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A Review On Green Methods for Synthesis of Silver Nano Particles

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Metal nano particles are one of the most attractive aspects of nano materials in recent years. The reason for this growing attraction is because of their special physical and chemical properties, which are more enhanced from bulk material. Hence they find wide application in various fields like catalysis, photonics, optoelectronics, information storage, antibacterial applications, etc. While considering metal nano particles, electrical conductivity is one of the most important properties that can be used for humans' benefit and should be enhanced. Silver nano particles can be used in the electronics industry as conductive fillers because of their unique properties such as high electrical and thermal conductivity, high resistance to oxidation. It is impressive that eco friendly methods are being developed for synthesizing these nano particles, using different kinds of plant extracts and water soluble component as capping agents, which results in different forms of particle morphologies.

Keywords: Silver nano particles, Green synthesis.

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1. INTRODUCTION

Electronic industry is currently one of the most practical industries and advancements in order to make the process of assembling a circuit board easier has become very attractive. Nano-particle metal inks are being developed for printed electronics, particularly on flexible plastic substrates, driving the need to understand their electrical performance [1].

Silver as the best conductor among metals is studied most intensively. Metal nano-inks consist of a colloidal suspension of nano-sized metal particles which was coated with a thin stabilizer shell. Very small particle sizes of silver, has the ability to sinter at exceptionally low temperatures due to their high surface area to volume ratio, so when the ink is exposed to heat, the nanoparticles diffuse in each other and form a continuous film (Fig.1) [1].

Changing the concentration ratio of the components used in synthesizing silver nano particles, such as silver nitrate, reducing agents, stabilizers and capping agents can cause the formation of a variety of morphologies for silver nano particles such as nano spheres, wires, plates and etc.

2. EXPERIMENTAL

2.1 Chemical Approach

The most common approach for synthesis of silver nanoparticles is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride (NaBH4), elemental hydrogen, polyol process, tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers are used for reduction of silver ions (Ag^{+}) in aqueous or non-aqueous solutions.

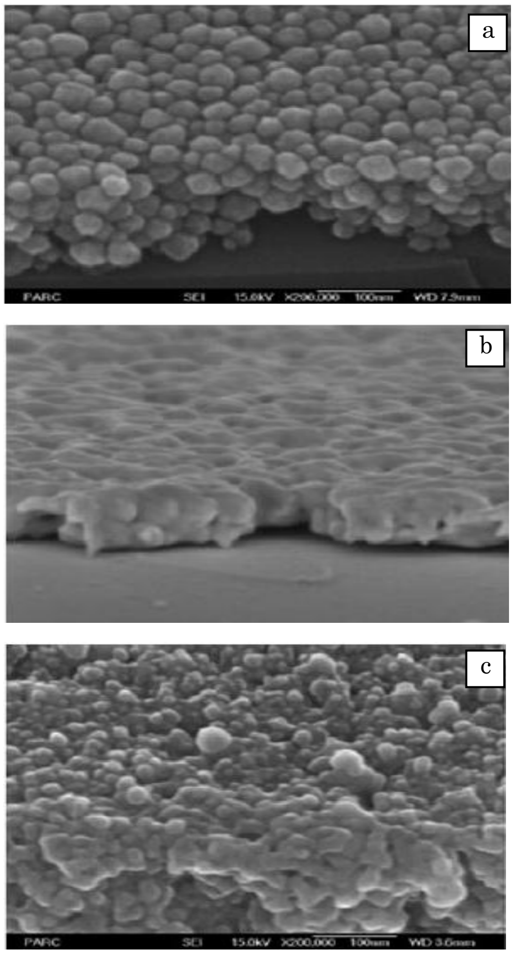

Fig. 1– SEM images of 100 nm silver nanoparticle film in as-dried condition (a), followed by curing at 150 for 5 min (b) and for 3 h (c) resulting in a continuous porous film [1]

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The aforementioned reducing agents reduce silver ions (Ag^+) and lead to the formation of metallic silver (Ag^0), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to formation of metallic colloidal silver particles [2].(Fig. 2)

