

When a photocatalytic reaction is conducted in an aqueous medium, the holes are effectively scavenged by the water and hydroxyl radicals OH* get generated; these are the strong and unselected oxidant species, in respect of the totally oxidative degradation of organic substrates (Fig. 5.2). Both holes and hydroxyl radicals have been proposed as the oxidizing species, responsible for the degradation (mineralization) of the organic substrates. The higher crystallinity combined with a good surface state improves the photocatalytic performance.

5.2 Fuel cells applications

Recent nanotechnology research has produced a number of promising nanomaterials which could make fuel cells cheaper, lighter and more efficient. Fuel cells are direct electrochemical fuel to electrical energy conversion devices and offer higher efficiency compared with conventional technologies such as internal combustion engines. If the waste heat of the fuel cell is also used, fuel efficiencies of 90% are possible. Fuel cells consist of an electropositive anode, where oxidation occurs to fuels (hydrogen, methanol, ethanol, methane, etc.), an electronegative cathode, where reduction occurs (to oxygen, air, etc.), and an electrolyte, where ions carry the current between the electrodes. The performance of a fuel cell electrode can be optimized in two ways; by improving the physical structure and by using more active electro catalyst. A good structure of electrode must provide ample surface area, provide maximum contact of catalyst, reactant gas and electrolyte, facilitate gas transport and provide good electronic conductance. In this fashion the structure should be able to minimize losses.

Among the various types of fuel cells, polymer electrolyte membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), and solid oxide fuel cell (SOFC) are actively under research and development as they employ solid electrolytes that could make the operation and maintenance of fuel cells easier. However, even like this, their commercialization is still hampered by high cost, poor durability issues, and operability problems that are directly linked to severe materials challenges and systems issues. For example, in low-temperature fuel cells, nearly half of the cost of the fuel cell is linked to the electro-catalyst cost. To reduce the cost, in PEMFCs and DMFCs, Pt catalyst with novel nanostructure and high performance have been developed to reduce the loading amount of Pt, or directly by using less expensive alternative nanostructured electrocatalysts, such as N-doped carbon nanotube (CNT) or iron-based catalysts.

Nanostructured materials are becoming increasingly important in the field of fuel cells and hence have attracted great interest in recent years. The variety of nanometer size effects in fuel cell materials can be divided into two types: (1) trivial size effects, which rely solely on the increased surface-to-volume ratio and (2) true size effects, which also involve the strong influence of surface properties on overall behavior, and the possibility of tailoring electrochemical and other properties when the dimensions of fuel cell systems are confined. There is a significant effect of spatial confinement and the surface on the physicochemical characteristics due to small particle size. New nanomaterials may allow fundamental advances in fuel cell performance. Further, nanostructured fuel cell electrodes increase the surface area (per unit weight) of catalysts and enhance the contact between fuels and catalysts, which leads to improved system efficiency.

5.3 Biosensor applications

Enormous efforts have been directed towards the development of diagnostic tools in order to improve the sensitivity of existing diagnostic techniques and to considerably reduce the time and labor required for analysis. Many biosensors take hours or even days and several successive steps and procedures are required to produce results, so there is a clear need for devices that operate on a short timescale. A combination of magnetic nanomaterials and ultrasensitive magnetic field sensors is nowadays showing a great potential as a perfect team to achieve these goals. In these biosensors, the nanoparticles are coated or functionalized with chemical groups or entities that will bind to the biomolecule that need to be detected. In the case of sensors on a substrate, these nanoparticles-biomolecule complexes then react with “probes” molecules that are fixed onto the surface of the magnetic sensor. The presence of the magnetic nanoparticles on the surface produces an output signal. In the case of label-free biosensors, the nanoparticle-biomolecule complexes are directly detected by probing changes in magnetic properties of the nanoparticles after the binding events. These kind of label-free biosensors are extremely promising, especially for point of care applications, where the assay should be simple, requiring no or minimum preparation. The possibility of analytes detection directly in biological samples will lead to more economic, simple to use, versatile and flexible sensors.

