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Nanoparticles: Synthesis, Characteristics, applications, Advantages and its toxicities

Dr Brajesh Singh¹

¹Assistant Professor Chemistry Government PG, College Musafirkhana Amethi Uttar Pradesh

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<u>Abstract</u>

The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs. Size of nanoparticle lies between 1nm to 100nm. NPs possess unique physical and chemical properties due to their high surface area and nanoscale size. Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region.

Their reactivity, toughness and other properties are also dependent on their unique size, shape and structure. Due to these characteristics, they are suitable candidates for various commercial and domestic applications, which include catalysis, imaging, medical applications, energy-based research, and environmental applications. Heavy metal like lead, mercury and tin are reported to be so rigid and stable that their degradation is not easily achievable, which can lead to many environmental toxicities.

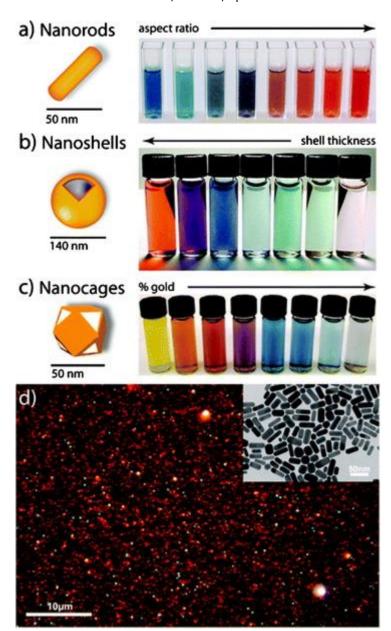
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Introduction

Nanotechnology produced materials of various types at nanoscale level. Nanoparticles (NPs) are wide class of materials that include particulate substances, which have one dimension less than 100 nm at least. Depending on the overall shape these materials can be 0D, 1D, 2D or 3D. The importance of these materials realized when researchers found that size can influence the physiochemical properties of a substance e.g. the <u>optical properties</u>. A 15-nm gold (Au), platinum (Pt), silver (Ag), and <u>palladium</u> (Pd) NPs have characteristic wine red colour, yellowish, grey, black and dark black colours, respectively, shows an example of this illustration, in which Au NPs synthesized with different sizes.

These NPs showed characteristic colours and properties with the variation of size and shape, which can be utilized in bio-imaging applications. As indicates, the colour of the solution changes due to variation in aspect ratio, <u>nanoshell</u> thickness and percentage gold concentration. The alteration of any of the above discussed factor influences the absorption properties of the NPs and hence different absorption colours are observed.

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2. Synthesis of nanoparticles

Various methods can be employed for the synthesis of NPs, but these methods are broadly divided into two main classes i.e. (1) Bottom-up approach and (2) Top-down. These approaches further divide into various subclasses based on the operation, reaction condition and adopted protocols.

2.1. Top-down syntheses

In this method, destructive approach is employed. Starting from larger molecule, which decomposed into smaller units and then these units are converted into suitable NPs. Examples of this method are grinding/milling, CVD, <u>physical vapor deposition</u> (PVD) and other decomposition techniques. This approach is used to synthesized coconut shell (CS) NPs. The milling method was employed for this purpose and the raw CS powders were finely milled for different interval of times, with the help of ceramic balls and a well-known planetary mill. They showed the effect of milling time on the overall size of the NPs through different characterization techniques. It was determined that with the time increases the NPs <u>crystallite size</u> decreases,

