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Overview of the Silver Oxide Nanoparticles

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Abstract: *The present review focuses on the green synthesis of silver nanoparticles by using an endophytic fungus, the properties of silver nanoparticles and the general techniques by which nanoparticles can well characterized. Silver has been used since ancient time due to its potent antimicrobial effect and now it is recognized as a non toxic and safe for human beings. Silver nanoparticles have attracted keen interest due to its specific size ranges 1-100 nm and its unique physical, chemical and biological properties. There are several methods reported for the synthesis of silver nanoparticles including physical, chemical and biological methods in which biological method are cheap, reliable, safe and non toxic over physical and chemical methods. Furthermore green synthesis technique is a promising approach for synthesis of silver nanoparticles showing antimicrobial effect as its not uses any toxic chemicals and specific higher temperature and pressure. But use of endophytic Fungi provides shield and survival condition to their host plants by secreting large amount of protein which can in a straight way convert to higher output of nanoparticles as well as can avoid the quick lessening of plant sources. These are characterized for physical and chemical properties of silver nanoparticles such as optical, magnetic and catalytic properties etc. by which nanoparticles shows influence in their reactivity as compared to macrostructure*

Keywords: Nanoparticles

I. INTRODUCTION

Nanoparticles are the clusters of atoms in the size range of 1–100 nm. In this size range, materials often develop useful attributes that are distinct from the properties of the bulk material. Metal particles in the nanometer size exhibit unique physical properties that are different from both the ion and the bulk material. Their uniqueness arises specifically from higher surface to volume ratio which results in increased catalytic activity due to morphologies with highly active facets; hence, the nanosize materials are more advantageous than their bulk materials [1]. As the size of matter is reduced to tens of nanometres or less, quantum effects can begin to play a role, and these can significantly change a material's optical, magnetic or electrical properties. In some cases, size-dependent properties have been exploited for centuries. For example, gold and silver nanoparticles (particles of diameter less than 100 nm; have been used as colored pigments in stained glass and ceramics since the 10th century AD (Erhardt 2003) The challenge for the ancient chemists was to make all nanoparticles the same size (and hence the same color), and the production of single-size nanoparticle is still a challenge today [2]. At the larger end of our size range, other effects such as surface tension or 'stickiness' are important, which also affect physical and chemical properties. For liquid or gaseous environments Brownian motion, which describes the random movement of larger particles or molecules owing to their bombardment by smaller molecules and atoms, is also important. This effect makes control of individual atoms or molecules in these environments extremely difficult. The concept of nanotechnology though considered to be a modern science has its history dating to as back as the 9th century. Nanoparticles (NPs) of gold and silver were used by the artisans of Mesopotamia to generate a glittering effect to pots. The first scientific description of the properties of nanoparticles was provided in 1857 by Michael Faraday in his famous paper "Experimental relations of gold (and other metals) to light". In 1959, Richard Feynman gave a talk describing molecular machines built with atomic precision. This was considered the first talk on nanotechnology. This was entitled "There's plenty of space at the bottom." [3] In last decay, application of nano material has been extensively increased in high demand leads to the bulk production of the nanomaterial. Classically, the nanoparticles are produced by physical method needs more energy and chemical methods are toxic but biological methods are clean, safe and cost effective. Biological methods of nanoparticles synthesis using microorganism, enzyme and plant or plant extract have been suggested as possible ecofriendly alternative to chemical and physical methods. It can also be suitable for large-scale synthesis of nanoparticles. There are several microorganisms from bacteria to fungi have been reported to synthesize inorganic materials either intra- or extracellularly, and thus to be potentially utilized as eco-friendly nanofactories. [4]A number of bacteria like Bacillus subtilis, Pseudomonas stutzeri, Thermonospora sp., Shewanella algae Lactobacillus strains, etc. have been studied for the synthesis of metallic nanoparticles. Yeast has also been explored for the biosynthesis of nanoparticles including Candida glabrata, Schizosaccaharomyces pombe, MKY3 etc. While, a number of plants like Medicago sativa, Pelargonium graveolans, Azadirachtaindica, Triticum, Cinnamomumcamphora, Capsicum annum have been used for the fabrication of metal nanoparticles [5]. Nanoparticles produced by a bio-enzymatic process are far superior, in several ways, to those particles produced by chemical methods despite the fact that the latter methods are able to produce large quantities of nanoparticles with a defined size and shape in a relatively short time. With an enzymatic process, the use of expensive chemicals is eliminated, and the