5.4 Information Technology

Nano-dimensional photonic crystals and quantum electronic devices plays a vital role in the recently developed computers. Further, they are used in chemical/optical computers. They are used in mobiles, lap-tops etc. Nanomaterials are used for data storage devices. They are used to make CD's and semiconductor laser. These materials are used to store the information in smaller chips. Nanomaterials are used to produce very tiny permanent magnets of high energy products. Hence, they are used in high-density magnetic recording. Magnetic devices made of nanoparticles of Cu-Fe alloy are used in RAM, READ/WRITE heads and sensors. Quantum dots, quantum wells and quantum wires are mainly produced from semiconductor nanomaterials. Hence, they are used in computer storage devices.

5.5 Next-Generation Computer Chips

The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. By achieving a significant reduction in their size, the microprocessors, which contain these components, can run much faster, thereby enabling computations at far greater speeds. However, there are several technological impediments to these advancements, including lack of the ultrafine precursors to manufacture these components; poor dissipation of tremendous amount of heat generated by these microprocessors due to faster speeds; short mean time to failures (poor reliability), etc. Nanomaterials help the industry break these barriers down by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity, and longer-lasting, durable interconnections (connections between various components in the microprocessors).

5.6 Data storage devices

Nanotechnology offers two unique opportunities to solve the problem of how to miniaturize storage devices. The first opportunity entails the use of a variety of chemical and physical processes to fabricate memory media capable of supporting nanoscale features that have reversible properties, be it magnetic, electric, or phase change. Such media should satisfy the first and second criteria, namely, a large data storage capacity and a small form factor. The second opportunity derives from the ability of scanning probe microscopy, the champion of nanotechnology, to characterize and modify structures down to atomic dimensions. Here, the use of a large number of probes operating in parallel should satisfy the third criterion, namely, fast access times. Also, because the fabrication of multiple cantilevers lends itself rather readily to mass production using currently available photolithographic processes, it should satisfy the fourth criterion: low cost.

5.7 Phosphors for High-Definition TV

The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render high-definition televisions (HDTVs) and personal computers affordable to be purchase.

5.8 Sun-screen lotion

Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO_2 provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO_2) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

5.9 Materials Technology

We can synthesis harder metals having hardness 5 times higher than normal metals using nanomaterials. Stronger, lighter, wear resistant, tougher and flame retardant polymers are synthesized with nanoparticles as fillers. They are used in replacement of body parts and metals (biomaterials). We can produce unusual colour paints using nanomaterials since nanomaterials exhibit entirely different optical properties. ZnO thermistors made of ZnO nanoparticles are used in efficient thermal protection and current controlling devices. Nanophase materials are used in nano-electronic devices such as nano-transistors, ceramic capacitors for energy storage, noise filters and stabilizers. The special features of these devices include smaller sizes and reduced power losses.

5.10 Gas sensing applications

During last few decades, the use of several kinds of gases in different areas like domestic, industries, food packaging, laboratories are creating a severe scene for us due to excess of these. So it is necessary to develop a device which is useful in detection of toxic and harmful gases. Many efforts have been done for developing such devices. But nanomaterials are playing a great role in developing these devices due to its potential applications. The sensing mechanism is based on changes in electrical resistance or conductance of nanomaterials due to chemical interaction in between the gaseous species and the nanomaterials. The charge transfer process induced by chemical interactions determines the resistance of the nanomaterials. If the nanomaterials are n-type the resistance decreases in presence of reducing gases such as Methane, Liquefied Petroleum gas (LPG), Ammonia gas (NH_3) while that of increases for p-type nanomaterials.