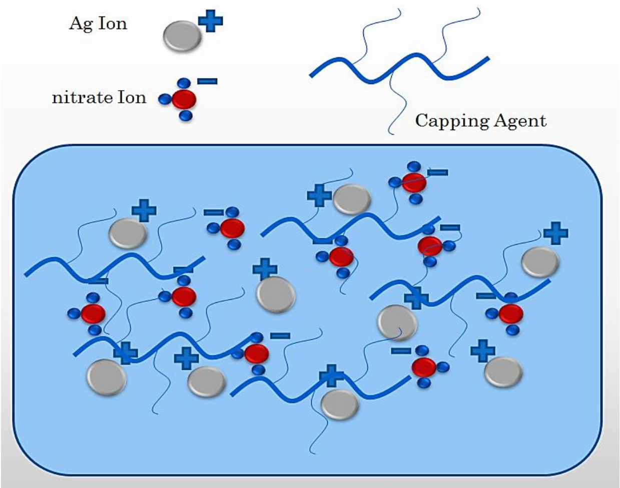

Fig. 2 – The schematic illustration of chemical reduction process for silver nitrate molecules, trapped among capping agents in water

2.2 Different Morphologies

Sintering temperature is one of the most important properties of silver nano particles. Different morphologies will result in different sintering temperatures, due to the amount of particles bulk that should be melted into each other during sintering process. The more the nano particles shapes becomes spherical, the more the particles become 3dimensional in nano scale. As illustrated in Fig.3 for spherical particles more energy and time is needed in sintering process than for planar particles that have 1dimension in nano scale.

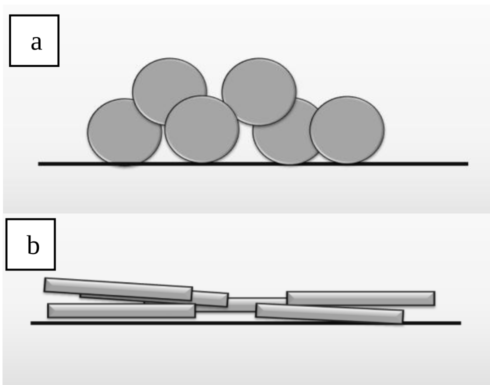

Fig. 3 – Illustration of nano particles sintering process for (a) 3dimensional nano particles and (b) 1dimensional nano particles

3. RESULT AND DISCUSSION

3.1 Articles on Green Synthesis

In 2009 Sharma et al. mentioned in their review article that Nanomaterials often show unique and considerably changed physical, chemical and biological properties compared to their macro scaled counterparts [3]. They also mentioned that synthesis of noble metal nanoparticles for applications such as catalysis, electronics, optics, and biotechnology is an area of constant interest for scientists.

Sharma et al. studied several synthetic methods for silver nano particles using inexpensive and nontoxic compounds in water environment. Rapid and green synthetic methods using extracts of bio-organisms have shown a great potential in synthesis of silver nano particles.It is also said that silver nano particles have advantages in antibacterial activities. Green synthetic methods include mixed-valence polyoxometallates, polysaccharide, Tollens, irradiation, and biological. The mixed-valence polyoxometallates method was carried out in water, an environmentally-friendly solvent [4].

In 2009 Rao et al. synthesized silver nano particles using silver nitrate, glucose, diethyl amine, sodium carbonate and sodium hydroxide. The different concentrations of aqueous solutions of silver nitrate and glucose solutions were mixed together and stirred to obtain a homogeneous solution. The result of this work was an eco friendly wet chemistry rout that produced spherical silver nano particles in suspension and as shown in Fig.4 [5].

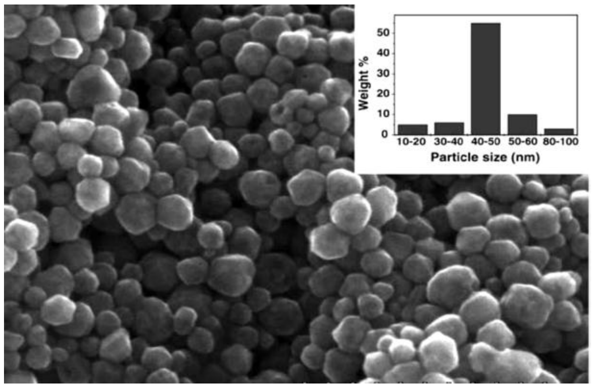

Fig. 4 – Spherical silver nano particles synthesized by using glucose and diethyl amine [5].

