ENGINEERED NANOPARTICLES: APPLICATIONS AND CONCERNS

Abstract

The unique optoelectronic, catalytic, and antimicrobial properties of nanoparticles (NPs) have made them one of the sought-after materials. They are now being employed in many consumer products like scratchproof eyeglasses, anti-stain paints and fabrics, self-cleaning windows and solar panels, transparent sunscreens, antifouling agents for refrigerators, washing machines, and cloths, antimicrobial agents for door knobs, etc. It is foreseeable that unabated applications of these NPs will eventually result in their concentration in to the environment. The environmental fate of these nanoparticles and their associated toxicity on various types of plant and animal life is not fully understood. The situation is further aggravated due to the ability of plants to absorb these nanoparticles through roots consequently making their way to the food chain. The continued exploration in the area is providing improved understanding ofthe toxicities of various nanoparticles toward aquatic and animal life. This review highlights recent reports on various toxic effects associated with various nanoparticles. Various mitigation strategies have also been highlighted which could enable safer application of these nanoparticles.

Keywords: Nanoparticles, toxicity, contaminant, water pollution

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I. INTRODUCTION

Nanotechnology has emerged as a renowned field of research in the last century which gained significant impetus after the famous lecture by Nobel laureate Richard P. Feynman in the year 1959 on top-down Nanotechnology in which he coined the phrase "*There's Plenty of Room at the Bottom*". Since then, numerous revolutionary advances have been made in the field of nanoscience and nanotechnology. Nanoscience deals with the study, synthesis, fabrication, and applications of objects that have dimensions in nanoscale. There are variety of nanomaterials of inorganic and organic origin such as carbon nanotubes, graphene, fullerene, metal and metal oxide nanoparticles, carbon-dots, quantum-dots, nanowires and cables, nanocages, core-shell structures, nanotriangles, nanocubes and other polyhedrons, nanopeapods, solid and hollow nanospheres, polymeric nanoobjects etc which have been synthesized and their properties have been explored. Table 1 summarizes different types of nanomaterials.

Table 1: Different Types of Nanomaterials

Nanomaterials		
Organic	**Inorganic**	**Hybrid**
Fullerene, Carbon Nanotubes (CNTs), Graphite and Graphene, Carbon Fibers, Carbon-dots, Polymer NPs	Metal NPs e.g. Ag NP, Au NP, Pt NP, Zn NP Metal Oxide NPs e.g. ZnO,TiO_2, BSnO, Fe_2O_3, CuO, CeO_2 Core Shell Structures	Polymer@TiO_2, Carbon@TiO_2 CNT@Metal NPs Quantum Dots e.g. CdSe, ZnS

In this chapter emphasis has been given on the application and toxicity of metal and metal oxide-based NPs. These engineered nanoparticles can be tailor-made to achieve the desired properties. The International Organization for Standardization defines nanoparticles (NPs) as "structures whose sizes in one, two, or three dimensions are within the range from 1 to 100 nm". Usually, nanoparticles are composed of three layers: (i) The inner core which is referred to as the nanoparticle itself and constitutes the is the central part of the NPs; (ii) The shell material which is essentially different from the nanoparticle in terms of chemical composition when core-shell NPs are being synthesized and (iii) The surface layer which is generally small organic molecule and helps in preventing the agglomeration of nanoparticle and also depending on the characteristic of the surfactant can result in a novel morphology, shape and size control. The dimensions and morphology of these designed nanoparticles, which are easily modifiable, have a significant impact on their distinctive physicochemical features that set them apart from the bulk phase materials from which they were created. For example, A 20-nmgold, platinum, silver and palladium nanoparticles have distinctive wine-red, yellowish-grey, black and dark-black colours, respectively which is in stark contrast to the colour of the bulk phase. This is because of an increase in the surface area, ensuing quantum effect, surface reactivity and hardness which results in improved electronic band gap, and superior electric, optic and magnetic properties. Due to these exceptional characteristics, the nanoparticle research has drawn attention from researchers from multidisciplinary fields. Continuous exploration has resulted significant scientific advancement in many fields ranging from polymer, textile, biology, medicine, drug deliverysensors,[1-3] optoelectronic devices, gas capture[4] and in catalysis.

The development of sophisticated fabrication and imaging techniques has made it easier and more reliable to synthesise and characterise range of nanomaterials. The effect of these development can be easily seen by the miniaturizations and development of electronic devices, computers and gadgets with enhanced performances. Similarly, the development of advanced functional materials in polymer, cosmetics, paints, ceramics, carbon fibre composites etc. has been realized as a direct consequence to the development of nanoscience.