Semiconducting metal oxide nanocomposites have been investigated extensively at elevated temperatures for the detection of simple gases. There are many parameters of materials for gas sensor applications, for example, adsorption ability, catalytic activity, sensitivity, thermodynamic stability, etc. Many different metal oxide materials appear favorable in some of the above said properties, but very few of them are suitable to all requirements. To evaluate the performance of gas sensing methods or gas sensors, several indicators should be considered: (i) sensitivity: the minimum value of target gases' volume concentration when they could be detected; (ii) selectivity: the ability of gas sensors to identify a specific gas among a gas mixture; (iii) response time: the period from the time when gas concentration reaches a specific value to that when sensor generates a warning signal; (iv) energy consumption; (v) reversibility: whether the sensing materials could return to its original state after detection; (vi) adsorptive capacity (also affects sensitivity and selectivity); (vii) fabrication cost. The most common gas sensing materials are metal oxide semiconductors, which provide sensors with several advantages such as low cost and high sensitivity. Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases by conductive measurements. The following oxides show a gas response in their conductivity: SnO_2, In_2O_3, WO_3, Cr_2O_3, Mn_2O_3, Co_3O_4, NiO, CuO, TiO_2, V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, Ta_2O_5, La_2O_3, CeO_2, Nd_2O_3. Metal oxides selected for gas sensors can be determined from their electronic structure. Generally, metal oxides can be classified into two types:

non-transition and transition. The d^0 configuration could be found in transition metal oxides (e.g., WO_3, V_2O_5 etc.), and d^{10} appears in post-transition-metal oxides (e.g., SnO_2, In_2O_3 etc.). Most common metal oxide semiconductors sensitive to gas concentration are n-type semiconductors. Oxide materials can present ionic or mixed ionic/electronic conductivity and it is experimentally well established than both can be influenced by the nanostructure of the solid. The number of electronic charge carriers in a metal oxide is a function of the band gap energy according to the Boltzmann statistics. The electronic conduction is referred to as n- or p-hopping-type depending on whether the principal charge carriers are electrons or holes respectively.

Four types of mechanism have been observed for ionic conduction: direct interstitial, interstitialcy, vacancy, and grotthus. As charge species (defects; impurities) in polycrystalline oxides typically segregate to particle boundaries to minimize strain and electrostatic potential contributions to the total energy, there is a contribution to the conductivity parallel to the surface which becomes important at the nanoscale regime. The charge carrier (defect) distribution also suffers strong modification from bulk materials as there is presence of charge carries through the whole material as a consequence of the shielded electrostatic potential depletion at surface layers of nanosized materials.

Different nanomaterials such as tin oxide (SnO_2), indium oxide (In_2O_3), tungsten oxide (WO_3), Zinc oxide (ZnO), chromium oxide (Cr_2O_3), Nickel oxide (NiO), Copper oxide (CuO), manganese oxide (Mn_2O_3), cerium oxide (CeO_2), lanthanum oxide (La_2O_3) etc. with various morphologies produced by using various synthesis processes are tested for reducing gases. Metal oxide nanorods produced by hydrothermal method were tested as LPG sensors. It is found that metal oxide nanorods provide a good response. The sensor response was found to be temperature dependent and exhibited maximum at 250°C. The role of metal oxide nanomaterials and their nanocomposites have been investigated for gas sensing application. Different metal oxide nanostructures like nanowires, nanobelts and tetrapod have been prepared and used for analyzing sensitivity to H_2S and NO gases. The effect of different nanostructures on response of n-type semiconductor metal oxide to both shows that the response to H_2S arises due to changes in grain boundary resistance while the response to NO arises due to changes in both intragrain and grain boundary resistances. The response of these structures to 4 ppm of H_2S shows that tetrapod have maximum while polycrystalline material has minimum sensitivity to H_2S. The films made up of tetrapod were found to be sensitive to 1 ppm due to oxygen vacancies and defects in lattice which create adsorption sites for oxygen. Several literatures reported that the use of catalyst or promoters because of good dispersion to the nanomaterials is the most effective way to enhance the sensitivity of nanomaterials. Ag nanoparticles embedded metal oxide nanorods developed by photochemical method were investigated for ethanol sensing. They are also found to be highly selective for ethanol in between the mixture of ethanol (C_2H_5OH), hydrogen (H_2), formaldehyde (HCHO), methane (CH_4), methanol (CH_3OH), carbon monoxide (CO), acetone (CH_3COCH_3) and ammonia (NH_3). One dimensional nanomaterials are very promising sensors, and some of their results have shown that the devices based on one dimensional nanostructures have great potential in overcoming the fundamental limitations of traditional nanomaterials based on sintered particles or thick-films such as low sensitivity, poor stability and high working temperature.