In 2010 Khan et al. synthesized silver nanoparticles were by a simple chemical reduction method using ascorbic acid and starch as reducing and stabilizing agents, respectively. The advantage of this green method was its simplicity, and room temperature conditions. nanoparticles which acted as a probable stabilizer and/or capping agent. The hydrophilic poly –OH groups were mainly responsible for the adsorption of amylose onto the surface of nanoparticles through electrostatic interactions. The size dispersity of quasi-spherical, triangular nano-plates and nano-rods of pure crystalline metallic silver could be synthesized in presence of starch [6] (Fig.5).

In 2011 Yi et al. synthesized silver nano plates, in room temperature, using tannic acid solution via chemical reduction method. The synthesis was a seedless process in which tannic acid was used as a reducing as well as a capping agent, and did not need any other surfactant or capping agent. The reason for this improvement lies in the structure of tannic acid (Fig.6), which has OH groups that participate in reduction reaction and also the branches in its structure that keep the Ag atoms from accumulation and growth [7].

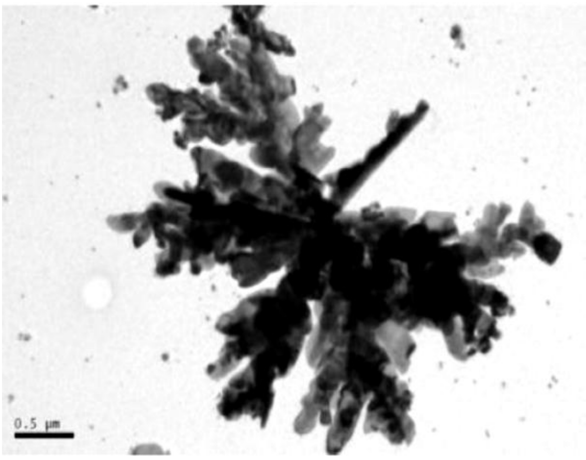

Fig. 5 – TEM image of silver nano crystals synthesized using ascorbic acid and starch [6]

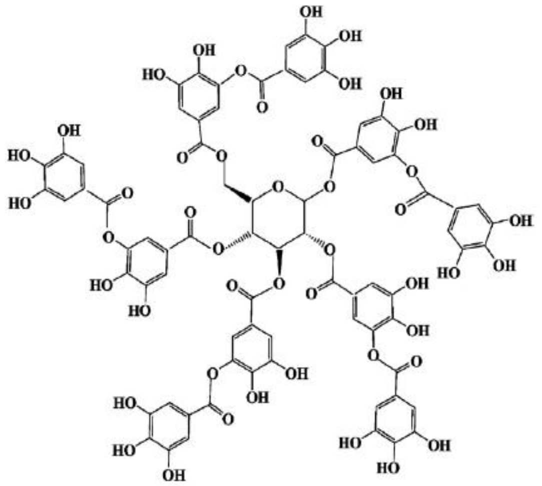

Fig. 6 – Chemical structure of tannic acid [7]

The result of this work was green synthesis of planar nano particles without introducing any surfactant or seed to direct the two-dimensional growth. The synthetic strategy presented was simple and environmentally friendly. Fig. 7 shows the TEM image of these planar particles.

