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Metal Coated Nanoparticles

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ABSTRACT

Metallic nanoparticles have fascinated scientist for over a century and are now heavily utilized in biomedical sciences and engineering. They are having focus of interest because of their huge potential in nanotechnology. Today these materials can be synthesized and modified with various chemical functional groups which allow them to be conjugated with antibodies, ligands and drugs of interest and thus opening a wide range of potential applications in biotechnology, magnetic separation, preconcentration of target analyte, targeted drug delivery, vehicles for gene drug delivery and more importantly diagnostic imaging. Moreover, different imaging modalities have been developed over the period of time such as MRI, CT, PET, ultrasound, SERS and optical imaging as an aid to image various disease states. These imaging modalities differ in both techniques and instrumentation and more importantly require a contrast agent with unique physiochemical properties. This led to the invention of various nanoparticulated contrast agent such as magnetic nanoparticles (Fe_3O_4), gold and silver nanoparticles for their application in these imaging modalities. In addition, to use various imaging techniques in tandem newer multifunctional nanoshells and nanocages have been developed. Thus in this review article, we aim to provide an introduction to various nanoparticles like gold, silver, platinum, copper, magnetic nanoparticles and their uses in the diagnosis of various diseases and therapy of cancer.

INTRODUCTION

Nanotechnology is the science that deals with matter at the scale of 1 billionth of a meter (i.e., 10^{-9} m = 1 nm), and is also the study of manipulating matter at the atomic and molecular scale. A nanoparticle is the most fundamental component in the fabrication of a nanostructure and is far smaller than the world of everyday objects that are described by Newton' s laws of motion, but bigger than an atom or a simple molecule that are governed by quantum mechanics. The United States instituted the National Nanotechnology Initiative (NNI) back in 2000, which was soon followed (2001) by a plethora of projects in nanotechnology in nearly most of the U.S. Departments and Agencies. In general, the size of a nanoparticle spans the range between 1 and 100 nm. Metallic nanoparticles have various physical and chemical properties different from bulk metals (e.g., lower melting points, higher specific surface areas, specific optical properties, mechanical strengths, and specific magnetizations), properties that might prove attractive in various industrial application.

Recently too much attention has been given towards controlling the shape and size of metal nanostructures because all the magnetic, catalytic, electrical and optical properties of metal nanostructures are influenced by their shape and size. Nanoparticles have wide applications in the field of biomedicine such as to deliver pharmaceutics, for diagnostic approaches as well as for the therapeutic purposes because nanoparticles have very small sized particles, they can be used for targeted drug delivery and the metallic nanoparticles respond resonantly to the magnetic field which varies with time so they transfer enough toxic thermal energy to the tumor cells as hyperthermic agents. Among these metal coated nanoparticles, gold and silver nanoparticles are found to have vast area of applications. Gold and silver nanoparticles are having wide applications than other metal coated nanoparticles

GOLD COATED NANOPARTICLES [1, 2]

Metal nanoparticles specifically gold nanoparticles have abundant use in the field of biotechnology and biomedicine because they have large surface bioconjugation with molecular probes and they also have many optical properties which are mainly concerned with localized plasmon resonance (PR).Properties of gold nanoparticles are different from its bulk form because bulk gold is yellow solid and it is inert in nature while gold nanoparticles are wine red solution and are reported to be anti-oxidant. Interparticle interactions and assembly of gold nanoparticles networks play key role in the determination of properties of these nanoparticles. They exhibit various sizes ranging from 1 nm to 8 µm and they also exhibit different shapes such as spherical, sub-octahedral, octahedral, decahedral, icosahedral multiple twined, multiple twined, irregular shape, tetrahedral, nanotriangles, nanoprisms, hexagonal platelets and nanorods (Figure 3).

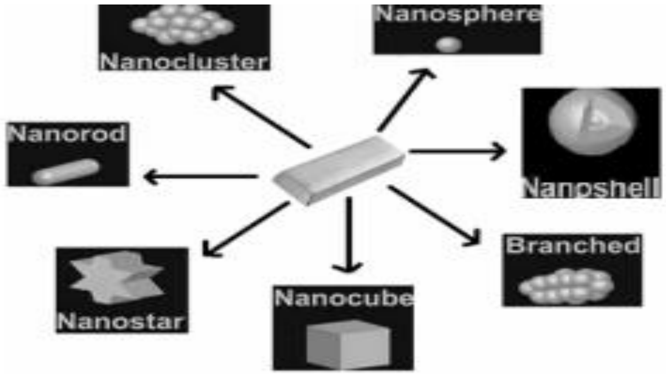


Figure 3: Various shapes of gold nanoparticles

Using of single active substance from plant extract in the synthesis of gold nanoparticles is an important biosynthesis technique to purify gold nanoparticles and to investigate about their medical uses. Gold nanoparticles have been widely used in the field of radiation medicine as radiation enhancer and also provide therapeutic enhancement in radiation therapy due to the efficient and targeted drug delivery to the tumor site. Gold nanoparticles have various applications as platform nanomaterials for biomolecular ultrasensitive detection, killing cancer cells by hyperthermal treatment, labeling for cells and proteins and delivering therapeutic agents within cells.

Advantages of gold coated nanoparticles

Gold nanoparticles have various advantages over conventional iodine-based agents as gold has higher absorption coefficient than iodine due to its higher atomic number and electron density so it enhances CT contrast more than iodine so they have been used in X-ray CT imaging as molecular probes. The second major advantage of gold nanoparticles is that they are non-cytotoxic and third most important benefit is regarding their surfaces, as they have large surface area due to which their surfaces are readily available for modification with targeting molecules or specific biomarkers and applicable in biomedical purposes.

