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SYNTHESIS METHODS OF METALLIC NANOPARTICLES - AN OVERVIEW

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Abstract: *In this work some of the synthesis methods of metallic nanoparticles are presented. There are two main ways to obtain nanoparticles, depending on the direction in which the processes take part, namely top-down (subtraction of material) and bottom-up (addition of material). Top-down methods include mechanical milling, while laser ablation and bioreduction are just a few techniques included in bottom-up approaches. The wide area of application of nanomaterials has led to a continuous development of the procedures used in their synthesis process.*

Key words: *synthesis methods, nanoparticles, bioreduction.*

1. Introduction

"Nano" is a linear dimension, derived from the Greek word "nanos" which means dwarf or extremely small. Nano (the symbol n) is a unitary prefix that means "one billionth". Used primarily with the metric system, this prefix is a factor of 10^{-9} [12].

The term nanotechnology was first used in the scientific field in 1974. At that time, Professor Nario Taniguchi defined nanotechnology as a production technology with a very high accuracy and ultra-fine dimensions, namely, precision and fineness being of the nanometer order. However, the first mentions of nano-scale technological processes, deliberately created and applied, but later referred to as nanotechnology, are found in Richard Feynman's well-known lecture "There's a Plenty of Room at the Bottom". The most common definitions of nanotechnology revolve around the study of technology that develops particles and materials on a nanoscale, under controlled conditions, not only the size but also their functionality. Nanoparticles have captured the interest of researchers over the last few years, due to their special properties, which are clearly superior to the same materials but in raw or bulk form [18].

Nowadays the nanomaterials can be synthesized and modified with different functional chemical groups that allow them to be conjugated to antibodies, ligands and drugs of interest, thus opening up a wide range of potential applications in biotechnology, magnetic separation and preconcentration of target analytes, drug delivery and vehicles for the administration of genes and drugs and, more importantly, diagnostic imaging [11].

The synthesis of metallic nanoparticles is an attractive subject due to their wide area of application. Several methods have been developed for the synthesis of these materials. The ability to obtain and influence the properties of the nano-sized materials due to their size and shape has led to an expansion of a variety of new possibilities in almost all

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industries and scientific efforts. Because nanotechnology is essentially a set of techniques that allow handling of very small scale properties, nanoparticles have many applications, such as those presented in Figure 1 [7], [16].

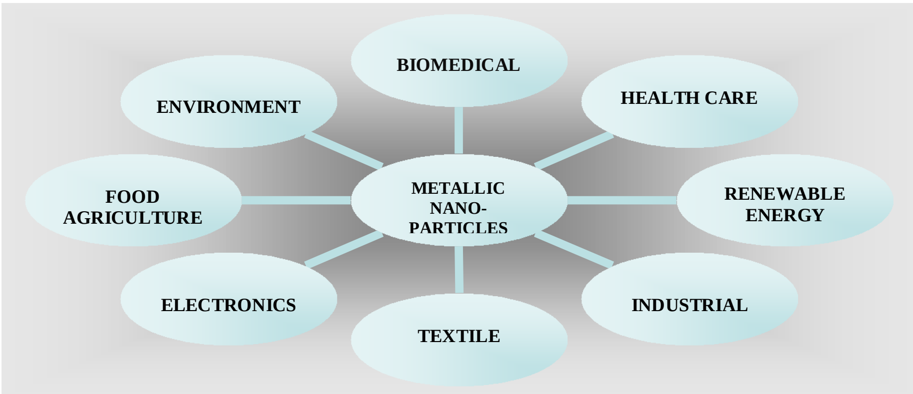


Fig. 1. *Application of nanoparticles*

Nanocrystalline materials can be synthesized either by reinforcing atoms /molecules/ clusters or by breaking down bulk materials into smaller sizes. Synthesis methods of nanoscale structures include both top-down and bottom-up approaches. In the first category, top-down synthesis, nanoparticles are obtained by reducing the size of macroscopic systems to nanoscale. The reduction in particle size can be achieved by various physical or chemical procedures.

In bottom-up synthesis processes, the individual manipulation of atoms and molecules through self-assembly processes leads to the formation of nanostructures. The latter approach can also be materialized by applying biological methods. Top-down synthesis methods are sought to be replaced or improved due to imperfections in the material structure. This is a major limitation because surface chemistry and other physical properties of nanoparticles are strongly dependent on the material structure. In addition, they can contain significant amounts of impurities. The particles have a relatively wide distribution of dimensions and different shapes. The bottom-up approaches have been proven to be more favourable, which is why a multitude of nanoparticle synthesis techniques have been developed following the principle of self-assembly [5], [10].