5.11 Pharmaceutical fields

Nanomaterials are increasingly used for manufacturing diverse industrial items such as cosmetics or clothes and for infinite applications in electronics, aerospace and computer industry. In addition, as the need for the development of new medicines is pressing and given the inherent nanoscale functions of the biological components of living cells, nanotechnology has been applied to diverse medical fields such as oncology and cardiovascular medicine. Indeed, nanotechnology is being used to refine discovery of biomarkers, molecular diagnostics, drug discovery and delivery, which could be applicable to management of these patients. The National Institutes of Health (USA) reviewing the use of nanotechnology in human diseases introduced the term of “nanomedicine” to describe such applications. To achieve these aims, nanotechnology strives to develop and combine new materials by precisely atoms and molecules to yield new molecular assemblies on the scale of individual cells, organelles or even smaller components, providing a personalized medicine.

5.12 Biomedical applications

One of the fields that can enormously benefit from the advancement in nanotechnology is biomedical research. In particular, highly specific medical interventions at the nanoscale for curing disease and repairing damaged tissues such as bones, muscles or nerves are emerging as nano-medicine area. Controlled drug delivery is possible using nanotechnology. Diffusion of medicine through nano-porous polymer reservoir as per the requirement is very useful in controlling the disease. Nanomaterials have wide-range applications and indications in a variety of areas, including chemistry, physics, electronics, materials science, optics and biomedical sciences. The nanomaterials exhibit solitary and considerably changed physical, chemical and biological properties, when compared to their macro-scaled, i.e. bulk compliments. The nanoparticles interaction with biological materials leads to the formation of new nanomaterials with control size, shape, surface chemistry, roughness and surface coatings. Antimicrobial agents are of great importance in several industries such as water disinfection, packaging, textiles, construction, medicine and food. The organic compounds traditionally used for disinfection produce several disadvantages, including toxicity to the human body, and sensitivity to high temperatures and pressures that are present in many industrial processes. For these reasons, the interest in inorganic disinfectants such as metal oxides is increasing. These inorganic compounds present strong antimicrobial activity at low concentrations. They are also much more stable in extreme conditions considered as non-toxic, and some of them even contain mineral elements essential to the human body.

Various nanoparticles of metal oxides such as Ag_2O, SnO_2, TiO_2, CuO, ZnO, Mn_3O_4, Co_3O_4, MgO, ZnO/CuO etc. have been synthesized and are found a good inhibitor of different bacterial strains. Activity of nanoparticles is directly dependent on the bacterial strain i.e. gram positive and gram negative as they have differences in their cell wall as shown in Fig. 5.3. Electrostatic interactions are directly responsible for the attachment of nanoparticles to bacteria. These interactions changes the integrity of cell membrane of bacteria and toxic free radicals are released which induce oxidative stress on bacteria.

Biomedical applications need nanosized particles with high magnetization value and narrow particle size distribution. Furthermore, these nanoparticles require a surface coating which must be biocompatible, nontoxic, and must also allow targeted drug delivery to specific area. Nanoparticles can be stabilized by various protection strategies which could be organic coating, such as polyethyleneglycol, polysaccharide, dodecanethiol - polymethacrylic acid, and chitosan, or a coating with an inorganic coating such as silica, metal or nonmetal, metal oxide or sulphide. This surface coating protects nanomaterials from agglomeration while at the same time functionalizing it. The functionalized magnetic nanoparticles can bind to drugs, proteins, enzymes, antibodies, or nucleotides and can be directed to an organ, tissues, or a tumor using an external magnetic field.