Gold nanoparticle-mediated drug delivery

Targeted drug delivery is better than conventional drug therapy because in targeted drug delivery drugs target the main effected area and delivered drug locally so it minimize the side effects caused by conventional drugs. Primary goal of developing anticancer agents is to minimize the various side effects caused by the conventional drugs and to improve selectivity and efficiency of drug. Gold nanoparticles have the ability of bio-imaging of the effected cancerous cells for therapy. For effective drug delivery system or drug therapy it is important to investigate about the biological effects of the nanoparticles as gold nanoparticles have unique physical and chemical properties and have strong binding attraction for thiols, proteins, carboxylic acid aptamers and disulfides so they have been extensively used in the field of biosciences especially in drug delivery for cancer therapy.

Some other advantages are listed here;

(i) Gold nanoparticles have unique optical, physical and chemical properties due to their size and shape.

(ii) Gold nanoparticles have high surface area which provide dense drug loading.

(iii) These particles are biocompatible and are readily available for conjugation with small biomolecules such as proteins, enzymes, carboxylic acid, DNA, and amino acids.

(iv) Khan et al Trop J Pharm Res, July 2014; 13(7): 1176 Gold nanoparticles have controlled dispersity;

(v) Due to small size and uniform dispersion they can easily reach to the targeted site with blood flow.

(vi) They are non-cytotoxic to the normal cells; and (vii) Gold nanoparticles are easily synthesized by various methods.

SYNTHESIS

General methods for the synthesis of gold nanoparticles include chemical, physical, and biological methods which are explained below.

Chemical methods

Gimenez et al proposed a method to synthesize gold nanoparticles supported on an insoluble thiolated chitosan derivative by reduction of the $HAuCl_4$ through thiolated chitosan (QTDT) as reducing and coupling agent for gold nanoparticles. Synthesized QT/Aunano is used as a good catalyst for the reduction of methylene blue. Citrate thermo reduction method can be used for the synthesis of gold nanoparticles having efficient SERS (surface enhanced Raman spectroscopy) in short reaction time by using a low cost reagent inositol hexaphosphate (IP6) as reduction agent for HAuCl4.

The synthesis of gold nanoparticles via seeding growth method has also been reported. Gold nanoparticles were grown from gold nanoparticles encapsulated in polyethylene glycol attached with dendrimers and have high near infra-red absorption by using formaldehyde as a reducing agent.

Physical methods

The γ-irradiation method was proved to be best for the synthesis of gold nanoparticles with controllable size and high purity. The γ-irradiation method is adopted to synthesize gold nanoparticles with size 5 - 40 nm. In this method natural polysaccharide alginate solution was used as stabilizer.

New technique of photochemical method has been reported for the preparation of gold-polyethylene glycol core-shell nanoparticles with size 10 - 50 nm in water by adopting redox and polymerization reactions. In this method gold salt was reduced by radical formation coated with polyethylene glycol diacrylate by UV-process with the help of photo-initiator 2-hydroxy-2- methyl-1-phenyl-1-propane.

Green methods

Green chemistry synthesis routes are environment friendly and non-toxic. A facile green synthesis method for the preparation of gold nanoparticles of size 25 + 7 nm was reported by using natural biomaterial egg shell membrane (ESM). In this method ESM was immersed in aqueous solution of $HAuCl_4$ without using any reductant. Another green synthetic approach was developed to synthesized gold sononanoparticles of size 5 - 17 nm by using high-power ultrasounds and sodium dehydrate.

Gold nanoparticles of size 15 - 80 nm are also synthesized via another green synthetic route. In this method $HAuCl_4$ was reduced by using citrus fruits juice extracts [Citrus limon, Citrus reticulate and Citrus sinensis]. Edible mushroom was also used for the synthesis of gold nanoparticles via sunlight exposure.

APPLICATIONS OF GOLD COATED NANOPARTICLES

Gold nanoparticles have unique electric and magnetic properties due to their shape and size so they have been received great attention in research areas especially in the field of biological tagging, chemical and biological sensing, optoelectronics, photo thermal therapy, biomedical imaging, DNA labelling, microscopy and photoacutisc imaging, surface-enhanced Raman spectroscopy, tracking and drug delivery, catalysis and cancer therapy(Table 1).

Table 1: Shapes of gold nanoparticles and their applications

Shape	Size	Application
Nano rod	2-5 nm	Drug delivery and photothermal therapy [15].
Hollow particle	25 nm	Photo-electronics, catalysis and cancer therapy [12]
Triangular particle	3.85-7.13 nm	Highly effective against *E. coli* and *K.* pneumonia [23]
Faceted particle	50-100 nm	Effective, reproducible, and stable large area substrates for NIR SERS [near infra-red surface enhanced Raman spectroscopy] [25]
Nanocube	50 nm	Field enhancement applications and refractive-index sensing [28]
Nanocage	50 nm	Effective molecular contrast agent for nonlinear endomicroscopy imaging [19] and in vivo medical applications [29]
Nanobelt	Thickness, ~80 nm, Width, ~ 20 μm, Length, ~0.15 m.	Strain sensors
Branched particle	90 nm	Substrates for SERS-based imaging of kidney cells [30]

Gold nanoparticles based sensors can detect various metal ions by working on the principle of colour change due to the aggregation of gold nanoparticles. Such types of sensors have been widely used for the detection of copper, mercury lead and arsenic in water.

Functionalized gold nanoparticles with calixarene derivatives, crown ethers DNA and peptides have been used for the sensing applications mainly for the recognition of amino acids, quaternary ammonium ions and pyridinium, indium tin oxide electrode modified with gold nanoparticles/TiO_2 composites has been used for the estimation of catechol (CC) and hydroquinone (HQ) with the help of voltametric method. Catechol has been successfully determined in tea sample by adopting this method.