II. CHARACTERIZATION

Numerous characterisation techniques are being used for evaluating different physicochemical properties of NPs. These are X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) for understanding the phase of the material and its purity and composition. The infrared (IR) spectrum provides the information about surface functionalities of NPs. Morphological investigations are generally carried out by scanning electron microscope (SEM) and transmission electron microscope (TEM) which provide insight into the shape and size of NPs which is of great importance since many of the properties of NPs are greatly influenced by morphology. Thus, these tools become indispensable for nanoscience research. Further, core shell structures, hollow and solid structures can be visualized by TEM microscopes. The in build EDX also provide information of different phases and compositions particularly in the case of composite materials. It also gives the information about the homogeneity of the sample under investigation. TEM studies are crucial studying the core shell structures where one material is encapsulated within other. This technique also offers unique advantages by providing information regarding the solid or hollow nanostructures which is not possible by other techniques.

III. APPLICATION OF NP’S

As the focus on exploring such materials increases as reflected by the number of publications in various journals, tremendous potential applications came into existence. Nowadays, several day-to-day life products utilize nanotechnologies in one way or the other such as nano silver-coated washing machines, and clothing to avoid foul odour.[5] Nanoparticles also find applications for making printer inks, paints and sunscreens where they are added to the colloids. Apart from this nanoparticles are being used for photocatalysis,[6] environmental remediation, biomedical science,[7] soil rejuvenation,[8] food technology,[9] cancer treatment,[10] oil and gas industry,[11]textile industry,[12] etc. For instance, zinc and titanium oxide sunscreens contain nanoparticles so small that they do not scatter light, resulting in a clear rather than a white final product..[13]

1. **Biomedical Applications:** Inorganic nanoparticles can be used to create nanodevices for a variety of biological and pharmacological purposes..[14]Several studies have demonstrated the efficiency of NPs as drug carriers by successfully delivering the optimum dosage, which results in improved therapeutic effectiveness, fewer adverse effects, and improved patient adherence..[15]Iron oxide based nanomaterials are at the forefront for their usage in biomedical application for enhancing the image quality of cells and tissues using magnetic resonance imaging tools.[16,17] Harisinghani et. al. has demonstrated the use of dextran coated superparamagnetic iron oxide NPs for the accurate detection of lymph-node metastases in prostate cancer which was undetectable by conventional MRI.[18] Similarly, Huh and co-workers have demonstrated in vivo

detection of human cancer cells implanted on live mice using iron oxide nanocrystals decorated with Herceptin functionalities as cancer-targeting antibody for desired receptors.[19]There finding suggested that iron oxide NPs have much higher relaxation time compared with gadolinium based MRI agents. The magnetic nature of iron oxide nanoparticles has also been exploited for developing magnetically guided and magnetically responsive drug carrier. The functionalized iron oxide NPs laden with drugs can be easily guided to specific site using external magnetic field. The similar property can also be exploited for control drug release.[20]

Due to the inherent characteristics of surface plasmon resonance (SPR), which intensifies the light scattering and absorption phenomenon, the majority of inorganic NPs have a tremendous promise in the detection and treatment of cancer. The Au NPs when exposed to irradiation, the surface electrons of AuNPs get highly excited and resonant, quickly converting light to heat in just one picosecond which has been exploited for selective laser induced photo thermal therapy for destroying the cancerous cells.[21] Application of Au NPs are advantageous over other nanoparticles due to well established synthetic protocols and size and shape control which can be used to finetune the absorption and scattering properties. The relative ease with which the Au NPs can be functionalized has made them material of choice for loading and control release of chemical drugs which can be delivered to the tumour site by functionalizing it with various ligands for improve selectivity.[22]

The antimicrobial properties of Ag NPs are exploited for wound dressing.[23] The Ag NPs are shown to possess broad range of antifungal, antibacterial, and antiviral properties apart from anticancer properties.[24] Morones and co-workers have studied the bactericidal effect of Ag NPs against several GRAM negative bacteria and found that the 75 mg/Ml was the cut-offs value for inhibiting the growth of all types of bacterial strains under investigation irrespective of the NP size, however, NPs in the size range of 1-10 nm have greater propensity for attaching to the cell membrane.[25] The Ag NPs have also demonstrated its antiviral activity against the very infectious COVID-19 disease which is due to the production of free radicals and reactive oxygen species (ROS), which cause apoptosis and hence prevent viral infection.[26]According to research by Jeremiah et al., the inhibitory concentrations of Ag NPs against SARS-CoV-2 ranged from 1 to 10 ppm, whereas the lethal effect was seen at concentrations of 20 ppm and beyond.[27] Similarly, the antifungal activities of silver nanoparticles have been demonstrated by several studies.[28]