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as calculated by Scherer equation. They also realized that with each hour increment the brownish color faded away due to size decrease of the NPs. The SEM results were also in an agreement with the X-ray pattern, which also indicated the particle size decreases with time .One study revealed the spherical magnetite <u>NPs</u> <u>synthesis</u> from natural <u>iron oxide</u> (Fe₂O₃) ore by top-down destructive approach with a particle size varies from ~10 to ~50 nm in the presence of organic <u>oleic acid</u>. A simple top-down route was employed to synthesize colloidal carbon spherical particles with control size. The synthesis technique was based on the continuous <u>chemical adsorption</u> of polyoxometalates (POM) on the carbon interfacial surface. Adsorption made the carbon black aggregates into relatively smaller spherical particles, with high dispersion capacity and narrow size distribution. It also revealed from the micrographs, that the size of the <u>carbon particles</u> become smaller with sonication time. A series of transition-metal dichalcogenide <u>nanodots</u> (TMD-NDs) were synthesized by combination of grinding and sonication top-down techniques from their bulk crystals. It was revealed that almost all the TMD-NDs with sizes <09 nm show an excellent dispersion due to narrow size distribution. Lately, highly photoactive active Co₃O₄ NPs were prepared via top-down laser fragmentation, which is a top-down process. The powerful laser irradiations generate well-uniform NPs having good <u>oxygen</u> <u>vacancies</u>. The average size of the Co₃O₄ was determined to be in the range of 5.5 nm \pm 1.2 nm.

2.2. Bottom-up syntheses

This approach is employed in reverse as NPs are formed from relatively simpler substances, therefore this approach is also called building up approach. Examples of this case are sedimentation and reduction techniques. It includes <u>sol gel</u>, green synthesis, spinning, and biochemical synthesis. Mogilevsky et al. synthesized TiO₂ anatase NPs with graphene domains through this technique . They used <u>alizarin</u> and titanium isopropoxide precursors to synthesize the photoactive composite for photocatalytic degradation of methylene blue. Alizarin was selected as it offers strong binding capacity with TiO₂ through their axial hydroxyl terminal groups. The anatase form was confirmed by <u>XRD pattern</u>. The SEM images taken for different samples with reaction scheme are provided in . SEM indicates that with temperature elevation, the size of NPs also increases .ham et al. In this method nucleation is the bottom approach followed by growth which is the up approach. The LDL NPs were obtained without using <u>phospholipid</u> and possessed high <u>hydrophobicity</u>, which is essential for drug delivery applications .

The monodispersed spherical <u>bismuth</u> (Bi) NPs were synthesized by both top-down and bottom-up approaches . These NPs have excellent <u>colloidal properties</u>. In the bottom-up approach bismuth acetate was boiled within ethylene glycol, while in top-down approach the bismuth was converted into molten form and then the molten drop was emulsified within the boiled diethylene glycol to produce the NPs. The size of the NPs obtained by both methods was varied from 100 nm to 500 nm . The details of this study are provided in 5 Green and biogenic bottom-up synthesis attracting many researchers due to the feasibility and less toxic nature of processes. These processes are cost-effective and environmental friendly, where synthesis of NPs is accomplished via biological systems such as using plant extracts. Bacteria, yeast, fungi, *Aloe vera*, tamarind and even human cells are used for the synthesis of NPs. Au NPs have been synthesis from the biomass of wheat and oat and using the microorganism and plant extracts as reducing agent provides the merits and demerits of various top-down and bottom-up techniques with general remarks

3. Physicochemical properties of NPs

As discussed earlier, various physicochemical properties such as large surface area, mechanically strong, optically active and chemically reactive make NPs unique and suitable applicants for various applications. Some of their important properties are discuss in the following section.

3.4. Thermal properties

It is well-known fact that <u>metals NPs</u> have <u>thermal conductivities</u> higher than those of fluids in solid form. For example, the thermal conductivity of copper at room temperature is about 700 times greater than that of water and about 3000 times greater than that of engine oil. Even <u>oxides</u> such as <u>alumina</u> (Al₂O₃) have thermal conductivity higher than that of water. Therefore, the fluids containing suspended solid particles are expected to display significantly enhanced <u>thermal conductivities</u> relative to those of conventional heat transfer fluids. Nanofluids are produced by dispersing the nanometric scales solid particles into liquid such as water, ethylene glycol or oils. Nanofluids are expected to exhibit superior properties relative to those of conventional heat transfer fluids and fluids containing microscopic sized particles. Because the heat transfer takes place at the surface of the particles, it is desirable to use the particles with large total surface area. The large total surface area also increases the stability suspension . Recently it has been demonstrated that the nanofluids consisting of CuO or Al₂O₃ NPs in water or ethylene exhibit advance thermal conductivity .