Another important application of gold nanoparticles is in memory devices. Gold nanoparticles coated with suitable insulator exhibit excellent stability for memory devices and this insulation helps in prevention of accumulation of charges when the applied field has been removed.

SILVER COATED NANOPARTICLES [3,4,5]

Silver nanoparticles (Ag-NPs or nanosilver) have attracted increasing interest due to their unique physical, chemical and biological properties compared to their macro-scaled counterparts. Ag-NPs have distinctive physico-chemical properties, including a high electrical and thermal conductivity, surface-enhanced raman scattering, chemical stability, catalytic activity and non linear optical behaviour.

Silver nanoparticles are nanoparticles of silver between 1 nm and 100 nm in size, while frequently described as being 'silver' some are composed of a large percentage of silver oxide due to their large ratio of surface-to-bulk silver atoms. Numerous shapes of nanoparticles can be constructed depending on the application at hand. Commonly used are spherical silver nanoparticles but diamond, octagonal and thin sheets are also popular.

Nanosilver can be used in a liquid form, such as a colloid (coating and spray) or contained within a shampoo (liquid) and can also appear embedded in a solid such as a polymer master batch or be suspended in a bar of soap (solid). Nanosilver can also be utilized either in the textile industry by incorporating it into the fiber (spun) or employed in filtration membranes of water purification systems. In many of these applications, the technological idea is to store silver ions and incorporate a time-release mechanism.

There are many consumer products and applications utilizing nanosilver in consumer products; nanosilver-related applications currently have the highest degree of commercialization. A wide range of nanosilver applications has emerged in consumer products ranging from disinfecting medical devices and home appliances to water treatments.

ADVANTAGES OF SILVER COATED NANOPARTICLES

Currently, the unique antimicrobial properties of AgNPs have led to their application in areas such as clothing manufacturing, food preservation, and water purification. More importantly, AgNPs are being increasingly utilized in the medical industry due to their antibacterial, antifungal, antiviral, anti-inflammatory, and osteoinductive effects as well as their ability to enhance wound healing.

1. Antibacterial Properties of AgNPs

Antibiotics are standard antimicrobials used in medicine that bind to specific chemical targets of bacteria not present in humans. However, this binding specificity narrows the number of bacterial species that are vulnerable to a specific antibiotic and contributes to the antibiotic resistance developed by bacteria, ultimately creating multidrug resistant bacteria. With the increasing number of infections due to multidrug resistant bacteria, there has been a need for effective antimicrobial alternatives. Thus, silver is a great alternative because it is an antiseptic that targets a broad spectrum of $Gram^+$ and $Gram^-$ bacteria as well as vancomycin-resistant strains.

Thus, neither the *in vitro* antibacterial action nor the clinical behaviour of non-nanoscale silver-coated stainless steel cortical screws significantly differed from that of the uncoated ones. Due to the greater surface-to-mass ratio, AgNPs offer greater active surface, higher solubility, and chemical reactivity.

2. Antifungal Properties of AgNPs

Long-term, repetitive administration of standard antifungal drugs leads to increased fungal resistance, especially by the Candida species. Therefore, new antifungal agents are constantly being investigated. AgNPs have displayed many antifungal properties against common fungi and thus offer potential as an effective antifungal agent. A recent study found that a AgNP-coated reverse osmosis membrane, which is used in water purification systems, exhibited good antifungal activities against fungal strains such as *Candida tropicalis, Candida krusei, Candida glabrata,* and *Candida albicans*.

3. Antiviral Properties of AgNPs

Various viruses, such as influenza, hepatitis, herpes simplex virus (HSV), and human immunodeficiency virus (HIV), can be life-threatening. Although many vaccines have been developed against various viruses, medicine has yet to develop a broad-spectrum antiviral vaccine. Furthermore, these viruses are developing antiviral resistance to current treatments and classical antiviral drugs, especially in immunocompromised patients. In light of this, there is a pressing need for the development of new antiviral agents against a broad spectrum of viruses. AgNPs act as a broad-spectrum agent against a variety of viral strains and are not prone to developing resistance. For example, studies have demonstrated antiviral activity of AgNPs against HSV-1, HSV-2, hepatitis B, and human immunodeficiency virus 1 (HIV-1).

4. Anti-Inflammatory Properties of AgNPs

Despite the billions of dollars that have been spent on immunological research, few effective anti-inflammatory drugs have emerged. Thus, an urgent need for new drugs exists, as many inflammatory diseases are insufficiently responsive to current medications. Recently, there has been increasing evidence that AgNPs are viable anti-inflammatory agents. Initially, anti-inflammatory properties of AgNPs were investigated by applying AgNP-coated, 0.5% silver nitrate ($AgNO_3$), or saline wound dressings to a porcine model of contact dermatitis .AgNP-coated wound dressings outperformed other wound dressings as erythema, edema, and histological data showed that AgNP-treated pigs had near-normal skin after 72 hours, while other treatment groups remained inflamed.

5. Osteoconductivity and Osteoinductivity of AgNP-Based Materials

Previously, by implanting AgNP/PLGA composite grafts for the healing of infected bone defects into grossly infected critical-sized bone segmental defects, we demonstrated that AgNP/PLGA composite grafts possess significant, antibacterial properties and osteoconductivity *in vivo* (Figure 2). AgNP/PLGA composite grafts displayed osteoconductive properties as they did not inhibit adherence, proliferation, alkaline phosphatase activity, or mineralization of on growth MC3T3-E1 preosteoblasts in vivo.