more acceptable "green" route is not as energy intensive as the chemical method and is also environment friendly. Nanoparticles are biosynthesized when the microorganisms grab target ions from their environment and then turn the metal ions into the element metal through enzymes generated by the cell activities. It can be classified into intracellular and extracellular synthesis according to the location where nanoparticles are formed [6]. The synthesis process is normally divided into two broad groups: the 'top-down' and the 'bottom-up' approaches. The top-down approach involves reducing the size of bulk materials by employing mechanical, chemical or other forms of energy. The breakdown of large structures can be achieved by use of ultra fine grinders, lasers and vaporization followed by cooling. Powerful techniques of lithography and etching start with large uniform pieces of material and generate the required nanostructures from them. The bottom-up approach on the other hand involves synthesizing nanomaterials from atomic or molecular species via self - assembly or chemical reactions allowing the precursor particles to increase in size. It is very powerful in creating identical structures with atomic precision [7]. The intend of the present review was focus on the green synthesis of silver nanoparticles by using an endophytic fungi, its properties and general characterization techniques

Silver Nanoparticle

The medical properties of silver have been known for over 2,000 years. Since the nineteenth centurysilver-based compounds have been used in many antimicrobial applications. Nanoparticles have been known to be used for numerous physical, biological, and pharmaceutical applications. Silver nanoparticles are being used as antimicrobial agents. Silver nanoparticles are nanoparticles of silver which are in the range of 1 and 100 nm in size. Silver nanoparticles have unique properties which help in molecular diagnostics, in therapies, as well as in devices that are used in several medical procedures [8]. 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. These properties make them of potential value in inks, microelectronics, and medical imaging. Besides, Ag-NPs exhibit broad spectrum bactericidal and fungicidal activity that has made them extremely popular in a diverse range of consumer products, including plastics, soaps, pastes, food and textiles, increasing their market value [9]. Silver is one of the basic elements that make up our planet. It is a rare, but naturally occurring element, slightly harder than gold and very ductile and malleable. Ag NPs of many different shapes (spherical, rod-shaped, truncated, triangular nanoplates) were developed by various synthetic routes. Truncated triangular silver nanoplates were found to show the strongest anti-bacterial activity. The Ag NPs have excellent antimicrobial property compared to other salts due to their extremely large surface area, which provides better contact with microorganisms [10].

PROPERTIES OF SILVER NANO- PARTICLES:

Many unusual properties of nanomaterials arise due to spatial confinement of electrons, photons, and electric fields around the particles as well as due to their large surface to volume ratio. The physical and chemical properties of nanoparticles depend on the type of motion its electrons can execute, which is dictated by the degree of their spatial confinement. When compared to macrostructures, larger proportions of constituent atoms or molecules lie at the surface of nanomaterials, leading to large surface to volume ratio, which can influence their reactivity, hardness, as well as magnetic, catalytic, and opto-electronic properties. [11] Some of the unique properties exhibited by such NPs are as follows:

OPTICAL PROPERTIES: Metal nanoparticles show different optical properties corresponding to their bulk form [12]. These properties are dependent on composition, size, shape and surrounding medium of the nanoparticles [13]. Depending on the size and shape of the nanoparticles, the optical properties vary from visible region to NIR region.The optical properties of colloidal nanoparticles in the UV-Vis-NIR spectral range are mainly determined by the so-called localized surface plasmon resonance (LSPRs) [14]

SURFACE PLASMON RESONANCE

Electromagnetic (EM) radiations cause oscillations of conduction electrons leading to a phenomenon called Surface Plasmon resonance (SPR). Free electrons on the metal nanoparticles have Plasmon resonances which are a result of EM radiations. When the frequency of the incident light photons matches with that of the free electrons oscillating, a resonance condition occurs. Unique intense colours are exhibited by gold and silver nanoparticles as they possess free electrons and the SPR bands can be observed by using spectrophotometry. The shape and size of the nanoparticles greatly affect the colour exhibited which is also reflected in the spectra. Slight modifications in the geometry of the nanoparticles can cause significant changes in the colour. Thus, the SPR exhibited by anisotropic nanoparticles is significantly distinguishable from that of isotropic (spherical) nanoparticles. While nanospheres typically have Plasmon resonance oscillations at one specific wavelength, anisotropic particles have both transverse and longitudinal oscillations that occur at different wavelengths of light. Thus, in the spectra of anisotropic nanoparticles, two separate SPR bands will be detected whereas only a single peak is displayed in case of spherical nanoparticles. While the longitudinal Plasmon band is related to the light absorption & scattering along the long axis of the particle, the transverse Plasmon band is contributed by the light absorption & scattering along the short axis of the particle. [15]

CATALYTIC ACTIVITY

Large surface areas of the nanomaterials make them good for adsorption at specific sites. Anisotropic nanostructures exhibit different crystal surfaces, and different fractions of atoms are located at different edges and corners. Thus, the catalytic efficiency is expected to be different in catalyzing the same reaction [16]. Different morphologies of platinum NPs had enhanced and selective catalytic activities when compared to their spherical counterparts [17].