4. Applications of NPs

Considering the unique properties discussed in Section 5, NPs can be used in variety of applications. Some important of these are given below.

4.1. Applications in drugs and medications

Nano-sized inorganic particles of either simple or complex nature, display unique, physical and chemical properties and represent an increasingly important material in the development of novel <u>Nano devices</u> which can be used in numerous physical, biological, biomedical and pharmaceutical applications.

NPs have drawn increasing interest from every branch of medicine for their ability to deliver drugs in the optimum dosage range often resulting in increased therapeutic efficiency of the drugs, weakened side effects and improved patient compliance. Iron oxide particles such as magnetite (Fe₃O₄) or its oxidized form maghemite (Fe₂O₃) are the most commonly employed for biomedical applications . The selection of NPs for achieving efficient contrast for biological and cell imaging applications as well as for photo thermal therapeutic applications is based on the optical properties of NPs. Mie theory and discrete dipole approximation method can be used to calculate absorption and scattering efficiencies and optical resonance wavelength for the commonly used classes of NPs i.e. Au NPs, silica-Au NPs and Au nanorods. The development of hydrophilic NPs as drug carrier has represented over the last few years an important challenge. Among the different approaches, polyethyleneoxide (PEO) and polylactic acid (PLA) NPs have been revealed as very promising system for the intravenous administration of drugs. Superparamagnetic iron oxide NPs with appropriate surface chemistry can be used for numerous in vivo applications such as MRI contrast enhancement, tissue repair, and immunoassay, detoxification of biological fluids hyperthermia, drugs delivery and cell separation. All of these biomedical applications require that the NPs have high magnetization value, a size smaller than 90 nm and a narrow particle size distribution. The detection of analytes in tissue sections can be accomplished through antigen-antibody interactions using antibodies labeled with fluorescent dyes, enzymes, radioactive compounds or colloidal gold.

Over past few decades these has been considerable interest in developing biodegradable NPs as effective drug delivery devices . Various polymers have been used in drug delivery research as they can effectively deliver the drugs to the target site thus increases the therapeutic benefit, while minimizing side effects. The controlled release of pharmacologically active drugs to the precise action site at the therapeutically optimum degree and dose regimen has been a major goal in designing such devices.

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<u>Liposomes</u> have been used as a potential drug carrier instead of conventional dosage forms because of their unique advantages which include ability to protect drugs from degradation, target to the site of action and reduce the noxiousness and other side effects. However developmental work on liposome drugs has been restricted due to inherent health issues such as squat encapsulation efficiency, rapid water leakage in the commodity of blood components and very poor storage, and stability. On the other hand, polymeric NPs promise some critical advantages over these materials i.e. liposomes. For instance, NPs help to increase the ratability of drugs or problems and possess convenient controlled drug release properties.

Most of the semiconductor and metallic NPs have immense potential for cancer diagnosis and therapy on account of their surface plasmon resonance (SPR) enhanced light scattering and absorption. Au NPs efficiently convert the strong absorbed light into localized heat which can be exploited for the selective laser photo thermal therapy of cancer . Beside this the antineoplastic effect of NPs is also effectively employed to inhibit the tumor growth. The multihydroxylated $[Gd@C_{82}(OH)_{22}]_n$ NPs showed antineoplastic activity with good efficiency and lower toxicity . Ag NPs are being used increasingly in wound dressings, catheters and various households' products due to their antimicrobial activity . Antimicrobial agents are extremely vital in textile, medicine, water disinfection and food packaging. Therefore, the antimicrobial characteristics of inorganic NPs add more potency to this important aspect, as compared to organic compounds, which are relatively toxic to the biological systems . These NPs are functionalized with various groups to overcome the microbial species selectively. TiO₂, ZnO, BiVO₄, Cu- and Ni-based NPs have been utilized for this purpose due to their suitable antibacterial efficacies.