2. **Industrial Applications:** Nanotechnologies are being used for the manufacturing of end products used in day-to-day life.[29]Nano-sized particles (NPs), which are typically added to final products to enhance their quality, can be found in a variety of items, such as cosmetics, medications, sunscreen, and powdered foods to name a few. Nanocomposite based scratch resistant coatings are used for creating transparent, durable, ultra-thin sun glasses without hampering its optical performance. Nanoparticles are also being prominently used in fashion industry to create wind- and water-resistant jackets, textiles and apparel that resist stains due to silica coatings, clothing that resists odour owing to microbe-killing silver nanoparticles, and even gears that offers sun protection.[12] Wrinkle and stain resistant fabrics are being manufactures by industries such as Nano-Tex and Gore-Tex which require less frequent washing. Similarly, stain resistant, hydrophobic shoes and other foot wears are also being developed exploiting nanotechnology which

also avoid foul odour.[30]The Use of ZnO and TiO_2 nanoparticles are used in the manufacturing of sunscreens which offer better UV protection. The antimicrobial properties of nanoparticles are being exploited for the manufacturing of paints and coating which resists development of stains due to bacterial and fungal growth on walls and furniture's.[31,32]

A range of wearable bands and watches are also commercially available which are decorated with variety of sensors to monitor vital signs such as respiratory rate, body temperature, and blood oxygen level in a real time health monitoring which employ nanotechnology in one form or other.[33]These features make them very crucial in the early detection of various diseases including COVID-19. Similarly, robust carbon nano tube and fibre based composite materials have been developed which are sturdier and avoid wear and tear. These materials are being used in sport industry for making tennis rackets (manufactured by Babolat) and aeronautics. A high-performance ski wax is developed which is employed for hard and fast-gliding surface by creating ultra-thin coatings. Copper nanoparticles are claimed to be used in growth inducing shampoo for treatment of baldness. Antibacterial Ag NPs in toothpastes and detoxifying gold NPs in skin creams are also being used.[34]

Maritime industry faces challenges form the hazardous sea environment as the navigational vessels, offshore rigs and marine platform are under constant attack from the marine microbial species, salty sea water and drastic temperature variations. Nanoparticle-based epoxy coating has been developed specifically for maritime components to combat biofouling and corrosions caused by marine environment. These epoxy coatings are impregnated with ZnO and silica nanoparticles and its coating on surfaces exposed to sea environment result in corrosion resistant surfaces which also avoid foul odouring and demonstrate biocidal activity as evident from the hindered bioaccumulation of microalgae and other species.[35]

Recent reviews highlight the use of nanomaterials in oil and gas industries besides for biofuelproduction.[36,37]Biofuels has gained significant attention as a renewable source due to dwindling reserves, unstable energy prices and pollution caused by burning conventional fuels. Researchers have explored the efficacy of nanoparticles along with other nanomaterials for the production of biofuels such as biohydrogen, biogas, biodiesel and bioethanol due to the catalytic properties.[36]Nanosilica (SiO_2) and aluminum oxide (Al_2O_3) NPs are primarily investigated for various applications in oil and gas industry.[37]

Water remediation is another aspect where nanoparticles are shown to exhibit high adsorption of pollutants and catalytic degradation of variety of organic colourant.[38]These engineered nanomaterials hold promise for waste water treatment because of their high efficiency as well as their economical production while simultaneously offering the manoeuvrability for in-situ or ex-situ use.[39]ZnO and TiO_2 NPs are frequently used for photocatalytic degradation of dyes whereas iron oxide NPs are used to develop easily separable adsorbents after remediation.[40-42]

The other areas where nanoparticles find increasing application is food processing and technology. NPs are designed to carry antimicrobial polypeptides which act against microbial deterioration of food quality in the food industry. Nanosensors find applications in the detection of harmful food pathogens and gases released due to food spoilages.[37]

3. **Nanoparticle Toxicity:** These engineered nanoparticles are relatively new entities, and a better understanding of their environmental fate is relatively unknown.[43]The increasing use in consumer products and other areas has increased the possibility of these nanoparticles to end up in the environment in general and in aquatic bodies in particular, which has raised concerns about environmental contamination by nanomaterial and its adverse effects on living things.[44,45]Toxicology is greatly influenced by the physicochemical characteristics of NPs, including their size, shape, surface area, surface charge, catalytic activity, and the presence or absence of a shell and active groups on the surface.[46] Because of their small size, NPs can be absorbed by cells and enter the circulation and can be transported to various organs and tissues.[47]Figure 1 schematically represent the applications of NPs in various areas and possible exposure scenarios to humans. Various research suggests that nanoparticles could exert toxic effect on marine life for example it has been shown that the zebra fish embryos get destroyed in presence of silver nanoparticles which probably generates silver ions in the environments which induces the toxicity.[48,49]Similarly, Ag NPS are also capable of damaging liver of adult zebrafish by causing oxidative stress and apoptosis.[50]Various nanomaterials show ecotoxicity against algae, aquatic plants and fungi.[51]The detailed mechanism of the toxicity caused by nanoparticles is not entirely understood, despite the large number of papers on in vitro and in vivo investigations.[52,53]