DISADVANTAGES OF AgNPs

Toxicity of AgNPs

Applying silver as an antimicrobial agent has been hindered by its potential toxic effects, such as argyria, an irreversible pigmentation of the skin and eyes due to inappropriate silver deposition. Thus, the toxicity of AgNPs must be investigated for commercial products and before widespread medical application. Also, environmental pollution must be considered to avoid ecological damage.

AgNPs enter the human body most often through the respiratory tract, gastrointestinal tract, skin, and female genital tract, as well as through systemic administration. Recently, an *in vivo* oral toxicity study of AgNPs on Sprague-Dawley (SD) rats demonstrated the accumulation of AgNPs in the blood, liver, lungs, kidneys, stomach, testes, and brain, but showed no significant genotoxicity function after oral administration of AgNPs of 60 nm average size for 28 days at different doses.

SYNTHESIS

Silver nanoparticles can be synthesized by several methods. They can be:

1. Chemical synthesis

Currently, many methods have been reported for the synthesis of Ag-NPs by using chemical, physical, photochemical and biological routes. Each method has advantages and disadvantages with common problems being costs, scalability, particle sizes and size distribution. Among the existing methods, the chemical methods have been mostly used for production of Ag-NPs. Chemical methods provide an easy way to synthesize Ag-NPs in solution.

Monodisperse samples of silver nanocubes were synthesized in large quantities by reducing silver nitrate with ethylene glycol in the presence of polyvinyl pyrrolidone (PVP), the so-called polyol process. In this case, ethylene glycol served as both reductant and solvent. It showed that the presence of PVP and its molar ratio relative to silver nitrate both played important roles in determining the geometric shape and size of the product. It suggested that it is possible to tune the size of silver nanocubes by controlling the experimental conditions.

2. Physical synthesis

For a physical approach, the metallic NPs can be generally synthesized by evaporation–condensation, which could be carried out by using a tube furnace at atmospheric pressure. However, in the case of using a tube furnace at atmospheric pressure, there are several drawbacks such as a large space of tube furnace, great consumption energy for raising the environmental temperature around the source material and a lot of time for achieving thermal stability. Therefore, various methods of synthesis of Ag-NPs based on the physical approach have been developed.

A thermal decomposition method was developed to synthesize Ag-NPs in powder form. The Ag-NPs were formed by decomposition of a Ag1+–oleate complex, which was prepared by a reaction with AgNO3 and sodium oleate in a water solution, at high temperature of 290 ◦C. Average particle size of the Ag-NPs was obtained of about 9.5 nm with a standard deviation of 0.7 nm. This indicates that the Ag-NPs have a very narrow size distribution.

In summary, the physical synthesis process of Ag-NPs usually utilizes the physical energies (thermal, ac power, arc discharge) to produce Ag-NPs with nearly narrow size distribution. The physical approach can permit producing large quantities of Ag-NPs samples in a single process.

3. Photochemical synthesis

The photo-induced synthetic strategies can be categorized into two distinct approaches, that is the photophysical (top down) and photochemical (bottom up) ones. The former could prepare the NPs via the subdivision of bulk metals and the latter generates the NPs from ionic precursors.

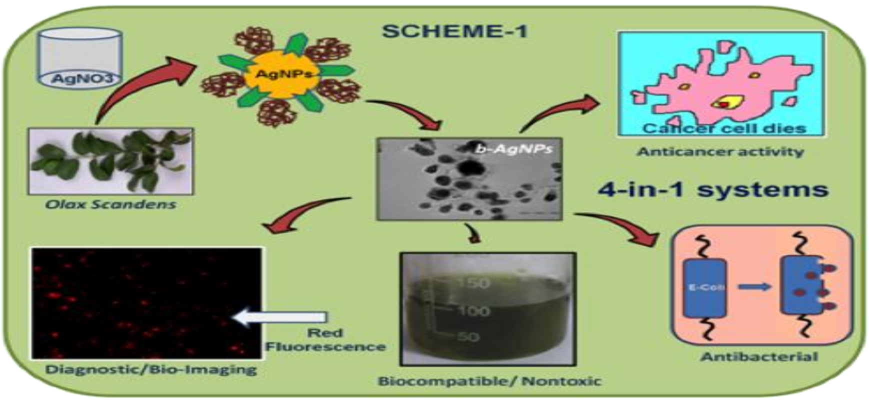
In summary, the main advantages of the photochemical synthesis are: (i) it provides the advantageous properties of the photo-induced processing, that is, clean process, high spatial resolution, and convenience of use, (ii) the controllable in situ generation of reducing agents; the formation of NPs can be triggered by the photo-irradiation and (iii) it has great versatility; the photochemical synthesis enables one to fabricate the NPs in various mediums including emulsion, surfactant micelles, polymer films, glasses, cells, etc.

4. Biological synthesis

As mentioned above, when Ag-NPs are produced by chemical synthesis, three main components are needed: a silver salt (usually $AgNO_3$), a reducing agent (i.e. ethylene glycol) and a stabilizer or aping agent (i.e. PVP) to control the growth of the NPs and prevent them from aggregating. In case of the biological synthesis of Ag-NPs, the reducing agent and the stabilizer are replaced by molecules produced by living organisms. These reducing and/or stabilizing compounds can be utilized from bacteria, fungi, yeasts, algae or plants.

A facile biosynthesis using the metal-reducing bacterium, Shewanellaoneidensis, seeded with a silver nitrate solution, was reported. The formation of small, spherical, nearly monodispersed Ag-NPs in the size range from ~2 to 11 nm (average size of 4 ± 1.5 nm) was observed.