4.2. Applications in manufacturing and materials

Nanocrystalline materials provide very interesting substances for material science since their properties deviate from respective bulk material in a size dependent manner. Manufacture NPs display physicochemical characteristics that induce unique electrical, mechanical, optical and imaging properties that are extremely looked-for in certain applications within the medical, commercial, and ecological sectors . NPs focus on the characterization, designing and engineering of biological as well as non-biological structures < than 90 nm, which show unique and novel functional properties. The potential benefits of nanotechnology have been documented by many manufacturer at high and low level and marketable products are already being mass-produced such as microelectronics, aerospace and pharmaceutical industries . Among the nanotechnology consumer products to date, health fitness products from the largest category, followed by the electronic and computer category as well as home and garden category. Nanotechnology has been touted as the next revolution in many industries including food processing and packing. Resonant energy transfer (RET) system consisting of organic dye molecules and noble metals NPs have recently gamed considerable interest in bio photonics as well as in material science . The presence of NPs in commercially available products is becoming more common.

Metals NPs such as noble metals, including Au and Ag have many colors in the visible region based on plasmon resonance, which is due to collective oscillations of the electrons at the surface of N. The resonance wavelength strong depends on size and shape of NPs, the interparticle distance, and the <u>dielectric property</u> of the surrounding medium. The unique plasmon absorbance features of these noble metals NPs have been exploited for a wide variety of applications including chemical sensors and biosensors.

4.3. Applications in the environment

The increasing area of engineered NPs in industrial and household applications leads to the release of such materials into the environment. Assessing the risk of these NPs in the environment requires on understanding

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of their mobility, reactivity, Eco toxicity and persistency. The <u>engineering material applications</u> can increase the concentration of NPs in groundwater and soil which presents the most significant exposure avenues for assessing environmental risks. Due to high surface to mass ratio natural NPs play an important role in the solid/water partitioning of contaminants can be absorbed to the surface of NPs, co-precipitated during the formation of natural NPs or trapped by aggregation of NPs which had contaminants adsorbed to their surface. The interaction of contaminants with NPs is dependent on the NPs characteristics, such as size, composition, morphology, porosity, aggregation/disaggregation and aggregate structure. The luminophores are not safe in the environment and are protected from the environmental oxygen when they are doped inside the silica network .

The removal of heavy metals such as mercury, lead, <u>thallium</u>, cadmium and arsenic from natural water has attracted considerable attention because of their adverse effects on environmental and human health. Superparamagnetic iron oxide NPs are an effective <u>sorbent</u> material for this toxic soft material. So, for no measurements of engineered NPs in the environment have been available due to the absence of analytical methods, able to quantify trace concentration of NPs . <u>Photodegradation</u> by NPs is also very common practice and many nanomaterials are utilized for this purpose. used NiO/ZnO NPs modified silica in the tandem fashion for photodegradation purpose. The high surface area of NPs due to very small size (<09 nm), facilitated the efficient photodegradation reaction . The same group has reported the synthesis of variety of NPs and reported their optical, florescence and degradation applications .

4.4. Applications in electronics

There has been growing interest in the development of printed electronics in last few years because printed electronics offer attractive to traditional <u>silicon</u> techniques and the potential for low cost, large area electronics for flexible displays, sensors. Printed electronics with various functional inks containing NPs such as metallic NPs, organic electronic molecules, CNTs and ceramics NPs have been expected to flow rapidly as a mass production process for new types of electronic equipment .Unique structural, optical and electrical properties of one dimensional semiconductor and metals make them the key structural block for a new generation of electronic, sensors and photonic materials .The good example of the synergism between scientific discovery and technological development is the electronic industry, where discoveries of new <u>semiconducting materials</u> resulted in the revolution from vacuumed tubes to diodes and transistors, and eventually to miniature chips .The important characteristics of NPs are facile manipulation and reversible assembly which allow for the possibility of in corporation of NPs in electric, electronic or optical devices such as "bottom up" or "self-assembly" approaches are the bench mark of nanotechnology .