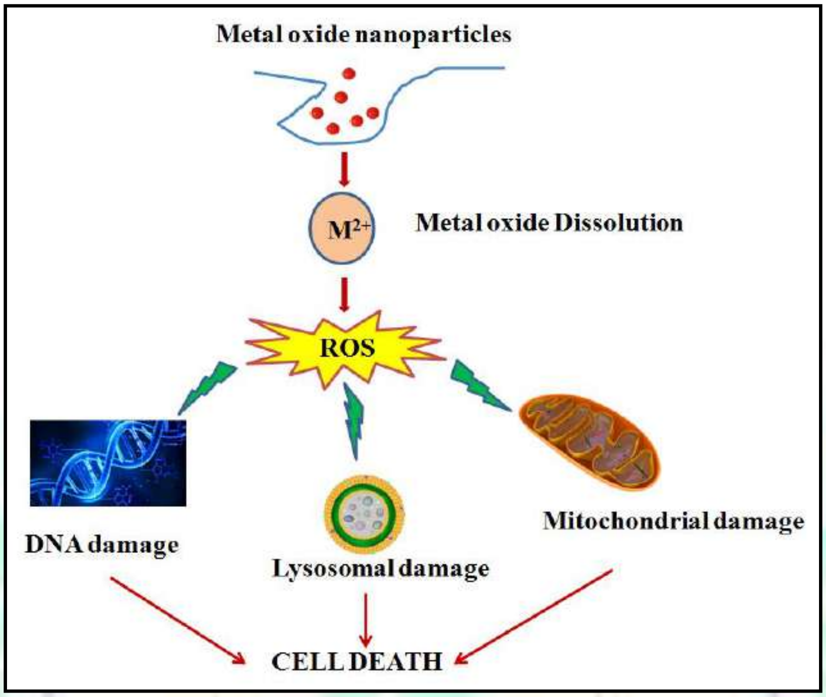

Fig. 5.3 Antimicrobial activities of nanomaterials

Silver nanoparticles are the most relevant nanoparticles for which to evaluate the effect on ecosystems because they exhibit a high level of toxicity at low concentration to a large diversity of microorganism. Microorganisms are key actors in many environmental, chemical and energetic cycles on which humans are dependent and at least in that respect major attention should be paid to the harmful effects of released anthropogenic nanomaterials into the environment. Silver nanoparticles possess several interesting properties for industrial applications (i.e., electrical, optical and catalytic properties) but the dominant one is its strong bactericidal effect. Silver nanoparticles are present in a large number of products spread across a diversity of applications that include: cosmetics, clothing, children goods, biomedical devices and electronics.

Nanomaterials have a great impact on biomedical research especially in the last few years: superparamagnetic iron oxide nanoparticles as MRI contrast agent were studied and today these are commercial products. The great advantages of nanomaterials in the biomedical research field lies in its ability to operate on the same small scale as all the intimate biochemical functions involved in the growth, development and ageing of the human body. Only in a few cases a particular nanostructured material was developed completely for a specific biomedical application. More frequently, nanomaterials discovered in the past are now further developed and applied in different biomedical fields. Still there are a lot of challenges for the use of nanoparticles in medical applications. One of the main issues is certainly related to long-term safety of nanomaterials, both developed for in vitro and in vivo applications. Super paramagnetic iron oxide nanoparticles are used in several biomedical applications, including the quantification of biomolecular targets in cell lysates and tissue extracts. They have also been used to detect larger biological entities, such as bacteria, in solutions. In most cases, commercial beads containing magnetic multicores with different surface layers have been used, but these detection systems have poor sensitivity and limited detection range due to a wide bead and magnetic domain size distribution. Moreover, the surface properties of nanomaterials can be modified for targeted drug delivery for e.g. nucleic acids, proteins, peptides, small molecules and loaded nanoparticles are not recognized by immune system and efficiently targeted to particular tissue types. Targeted nano drug movers' decreases drug toxicity and offer the more efficient drug distribution. The nanocarriers' embraces potential to transport biotech drugs above various an atomic limits of body such as blood brain barrier.

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