MAGNETIC PROPERTIES:

Super paramagnetism is a form of magnetism that is a special characteristic of small ferromagnetic or ferromagnetic nanoparticles. In such super paramagnetic nanoparticles, magnetization can randomly change direction under the influence of temperature. Super paramagnetism occurs when a material is composed of very small particles with a size range of 1- 10nm. In the presence of an external magnetic field, the material behaves in a manner similar to paramagnetism with an exception that the magnetic moment of the entire material tends to align with the external magnetic field [3].

MELTING TEMPERATURE:

The bulk melting temperature is independent on its size. However, melting temperature for NP depends on its dimension and their melting temperature is lower than the corresponding bulk materials. It is known that the melting temperature depression result from the high surface-to-volume ratio and the surface substantially affects the interior "bulk" properties of these materials. Since the melting temperature depression results from the large surface-to-volume ratio, the surface areas of nanoparticles in different shape will be different even in the identical volume, and the area difference is large especially in small particle size. The melting temperature depression of nanoparticles is apparent only when the particle size is smaller than 100 nm. If the particle size is larger than 100 nm, the melting temperature of the particles approximately equals to the corresponding bulk materials, and in other words, the melting temperature of nanoparticles is independent of the particle size. It is found that the particle shape can affect the melting temperature of nanoparticles, and this effect on the melting temperature become larger with decreasing of the particle size [18].

PHYSICAL APPROACHES:

Most important physical approaches include evaporation-condensation and laser ablation. Various metal nanoparticles such as silver, gold, lead sulfide, cadmium sulfide have previously been synthesized using the evaporation-condensation method. The absence of solvent contamination in the prepared thin films and the uniformity of nanoparticles distribution are the advantages of physical approaches in comparison with chemical processes. Physical synthesis of silver nanoparticles using a tube furnace at atmospheric pressure has some disadvantages, for example, tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a great deal of time to achieve thermal stability. Moreover, a typical tube furnace requires power consumption of more than several kilowatts and a preheating time of several tens of minutes to reach a stable operating temperature [19].

II. CHEMICAL APPROACHES

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 polyvinylpyrrolidone (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. Spherical Ag-NPs with a controllable size and high monodispersity were synthesized by using the polyol process and a modified precursor injection technique. In the precursor injection method, the injection rate and reaction temperature were important factors for producing uniform-sized Ag-NPs with a reduced size. Ag-NPs with a size of 17±2 nm were obtained at an injection rate of 2.5 ml s^{-1} and a reaction temperature of 100 °C. The injection of the precursor solution into a hot solution is an effective means to induce rapid nucleation in a short period of time, ensuring the fabrication of Ag-NPs with a smaller size and a narrower size distribution. Nearly monodisperse Ag- NPs have been prepared in a simple oleylamine-liquid paraffin system. It was shown that the formation process of Ag-NPs could be divided in the three stages: growth, incubation and Ostwald ripening stages. In this method, only three chemicals, including silver nitrate, oleylamine and liquid paraffin, are employed throughout the whole process. Generally, the chemical synthesis process of the Ag-NPs in solution usually employs the following three main components: (i) metal precursors, (ii) reducing agents and (iii) stabilizing/ capping agents. The formation of colloidal solutions from the reduction of silver salts involves two stages of nucleation and subsequent growth. It is also revealed that the size and the shape of synthesized Ag- NPs are strongly dependent on these stages. Furthermore, for the synthesis of monodispered Ag-NPs with uniform size distribution, all nuclei are required to form at the same time. In this case, all the nuclei are likely to have the same or similar size, and then they will have the same subsequent growth. The initial nucleation and the subsequent growth of initial nuclei can be controlled by adjusting the reaction parameters such as reaction temperature, pH, precursors, reduction agents (i.e. $NaBH_4$, ethylene glycol, glucose) and stabilizing agents (i.e. PVA, PVP, sodium oleate [20].

GREEN SYNTHESIS OF SILVER NANOPARTICLES:

In recent years, the development of efficient green chemistry methods employing natural reducing, capping, stabilizing agents to prepare silver nanoparticles with desired morphology and size have become a major focus of researchers. Biological methods can be used to synthesize silver nanoparticles without the use of any harsh, toxic and expensive chemical substances [21-22].