In summary, the biological method provides a wide range of resources for the synthesis of Ag-NPs, and this method can be considered as an environmentally friendly approach and also as a low cost technique. In biological synthesis, the cell wall of the microorganisms plays a major role in the intracellular synthesis of NPs. The negatively charged cell wall interacts electrostatically with the positively charged metal ions and bioreduces the metal ions to NPs. When microorganisms are incubated with silver ions, extracellular Ag-NPs can be generated as an intrinsic defence mechanism against the metal's toxicity. Other green syntheses of Ag-NPs using plant exacts as reducing agents have been performed.



A general representation of the synthesis and applications of biogenically synthesized silver nanoparticles using plant extract.

5. Ion implantation

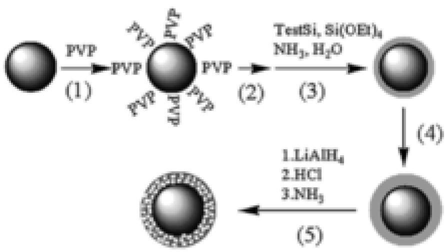
Ion implantation has been used to create silver nanoparticles embedded in glass, polyurethane, silicone, polyethylene, and polymethylmethacrylate. The particles grow in the substrate with the bombardment of ions. The existence of nanoparticles is proven with optical absorbance, though the exact nature of the particles created with this method is not known.

6. Wet chemistry

Wet chemical methods for creating silver nanoparticles typically involve the reduction of a silver salt such as silver nitrate with a reducing agent like sodium borohydride in the presence of colloidal stabilizer. Sodium borohydride has been used with polyvinyl alcohol, poly(vinylpyrrolidone), bovine serum albumin (BSA), citrate and cellulose as stabilizing agents. In the case of BSA, the sulfur-, oxygen- and nitrogen-bearing groups mitigate the high surface energy of the nanoparticles during the reduction. The hydroxyl groups on the cellulose are reported to help stabilize the particles. Citrate and cellulose have been used to create silver nanoparticles independent of a reducing agent as well.

7. Coating with silica

In this method, polyvinylpyrrolidone (PVP) is dissolved in water by sonication and mixed with silver colloid particles. Active stirring ensures the PVP has adsorbed to the nanoparticle surface. Centrifuging separates the PVP coated nanoparticles which are then transferred to a solution of ethanol to be centrifuged further and placed in a solution of ammonia, ethanol and $Si(OEt_4)$ (TES. Stirring for twelve hours results in the silica shell being formed consisting of a surrounding layer of silicon oxide with an ether linkage available to add functionality. Varying the amount of TES allows for different thicknesses of shells formed.This technique is popular due to the ability to add a variety of functionality to the exposed silica surface.



General procedure for coating colloid particles in silica. First PVP is absorbed onto the colloidal surface. These particles are put into a solution of ammonia in ethanol. The particle then begins to grow by addition of Si(OET4).

8. Alternative methods

Bacterial and fungal synthesis of nanoparticles is praccalti because bacteria and fungi are easy to handle and can be modified genetically with ease. This provides a means to develop biomolecules that can synthesize AgNPs of varying shapes and sizes in high yield, which is at the forefront of current challenges in nanoparticle synthesis. Fungal strains such as *Verticillium* and bacterial strains such as *K. pneumoniae* can be used in the synthesis of silver nanoparticles. When the fungus/bacteria is added to solution, protein biomass is released into the solution. Electron donating residues such as tryptophan and tyrosine reduce silver ions in solution contributed by silver nitrate. This again causes colloid crystallization and thus the formation of nanoparticles similar to the previous methods.

APPLICATIONS OF AgNPs

Silver nanoparticles in environmental treatments

Air disinfection

Bioaerosols are airborne particles of biological origins including viruses, bacteria, fungi, which are capable of causing infectious, allergenic or toxigenic diseases. Particularly, indoor air bioaerosols were found to accumulate in large quantities on filters of heating, ventilating, and air-conditioning (HVAC) systems. It is found that outdoor air pollution and insufficient hygiene of an HVAC installation often resulted in the low quality of indoor air. Moreover, the organic or inorganic materials deposited on the filter medium after air filtration contribute to microbial growth. To reduce the microbial growth in air filters, the integration of antimicrobial Ag-NPs in air filters has been proposed and developed. The antimicrobial effect of Ag-NPs on bacterial contamination of activated carbon filters (ACF) was studied. The results showed that Ag-deposited ACF filters were effective for the removal of bioaerosols.

Water disinfection

- **Drinking water disinfection.**

The chemically produced nanosilver (*chem*-Ag-NPs) can be uniformly decorated onto porous ceramic materials to form an Ag-NPs–porous ceramic composite by using 3-aminopropyltriethoxysilane (APTES) as a connecting molecule. This composite can be stored for long periods and is durable under washing without loss of NPs. The sterilization property of Ag-NPs–porous ceramic composite as an antibacterial water filter was tested with *E. coli*. It was found that at a flow rate of 0.01 l min−1, the output count of E. *coli* was zero when the input water had a bacterial load of _105 CFU ml−

In summary, the silver-based NPs are very ideal for use in water disinfection. The silver-based NPs can be incorporated to core materials and polymeric membranes to disinfect the water contaminated with the bacteria and viruses. The application of silver-based NPs is of utmost importance to prevent outbreaks of waterborne diseases related to poor treatment of drinking water. Moreover, the addition of silver-based NPs could prevent bacterial/viral attachment and biofilm formation infiltration medium.