2. Materials and Methods

2.1. Mechanical Milling

This process was discovered by Benjamin and his collaborators at the Nickel International Company in the 1970s. At first, the method was called "mechanical alloying" as it could produce fine and uniform dispersions of oxide particles in nickel superalloys [19].

Nowadays, there are different types of milling equipment used to mix, alloy or reduce in particle size. Particle shape changes are of particular interest in the synthesis of nanomaterials. These aspects differ in particular, depending on the capacity and efficiency of grinding, but the arrangements can also be easily influenced by the heat transfer involved [4].

High-energy ball milling is the most commonly used milling technique for obtaining nanoparticles, but it was initially considered to be a "dirty" technique due to iron contamination issues. However, the use of tungsten carbide or steel carbide components and inert atmosphere and/or high vacuum processes have reduced the level of impurities within acceptable limits [4]. In Figure 2 is shown a schematic representation of the working principle of ball milling process.

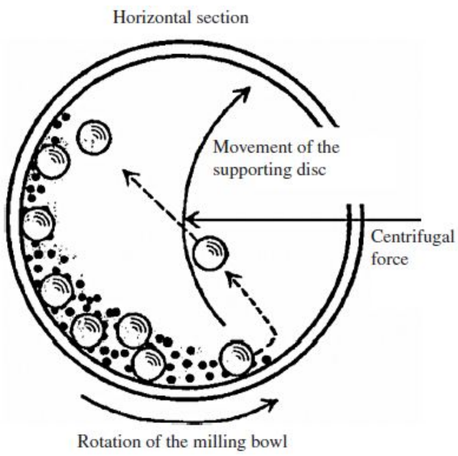


Fig. 2. *Schematic view of motion of the ball and powder mixture* [21]

The process is carried out by loading in a high-energy ball mill a batch of metallic powder along with a special grinding medium. The grinding balls used in the synthesis of nanomaterials act directly on the powder charge. Grinding bodies are made of high density materials, such as steel or tungsten carbide. The kinetics of the mechanical grinding process depends on the energy transferred from the balls to the powder. The energy transfer is driven by a number of process parameters such as the type of powder used in the milling chamber, the grinding speed, the size and distribution of grinding balls by size, the type of milling: dry or wet, the temperature and the duration of the milling process [19].

In order to improve the process of nanoparticles synthesis by mechanical milling, surfactants are currently used, which help to obtain particles with precise sizes and superior characteristics. Surfactants are surface active agents that can exhibit both hydrophobic and hydrophilic properties. A major classification of these is defined on the basis of the type of surface load, namely, anionic, cationic, amphionic and ionic surfactants [17].

2.2. Laser Ablation

Synthesis by laser ablation has emerged as a reliable alternative to traditional methods of chemical reduction for the production of metallic nanoparticles. Depending on the state of aggregation of systems with which the laser beams interact during the ablation process, several studies have categorized this method as feasible in various environments: from ambient air or the use of different gases (He, Ne, Ar, Kr, Xe and N), to vacuum or liquid media. The use of different mechanisms in laser ablation corresponding to the media used implicitly led to different results. Although the media described above have a wide range of development and applicability, the greatest interest is the development of the method in liquid media, the optimal environment for the synthesis of nanoparticles being deionized water [2].

Laser ablation in liquid medium was first described in 1987 by P.P. Patil et al., who reported the synthesis of iron oxide in metastable form by laser pulsing of an iron target in interdependence with water, the liquid medium used during the process [13].

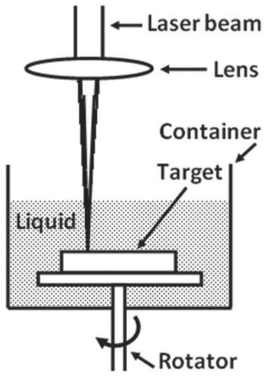


Fig. 3. *Experimental setup for nanoparticles synthesis by laser ablation in liquid* [13]

Figure 3 shows the two essential parts of the equipment used for laser ablation, namely a laser beam and an ablation chamber. The principle underlying the process consists in the fact that the high intensity of the laser beam causes an increased absorption of the luminosity at the surface of the target material, where there is a rapid increase in temperature, making possible the surface evaporation of the target material. Laser ablation of solid targets in liquid media can result in nanostructures with different compositions (metals, alloys, oxides, carbides etc.) and various morphologies (nanoparticles, nanocomposites etc.). Particle synthesis is accomplished by condensation of the removed material from the surface of the target as a result of the interaction of the laser radiation, leading to the formation of nanoparticles in the liquid [20], [15].