4.5. Applications in energy harvesting

Recent studies warned us about the limitations and scarcity of <u>fossil fuels</u> in coming years due to their nonrenewable nature. Therefore, scientists shifting their research strategies to generate renewable energies from easily available resources at cheap cost. They found that NPs are the best candidate for this purpose due to their, large surface area, optical behavior and catalytic nature. Especially in photocatalytic applications, NPs are widely used to generate energy from photoelectrochemical (PEC) and electrochemical water splitting

4.6. Applications in mechanical industries

As revealed from their mechanical properties through excellent <u>young modulus</u>, stress and strain properties, NPs can offer many applications in mechanical industries especially in coating, lubricants and adhesive applications. Besides, this property can be useful to achieve mechanically stronger nanodevices for various

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purposes. Tribological properties can be controlled at nanoscale level by embedding NPs in the metal and <u>polymer matrix</u> to increase their <u>mechanical strengths</u>. It is because, the rolling mode of NPs in the lubricated contact area could provide very low friction and wear. In addition, NPs offer good sliding and <u>delamination</u> properties, which could also effect in low friction and wear, and hence increase <u>lubrication</u> effect . Coating can lead to various mechanically strong characteristics, as it improves toughness and wear resistance. Alumina, Titania and carbon based NPs successfully demonstrated to get the desirable mechanical properties in coatings.

5. Toxicity of NP

Beside many industrial and medical applications, there are certain toxicities which are associated with NPs and other nanomaterials and basic knowledge is required for these toxic effects to encounter them properly. NPs surreptitiously enter the environment through water, soil, and air during various human activities. However, the application of NPs for environmental treatment deliberately injects or dumps engineered NPs into the soil or aquatic systems. This has resultantly attracted increasing concern from all stakeholders. The advantages of magnetic NPs such as their small size, high reactivity and great capacity, could become potential lethal factors by inducing adverse cellular toxic and harmful effects, unusual in micron-sized counter parts. Studies also illustrated that NPs can enter organisms during ingestion or inhalation and can translocate within the body to various organs and tissues where the NPs have the possibility to exert the reactivity being toxicology effects. Although some studies have also addressed the toxicological effects of NPs on animal cells and plant cells the toxicological studies with magnetic NPs on plants to date are still limited. The uses of Ag NPs in numerous consumer products lead them to their release to the aquatic environment and become a source of dissolved Ag and thus exert toxic effects on aquatic organisms including bacteria, algae, fish and daphnia. The respiratory system represents an unique target for the potential toxicity of NPs due to the fact that in addition to being the portal of entry for inhaled particles, it also receives the entire cardiac output . NPs are used in bio applications widely but despite the rapid progress and early acceptance of <u>nanobiotechnology</u> the potential for adverse health effects due to prolong exposure at various concentrations levels in human in the environment has not yet been established. However, the environmental impact of NPs is expected to increase in the future. One of the NPs toxicity is the ability to organize around the protein concentration that depends on particles size, curvature, shape and surface characteristics charge, functionalized groups, and free energy. Due to this binding, some particles generate adverse biological outcomes through protein unfolding, fibrillation, thiol crosslinking, and loss of enzymatic activity. Another paradigm is the release of toxic ions when the thermodynamic properties of materials favor particles dissolution in a suspending medium or biological environment.

NPs tend to aggregate in hard water and <u>seawater</u> and are greatly influenced by the specific type of organic matter or other natural particles (colloids) present in fresh water. The state of dispersion will alter the ecotoxicity, but many abiotic factors that influence this, such as pH, salinity, and the presence of organic matters remain to be systematically investigated as part of ecotoxicological studies .