- **Groundwater and biological wastewater disinfection**

The impact of Ag-NPs on microbial communities in wastewater treatment plants was evaluated. It was found that original wastewater biofilms are highly tolerant to Ag-NP treatment. With an application of Ag-NPs of 200 mg l−1, the reduction of biofilm bacteria measured by heterotrophic plate counts was insignificant after 24 h. Biofilm can provide physical protection for bacteria under Ag-NP treatment, and extracellular polymeric substances (EPS) may play an important role in this protection. Susceptibility to Ag-NPs is different for each microorganism in the biofilm microbial community. This study showed two suggestions:

(i) Ag-NPs could impact wastewater biofilm microbial community structures, depending on the characteristics of each strain, e.g., its ability to produce EPS and growth rate, and the community interactions among these strains; and
(ii) the effects of Ag-NPs on planktonic cells were different to those on wastewater biofilms. Biofilm bacteria treated as isolated pure culture are much more sensitive to Ag-NPs, compared with mixture of bacteria in the biofilm.

Surface disinfection

- **Silver-nanoparticle-embedded antimicrobial paints.**

Developing bactericidal coatings on surfaces has attracted increasing interest to protect human health and the environment. Among them, Ag-NPs-embedded paints are of particular interest owing to their potential bactericidal activity. The results showed that the surfaces coated with silver-nanoparticle paint showed excellent antimicrobial properties by killing both gram-positive human pathogens (*S. aureus*) and gram-negative bacteria (*E. coli*).

- **Antimicrobial surface functionalization of plastic catheters**

Ag-NPs were used as antimicrobial coatings in medical devices to reduce nosocomial infections at hospitals. Catheters were coated with Ag-NPs. Silver release from the catheters was determined *in vitro* and *in vivo* using radioactive silver. Silver-coated catheters showed significant *in vitro* antimicrobial activity and prevented biofilm formation against pathogens (*E. coli, Enterococcus, S. aureus, coagulase-negative Staphylococci, P. aeruginosa and C. albicans*); most of them involved in catheter-related infections.

- **Antimicrobial gel formulation for topical use.**

In addition, Ag-NPs were also used in therapeutics, especially for treating burn wounds. In order to develop this test, a gel formulation containing Ag-NPs (S-gel) was developed. As part of toxicity studies, localization of Ag-NPs in Hep G2 cell line, cell viability, biochemical effects and apoptotic/necrotic potential were assessed. It was found that Ag-NPs get localized in the mitochondria and have an IC50 value of 251μg ml−1. Further, it was obvious that Ag-NPs induced apoptosis at concentrations up to 250μg ml−1, which could favor scarless wound healing.

- **Antimicrobial packing paper for food preservation.**

In addition to the above described applications of Ag-NPs as antimicrobial coatings for household paints, biomedical and therapeutic fields, Ag-NPs-coated paper could be useful for preventing microbial growth for longer periods in food preservation by providing a reservoir for slow releasing of ionic silver from the surface to the bulk as well as preventing growth on the surface itself. A simple method to develop coating of colloidal silver on paper using ultrasonic radiation was reported called the sonochemical coating.The results showed that such Ag-NPs-coated paper has potential application in the food industry as a packing material with a long shelf life and antifouling properties.

- **Silver-impregnated fabrics for clinical clothing**

Progressive contamination of clinical clothing with a mixture of bacteria from the wearer and the environment is a common occurrence. Freeman *et al* investigated the effect of silver impregnation of surgical scrub suits on surface bacterial contamination during use in a veterinary hospital. It was found that silver-impregnated scrubs had significantly lowered bacterial colony counts (BCC) compared with polyester/cotton scrubs. The results showed that silver impregnation appeared to be effective in reducing bacterial contamination of scrubs during use in a veterinary hospital.

PLATINUM NANOPARTICLES[6,7,8]

The search for new functional materials is one of the defining characteristics of modern science and technology. Metal nanoparticles (MNPs), in particular, platinum nanoparticles (PtNs) can possess a wide range of properties that can be used for many practical applications. Due to potential technological interests of PtNs, the synthesis and study of nanoparticles was a very active field of research during last years. Platinum containing films could be used for enzyme immobilization, optical applications, and catalytic activity. For instance, the enhanced catalytic activity of PtNs plays an important role in the reduction of pollutant gases exhausted from automobiles. Also, the stability of PtNs is of great importance to the development of efficient and durable proton exchange membrane fuel cells and the coalescence of PtNs is responsible for a reduction in the electrochemically active surface area that reduces cell performance. Furthermore, PtNs is used widely in the electronics industry for the manufacture of conductive thick film circuits and internal electrodes of multilayer ceramic capacitors.

PHYSICAL PROPERTIES AND APPLICATIONS

1. Optical properties
2. Nonlinear optical properties
3. Catalysis
4. Conductivity
5. Single electron tunneling

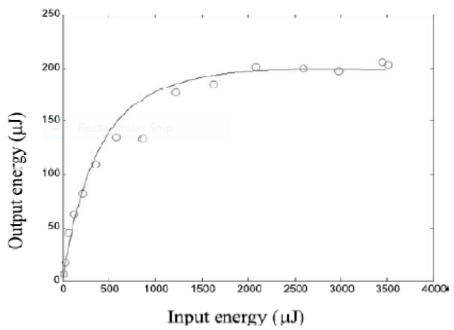
Optical properties

Nanometer-sized particles of free electron metals, such as Ag, Au, Cu, and Pt display interesting and useful optical properties. Their linear optical response is dominated by the surface plasmon resonance associated with the collective oscillation of state experimental extinction spectrum of PtNs invisible area and to compare this spectrum with another noble metal nanoparticles, various simplest MNPs suspensions in water were prepared in similar conditions. An optical absorption of particles in a solution with smaller diameters than the wavelength of an incoming light (<500 nm) is given by the Mie theory, where the dielectric function of MNPs is written as a combination of an interband term and a Drude term for the conduction electrons in the particles.