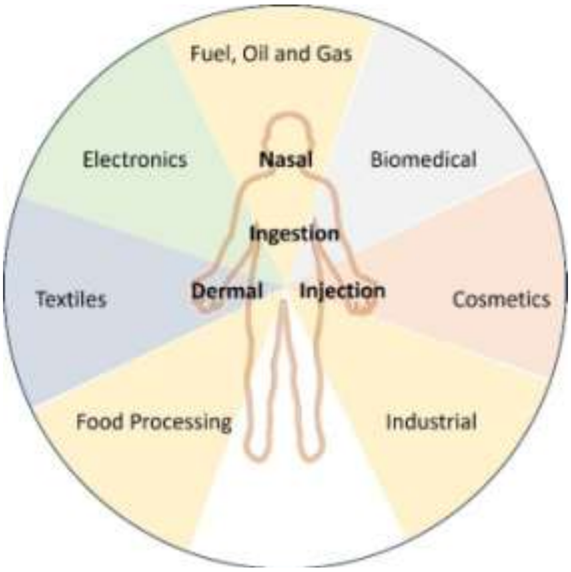

Figure 1: Application Areas of NPs and Possible Exposure Route to Human Body.

However, the main problem preventing their application in the treatment and diagnosis of diseases is NP toxicity against living things. Consequently, researchers frequently struggle to strike a compromise between NPs' beneficial therapeutic effects and their toxicity-related adverse effects. Regulation has been in place to assess the health risk posed by nanoparticles present in the consumer products and therapeutics including their effect on fertility and reproductivity. Asare and coworkers have examined the effect of Ag NPs and TiO_2 NPs on cellular and genotoxicity against testicular cell lines and found that Ag NPs exert more toxicity compared to TiO_2 NPs causing apoptosis and necrosis.[54] The situation becomes more alarming as few studies suggest that Ag NPs are capable of crossing blood–testis and blood–brain barrier in rats and mice.Toxicity studies on starch coated Ag NPs showed that damage to the mitochondria and increased production of reactive oxygen species leading to DNA damage in human lung fibroblast cells and human glioblastoma cells.[55]Studies have shown that PEG-coated gold nanoparticles and silver nanoparticles are unsafe because they accumulate in the liver, spleen, and other organs after controlled injection for up to seven days in the case of Au NPs and up to sixteen days in the case of Ag NPs. They also cause acute inflammation and apoptosis in the liver.[56,57]

Nanomaterials have a tendency to partition into sediments and soils, which exacerbates the pollution of agricultural areas potentially endangering the associated food webs. Consequently, study of NPs' biodistribution in the food chain is crucial for assessing their toxicity and bio-accumulation.[58]Various research indicate that the crops can take up and accumulate these nanoparticles resulting entry into the food chain which could have drastic effect on human health due to induced toxicity.[59]In a controlled experiments, Ferry and coworkers have found that the gold nanorods can readily pass from water column to marine food web by studying the effect on laboratory constructed estuarine ecosystem consisting range of flora and fauna like sea grass, microbes, biofilms, snails, clams, shrimp and fish along with sea water and sediments.[60]The kidney bean plants grown innano CeO_2 contaminated soilindicates accumulation of Ce in the plant which was higher in the roots. The exposure of Mexican bean beetles (Epilachna varivestis), to the contaminated plant and consequent feeding of beetles to spined soldier bugs (Podisus maculiventris) indicated 5.3 fold biomagnification from the plants to adult beetles and further to bugs.[61]In another study, scientist have germinated and grown soybean (Glycine max) plants in soil contaminated with ZnO or CeO_2 nanoparticles. In Situ Synchrotron X-ray Fluorescence Mapping suggest that ZnO NPs are accumulated in the entire plant as zinc ions which could be due to dissolution. However, CeO_2 NPs were detected in plant tissues of reproductive/edible portion of the soybean plant. This study highlighted the plant toxicity of nanoparticles and entry of engineered nanoparticles into the food chain directly concerning humans.[62]

Because NPs can spread widely and enter the water system through a variety of channels, manufactured nanoparticles are therefore regarded as a new class of contaminants. Thus, there must be conscious use of NPs in consumer products and therapeutics with proper studies which can fill the knowledge gap and also provide ways to mitigate its adverse effect on environment and human health.

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