5.1. Electronic and optical properties

The optical and electronic properties of NPs are inter-dependent to greater extent. For instance, noble <u>metals</u> <u>NPs</u> have size dependent optical properties and exhibit a strong UV–visible extinction band that is not present in the spectrum of the bulk metal. This excitation band results when the incident photon frequency is constant with the collective excitation of the conduction electrons and is known as the localized surface plasma resonance (LSPR). LSPR excitation results in the wavelength selection absorption with extremely large molar

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excitation coefficient resonance Ray light scattering with efficiency equivalent to that of ten fluorophores and enhanced local electromagnetic fields near the surface of NPs that enhanced spectroscopies. It is well established that the peak wavelength of the LSPR spectrum is dependent upon the size, shape and interparticle spacing of the NPs as well as its own <u>dielectric properties</u> and those of its local environment including the substrate, solvents and adsorbates . Gold <u>colloidal NPs</u> are accountable for the rusty colors seen in blemished glass door/windows, while Ag NPs are typically yellow. Actually, the free electrons on the surface in these NPs (d electrons in Ag and gold) are freely transportable through the nanomaterial. The mean free path for Ag and gold is ~40 nm, which is more than the NPs size of these materials. Thus, no scattering is expected from the bulk, upon light interaction, instead they set into a standing resonance conditions, which is responsible for LSPR in these NPs

5.2. Magnetic properties

<u>Magnetic NPs</u> are of great curiosity for investigators from an eclectic range of disciplines, which include heterogenous and homogenous catalysis, biomedicine, magnetic fluids, data storage magnetic resonance imaging (MRI), and environmental remediation such as water decontamination. The literature revealed that NPs perform best when the size is <critical value i.e. 10-20 nm. At such low scale the magnetic properties of NPs dominated effectively, which make these particle priceless and can be used in different applications. The uneven electronic distribution in NPs leads to magnetic property. These properties are also dependent on the synthetic protocol and various synthetic methods such as solvothermal, co-precipitation, micro-emulsion, thermal decomposition, and flame spray synthesis can be used for their preparation.

5.3. Mechanical properties

The distinct mechanical properties of NPs allow researchers to look for novel applications in many important fields such as <u>tribology</u>, surface engineering, nanofabrication and <u>nanomanufacturing</u>. Different <u>mechanical parameters</u> such as <u>elastic modulus</u>, hardness, stress and strain, adhesion and friction can be surveyed to know the exact mechanical nature of NPs. Beside these parameters <u>surface coating</u>, coagulation, and <u>lubrication</u> also aid to mechanical properties of NPs . NPs show dissimilar mechanical properties as compared to <u>microparticles</u> and their bulk materials. Moreover, in a lubricated or greased contact, the contrast in the stiffness between NPs and the contacting external surface controls whether the NPs are indented into the plan surface or deformed when the pressure at contact is significantly large. This important information could divulge how the NPs perform in the contact situation. Decent controls over mechanical features of NPs and their interactions with any kind of surface are vital for enlightening the surface quality and elevating material removal. Fruitful outcomes in these fields generally need a deep insight into the basics of the mechanical properties of NPs, such as elastic modulus and hardness, movement law, friction and interfacial adhesion and their size dependent characteristics .

6. Conclusion

In this review, we presented a detail overview about NPs, their types, synthesis, characterizations, physiochemical properties and applications. Through different characterization techniques such as SEM, TEM and XRD, it was revealed that NPs have size ranges from few nanometer to 480 nm. While the morphology is also controllable. Due to their tiny size, NPs have large surface area, which make them suitable candidate for various applications. Beside this, the optical properties are also dominant at that size, which further increase the importance of these materials in photocatalytic applications. Synthetic techniques can be useful to control the specific morphology, size and <u>magnetic properties</u> of NPs. Though NPs are useful for many

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applications, but still there are some health hazard concerns due to their uncontrollable use and discharge to natural environment, which should be consider for make the use of NPs more convenient and environmental friendly.

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