Nonlinear optical properties

Optical limiters in the visible domain with a broad nonlinear optical spectrum and short response time are required for eye protection and switching applications. Study of optical properties of materials with ideal optical limiting performances has attracted substantial attention. With such aim, an optical limiting performance of PVP-stabilized PtNs in methanol was analyzed with 8 ns pulses from a frequency doubled,Q-switched Nd:YAG laser at 532 nm. The average size of PtNs was estimated by TEM to be of the order of 2 nm. As result Fig.4 gives the optical limiting experimental dependence of PtNs-PVP. The transmitted energy shows a clamped curve as the input energy increases. The highest input energy was estimated to be of 3.5 mJ here used. It was found that the nonlinear transmittance decreases to 6.0%. Namely, it gives near 10 times attenuation of the incident energy. The main nonlinear optical process responsible for strong optical limiting effect can be attributed to interband transition of platinum during the excitation of nanosecond pulses.

Fig:4 The theoretical and experimental optical limiting results of PtNs-PVP in methanol with a linear transmission of 59%measured at the wavelength of 532 nm.



Catalysis

PtNs were specially studied in the field of catalysis because of their important industrial applications, including the reduction of pollutant gases from automobiles. PtNs have shown catalytic reactivity highly dependent on particle morphology and the importance of a detailed understanding of these systems. One of the most important problems, whose solution is needed for many practical applications of metal nanoparticles, is the formation and sembles on various planar substrates. Successful preparation of such-type composites is a promising as convenient and inexpensive active elements of catalytic reactors, various sensors, etc. As example, it is possible to consider catalytic properties of PtNs deposited onto polystyrene surface from a colloidal hydrosol solution. During the adsorption on polymer substrate, PtNs form rather densely packed ordered monolayer ensembles with high catalytic activity in the model reaction of hydrogen reduction of methyl viologen (dimethyl-4,4'-bipyridine) in aqueous alkaline solutions. The synthesized platinum particles have and their average diameter is approximately 7 nm. The AFM experiments demonstrated that PtNs styrene surface (Fig. 5).

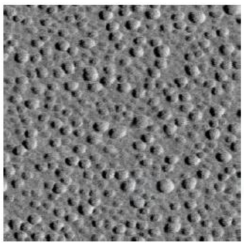


Fig. 5: The AFM image of deposited PtNs onto polystyrene surface.

Conductivity

Rapid improvement in recent years of the performance of zinc oxide (ZnO) in transparent conducting oxides has distinguished ZnO as a promising material alternative to indium tin oxide (ITO). There are many characteristics of ZnO that may enable its efficient utilization in various novel devices. ZnO is an n-type semiconductor with a wide bandgap of 3.37 eV.

SYNTHESIS

Chemical Preparation

Chemical preparation method means a synthesis of MNPs in chemical solution and quite often such MNPs called as colloid metal particles. In such case, the main variations in chemical preparation of colloidal particles are going from the different chemical reactions and chemical compositions, which are used for these purposes. For instance, chemical reduction of metal ions inside reversed micelles in a nonpolar solvent is most commonly employed in the preparation of MNPs. A metal salt dissolved in water is confined inside the reversed micelles and is reduced into MNPs by chemical reduction.

1. Shape-controlled synthesis

Shape control of MNPs is much more difficult to achieve. Therefore, the influence of particle shape on catalytic activity was not reported to date. However, authors of the work describe a novel approach for synthesis of colloidal PtNs with controlled shapes and sizes by changing the ratio of the concentration of the capping polymer material to the concentration of the cations Pt2+ in solution at room temperature. For that purpose, the PtNs A solution of 1M-4M K2PtCI4 was prepared in 250 ml of water, to which we added 0.2 ml of 0.1 M sodium polyacrylate (sample 1). As seen from TEM sample 1 predominately containing particles with a square outline (Fig. 1, left) whereas sample 2 contained high proportion of particles with a triangular outline (Fig. 1, right). By tilting the samples in the TEM, it was detected that square outline was found to be cubic, and those triangular outlines were tetrahedral.

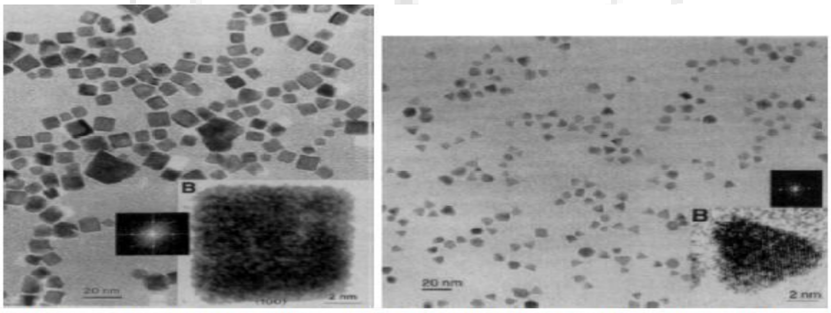


Fig. 1. TEM images of sample 1 (left) and sample 2 (right), indicating the cubic particles and the abundance of tetrahedral, respectively. Insets show high-resolution lattice images. Replotted from Ref. [7].