2.3. Green Synthesis of Metallic Nanoparticles

Nowadays, the biological synthesis is an attractive alternative to traditional methods (physical and chemical approaches) for the production of nanoparticles. The bio-reduction synthesis involves the use of different biological entities, such as, plant extracts, bacteria, fungi, and yeasts.

Bioreduction using plant extracts. The plant extracts contain bioactive alkaloids, phenolic acids, polyphenols, proteins, sugars and terpenoids which confer the ability to reduce the metal ions to nanoparticles. The plants were considered an ecological way for nanoparticles synthesis, especially for those materials which have to be used in the biomedical field [10].

Bioreduction using microorganisms. Microorganisms can survive and grow in high concentrations of toxic metals due to their chemical detoxification potential, as well as their energy-dependent efflux in the cell by membrane protein, that functions either as

ATPase or as chemo-osmotic or proton anti-transporter agents. Biosynthesis is the phenomenon that occurs through biological or enzymatic reaction [6].

The exact mechanism for the synthesis of nanoparticles using biological agents has not yet been perfected, as the different biological agents are using a different mechanism with different metals, and there are also different biomolecular responses for nanoparticle synthesis.

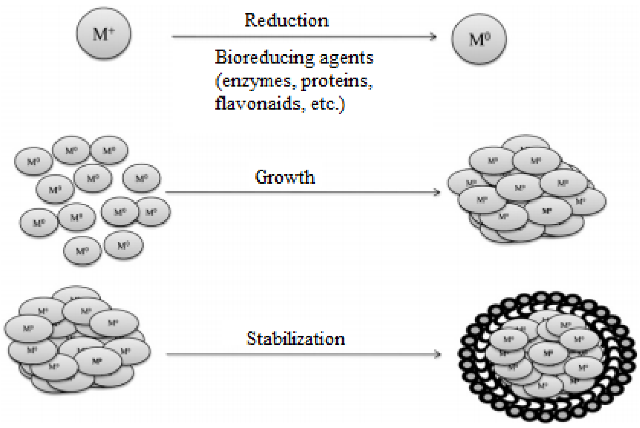


Fig. 4. *Possible mechanisms of nanoparticle synthesis (M^+-metal ion)* [10]

In Figure 4 is presented the probable mechanism of nanoparticle synthesis by bottom-up approach thought by Mittal and co-authors.

3. Results and Discussion

Khayati and Janghorban have reported the mechanical reduction of Ag_2O using graphite in a high energy planetary ball mill. They have observed that by increasing milling time, ultra-fine Ag powders were obtained. The prepared silver powder was mechanically deformed and refined with increasing milling time until all the silver oxide was reduced to silver.

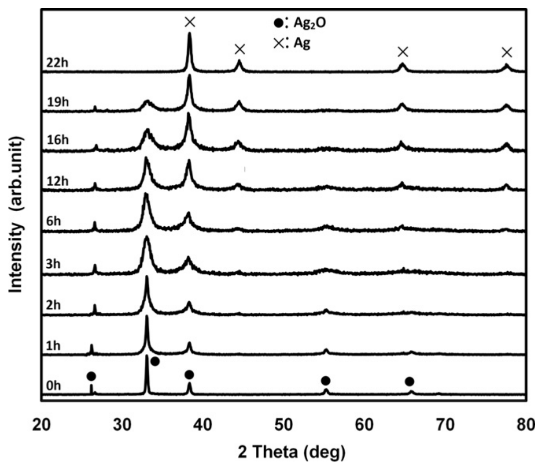
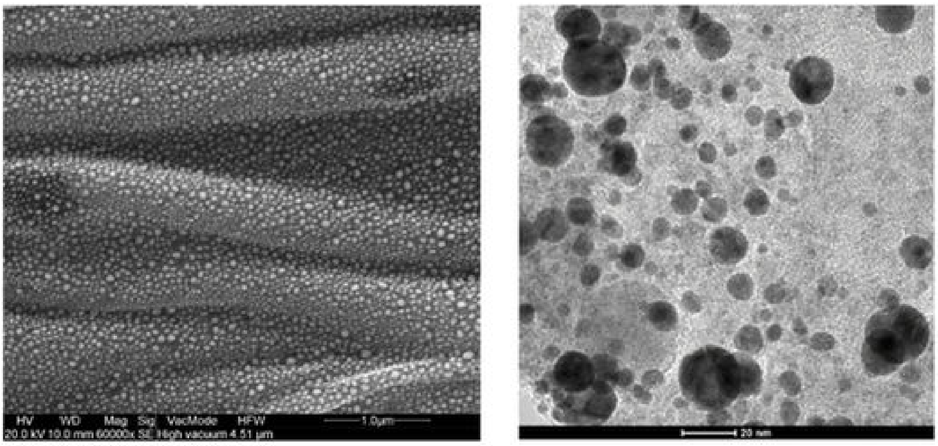