SYNTHESIS OF SILVER NANOPARTICLES BY PLANTS:

The major advantage of using plant extracts for silver nanoparticle synthesis is that they are easily available, safe, and nontoxic in most cases, have a broad variety of metabolites that can aid in the reduction of silver ions, and are quicker than microbes in the synthesis. The main mechanism considered for the process is plant-assisted reduction due to phytochemicals. The main phytochemicals involved are terpenoids, flavones, ketones, aldehydes, amides, and carboxylic acids. Flavones, organic acids, and quinones are water-soluble phytochemicals that are responsible for the immediate reduction of the ions. Studies have revealed that xerophytes contain emodin, an anthraquinone that undergoes tautomerization, leading to the formation of the silver nanoparticles. In the case of mesophytes, it was found that they contain three types of benzoquinones: cyperoquinone, dietchequinone, and remirin. It was suggested that the phytochemicals are involved directly in the reduction of the ions and formation of silver nanoparticles [23].

SYNTHESIS OF SILVER NANOPARTICLES BY BACTERIA:

Bacteria are known to produce inorganic materials either intra- or extracellularly. This makes them potential biofactories for the synthesis of nanoparticles like gold and silver. Silver is well known for its biocidal properties; however, some bacteria are known to be silver resistant and can accumulate silver on the cell wall to as much as 25% of their dry weight biomass, thus suggesting their use in industrial recovery of silver from ore materials. Therefore, the use of prokaryotic bacteria as nanofactories was first studied [24]. The first evidence of bacteria synthesizing silver nanoparticles was established using the Pseudomonas stutzeriAG259 strain that was isolated from silver mine [25]. There are some microorganisms that can survive metal ion concentrations and can also grow under those conditions, and this phenomenon is due to their resistance to that metal. The mechanisms involved in the resistance are efflux systems, alteration of solubility and toxicity via reduction or
oxidation, biosorption, bioaccumulation, extracellular complex formation or precipitation of metals, and lack of specific metal transport systems [26].

SYNTHESIS OF SILVER NANOPARTICLES BY FUNGI:

When in comparison with bacteria, fungi can produce larger amounts of nanoparticles because they can secrete larger amounts of proteins which directly translate to higher productivity of nanoparticles [27]. The mechanism of silver nanoparticle production by fungi is said to follow the following steps: trapping of Ag^+ ions at the surface of the fungal cells and the subsequent reduction of the silver ions by the enzymes present in the fungal system [28]. The extracellular enzymes like naphthoquinones and anthraquinones are said to facilitate the reduction. Considering the example of F. oxysporum, it is believed that the NADPH-dependent nitrate reductase and a shuttle quinine extracellular process are responsible for nanoparticle formation [29].

SYNTHESIS OF SILVER NANOPARTICLES USING ENDOPHYTIC FUNGI:

Endophytic fungi are microorganisms which spend the whole or part of their life-cycle residing symbiotically within the healthy tissues of host plants, inter-and/or intra- cellularly and produce bioactive natural products or drugs and derivatives; meanwhile causing no damage or disease to their hosts [30]. Taken literally, the word endophyte means “in the plant” (endon Gr.= within, phyton = plant). The usage of this term is as broad as its literal definition and spectrum of potential hosts and inhabitants, e.g. bacteria (Kobayashi and Palumbo 2000), fungi (Stone et al. 2000), plants (Marler et al. 1999) and insects in plant(Feller 1995), but also for algae within algae (Peters 1991). Endophytic fungi are an ecological, polyphyletic group of highly diverse fungi, mostly belonging to ascomycetes and anamorphic fungi.

Approximately, there are near to 300,000 plant species on earth and each individual plant is the host to one or more endophytes, and many of them may colonize certain hosts. It has been estimated that there may be as many as one million different endophytic fungal taxa, thus endophytes may be hyperdiverse. The presence of biodiverse endophytes in huge number plays an important role on ecosystems with greatest biodiversity. Endophytes provide a broad variety of bioactive secondary metabolites with unique structure, including alkaloids, benzopyranones, flavonoids, phenolic acids, quinones, steroids, terpenoids, tetralones, xanthones, and others [31]. The endophytes may provide protection and survival condition to their host plant by producing a plethora of substances which once isolated and characterized, may also have potential for use in industry, agriculture and medicine [32]. Some species of endophytic fungi have been identified as sources of anticancer, antidiabetic, insecticidal and immuno- suppressive Some studies show that the endophytes are not host specific a single endophyte can survive a wide range of host. A large number of fungi isolated from the different parts of the same plants which differ in their ability to utilize different substances [33]. Therefore, a number of fungi can be isolated from different plant belonging to different genera and grow under different climatic conditions. The host and endophytes relationship varies from host to host and endophytes. Some studies show that host plant and endophyte relationship also able to maintain the pathogen host antagonism [34].

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