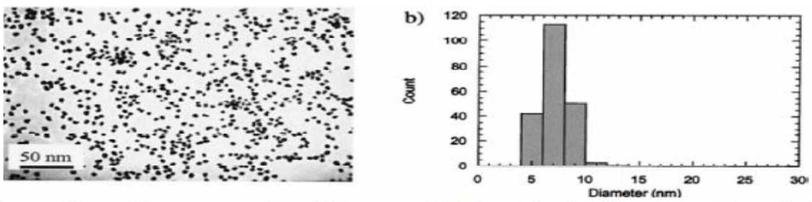


Fig. 2. Micrographs and the corresponding histograms of PtNs synthesized from hexachloro platinic acid in ethylene glycol in the presence of PVP (500 mg. c). Replotted from Ref. [11].

Physical technique of nanoparticle preparation

There are a variety physical methods for preparation of MNPs in substrates or deposited on them.

1. Ion implantation

Ion implantation offers a relatively simple and flexible means of fabricating MNPs in different host materials and is therefore a useful tool for exploring such systems. The main advantages of using ion implantation are that concentration and depth distribution of implanted ions can easily be controlled accurately.

Ion implantation can be also used for fabrication of PtNs in SiO_2 matrix. For such purpose SiO_2 film thermally grown on Si substrate was implanted by Pt ions with high energy between 3.4 and 5.6MeV and a dose range of 2-1016 ion/cm2 at liquid nitrogen temperature of irradiated substrate and followed by thermal annealing during one hour at temperature 1100-1300^{o}C. TEM analysis revealed that the PtNs are spherical in shape. The mean size of the PtNs varied between 2.8 and 3.6 nm for the highest and lowest ion energy, respectively, as determined with both TEM and X-ray scattering

COPPER NANOPARTICLES[9,10]

Amongst other metals, copper nanoparticles are of great interest due to its low cost and easy availability with the property like other metal nanoparticles. The synthesis of stable, monodisperse, and uniformly-shaped copper nanoparticles has proven difficult because of the tendency for copper to rapidly oxidize. Nanoparticles of copper and its alloys have been applied more often as catalysts due to their high surface-to-volume ratio and less cost compared to noble metals. They are used as water gas shift catalysts and gas detoxification catalysts. copper is a promising alternative material due to its high conductivity and lower cost. For example, replacement of noble metal powders such as gold or silver with copper powder for the metallisation of multilayer ceramic capacitors (MLCC) is a current trend in the electronics industry.

Furthermore, copper nanowires may play an essential role in connecting the next generation of electronic nanodevices. Use of plants for nanoparticle synthesis can have advantages over other biological processes because it eliminates the elaborate process of maintaining cell cultures and can also be suitably scaled up for large-scale nanoparticle synthesis.

SYNTHESIS

1. Synthesis of copper nanoparticles by Green Chemistry

In a typical experiment, 0.01 M of $CuSO_4 \cdot 5H_2O$ and 0.11 M of ascorbic acid were dissolved in 100 ml of deionised water in a 250 ml flat-bottom flask equipped with a hot plate, a small magnetic stir bar, and a thermometer. The 0.03 M of CTAB was introduced into the solution with rapid stirring at room temperature. Aqueous NaOH was employed to control pH 6.5. Before starting the reactions, the pH of reaction mixture of all three chemicals was monitored by handy pH meter and then during the reaction it was monitored by pH strip (broad range [pH 2 to 10] strip was used; the medium dark green colour was observed on pH strip). The mixture was agitated at 85°C without any inert gas protection. The temperature was monitored with thermometers.

In this process, the blue coloured mixture turned brick red, then reddish (Fig.1.1). Copper particles were separated by filtrating, washed with deionised water and ethanol. Copper particles were kept in dialysis bag 70 KD (Kilo Dalton), in a 250ml glass beaker with distilled water in refrigerator for around 2.5 weeks. Then the dialysis bag content copper particles solution was filtered by a filter assembly with 0.2 um nylon membrane.

Figure 1.1 :Synthesis of copper nanoparticles by Green Chemistry

2. Biological synthesis of copper nanoparticles

For biological synthesis of copper nanoparticles, Nag champa (*Artabotrys odoratissimus*, Family: Annonaceae), (Fig.1.4) leaves were collected and dried for 4 days at room temperature. The plant leaf broth solution was prepared by taking 25 g of thoroughly washed and finely cut leaves in a 1 L beaker with 500 mL of sterile distilled water and then boiling the mixture for 5 min before finally decanting it. It was stored at 4 0C and used within a week. Typically, 30mL of leaf broth was added to 170 mL of 1 mmol L−1 aqueous $CuSO_4 \cdot 5H_2O$ solution for the reduction of copper ions. The effects of temperature on synthesis rate and particle size of the prepared copper nanoparticles were studied by carrying out the reaction in a water bath at 95^0C with reflux. The copper nanoparticle solution thus obtained was purified by repeated centrifugation at 15,000 rpm for 20 min followed by redispersion of the pellet in deionized water (Fig.1.2).

Figure 1.2 : Biological synthesis of copper nanoparticles

Between both methods, the synthesis by Green Chemistry method was best for the formation of copper nanoparticles. The average size was found 35 nm. While the results of Biological method showed the more than 100 nm size particles. We have also tried to synthesize copper nanoparticles by quick and instant chemical reactions which gives pure copper particles, but with higher average size 743nm.

CONCLUSION

It has been discovered that the metal coated nanoparticles handle vital role in current as well as the future trends in drug delivery systems. Among them, silver and gold coated nanoparticles have significant applications. They have been widely used for antimicrobial, electronic and biomedical products. In this review, we provide a comprehensive understanding of various metallic NPs like Ag-NPs, gold, platinum and copper NPs from synthesis methods, antimicrobial effects and possible toxicology considerations of these nanoparticles to both humans and ecology. Other metals such as titanium, iron etc are also found to be used as these type of NPs.

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