Fig. 5. *XRD spectra of powder mixture milled as a function of milling time* [8]

In Figure 5 the XRD patterns of the powder mixture milled for various times can be observed, revealing the structural evolution as a function of milling time in the powder mixture. As milling time increased, the peaks of Ag_2O are gradually broadened and their height decreased. The Ag peaks appear between 3 and 6 h milling. Further milling resulted in an increase in the Ag peaks intensities, and single phase of Ag appeared after 22 h milling time [8].

In case of laser ablation, the wavelength and laser pulse interval and ablation period are just a few of the factors that directly influence the process yield, and hence the particularities of the nanoparticles produced. Barberio and Antici have presented a method to control, with very high precision, the starting of the aggregation phase during the laser ablation in solution. They have obtained the results due to the monitoring of the optical absorption of the colloidal solution. Morphological analysis, conducted by SEM and TEM, for short irradiation times (15 sec) are presented in Figure 6a. For irradiation times greater than 30 s, the morphological analysis (Figure 6b) shows the presence of large amorphous aggregates with NP (nanoparticle) dimensions varying from a few tens of nm to hundreds of nm, without any sign of a regular distribution [2].



a) b)

Fig. 6. *SEM image of Ag NPs obtained after an irradiation time of 15 s* (a); *TEM images of Ag NPs collected after 30 s of irradiation* (b) [2]

A laser irradiation applied after the nanomaterials are suspended in colloid (Figure 5) can influence and alter the shape, size and composition of the material.

Natural products or those derived from natural products, such as extracts from several plants or parts of plants, tea, coffee, bananas, plain amino acids, as well as wine, table sugar and glucose, have been used as reducing agents and as agents for coating during the bioreduction synthesis method [7].

More specifically, the synthesis of noble metal using *Hyacinthus orientalis* and *Dianthus caryophyllus* has been reported [3].

The first bacteria which have presented that they have the ability to synthesize nanocrystals, was the *Pseudomonas stutzeri A259* [9]. Eukaryotic organisms, such as mushrooms, have been thoroughly investigated for their ability to form nanoparticles with different elements in compositions and sizes. In a large study involving nearly 200 different genres, Sastry et al. have found that the mushrooms are excellent candidates for the synthesis of metallic nanoparticles and metallic sulphides because of the variety of enzymes and their relatively simple manipulation. Of all eukaryotes, yeasts are probably the most studied and applied in bioprocesses. Furthermore, their potential to produce semiconductor nanoparticles is well known and investigated. Although yeast is known to predominantly produce intracellular nanoparticles, recent studies have revealed the extracellular effect in the formation of silver nanoparticles in the 2-5 nm range using the silver-tolerant yeast strain MKY3 [14].

Absar Ahmad reported intracellular synthesis of relatively monodispersive gold nanoparticles by the reaction of aqueous AuCl-4 ions with *Rhodococcus sp*. The reduction of noble metal ions occurs both on the surface of the mycelium and on the cytoplasmic membrane, which leads to the formation of gold nanoparticles with fairly well-defined dimensions between 5-15 nm and good monodispersity [1].

4. Conclusions

The synthesis of metal nanoparticles is one of the most important points in the materials field. Because there are different kinds of synthesis methods, by which the nanoparticles can be obtained, the focus should be on the methods that can offer a production low-cost, coupled with desired properties, but also are environment-friendly. The green methods, using plant extracts and microorganisms are a good alternative for the synthesis of nanoparticles. It is worth mentioning the fact that combining two or more methods the synergistic effect could exceed the expectations.

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