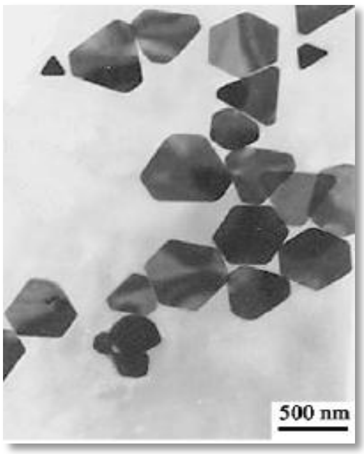

Fig. 7 – TEM image of silver nano plates synthesized using tannic acid [7]

In 2011 Zhang et al. stated that the main problem in preparing stable nanoparticles for inkjet printing is to overcome the strong agglomeration of the particles in dispersion medium. Good dispersion of metal particles in the ink with a low viscosity is essential to achieve. Nanoparticles tend to cluster and agglomerate if they are not prevented to do so. Particle agglomeration causes the system to change to the one with fewer but larger particles. Hence, it is necessary to modify the surface of the particles so that the agglomeration or clustering can be delayed [8].

The result of this work was eco friendly method for synthesis of sphere shaped nano particles. Fig.8 shows the SEM image of these particles.

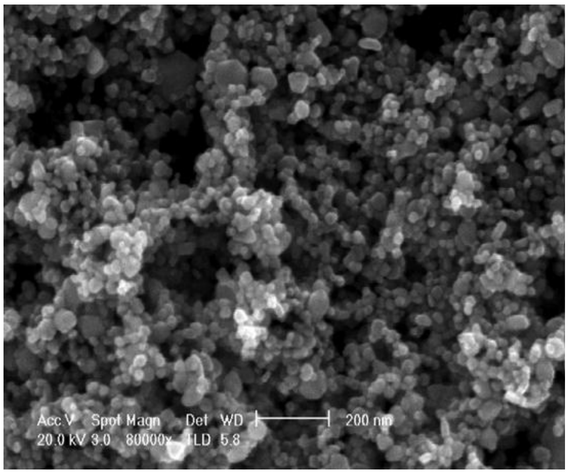

Fig. 8 – SEM image of silver nano particles [8]

printable fluid and assure its performance. Due to agglomeration of particles, the viscosity tends to increase during storage.One of the advantages coming from the nano-size of material is a dramatic reduction in melting point. Films printed using such small particles can be annealed at lower temperatures to form conductive films of low resistance [8].

In 2011 Philip et al. developed a green synthesis of noble metal nanoparticles. This method contained using aqueous seed extract of Macrotyloma uniflorum [9]. Before that many other methods were employed to enhance the green preparation of nanosized silver nano particles using plant extracts including honey [10], mangifera indica [11], hibiscus leaf extract [12], Cashew leaf [13], murraya koenigii leaf [14], glucose in the presence of soluble starch as a stabilizing agent [15–16], sucrose and maltose [17], aloevera plant extracts [18] and etc.

In their research, Philip et al. used plant extract from Macrotyloma uniflorum, which is an herbaceous plant with lots of medicinal properties. The plant extract was used as capping agent for synthesizing silver nano particles (Fig.9). It was concluded in this work, that several factors influence the formation of silver nanoparticles such as plant source, organic compound in plant extract. Organic compounds like alkaloids, polyphenols, proteins and even some natural pigments are present in plant extracts [9].

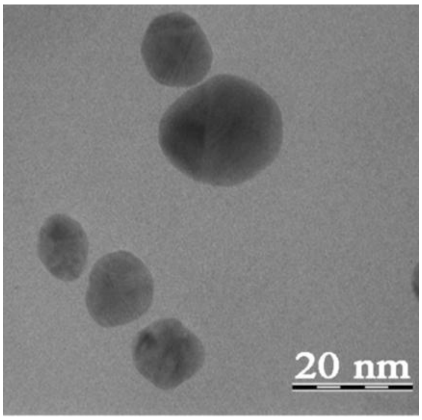

Fig. 9 – TEM image of silver nano particles, using Macrotyloma uniflorum extract as capping agent [9]

In 2012 Vijayaraghavan et al. stated that nanoparticles can be synthesized intracellularly or extracellularly using bacteria, yeast, fungi and plant materials [18]. These green synthesizing methods can also find wide applications [20].

In their research Vijayaraghavan et al. used the extract of Syzygium aromaticum plant as reducing and capping agent and the reduction reaction was performed in the presence of different bacteria. The result of their work was colloidal silver nano particles as illustrated in Fig. 10 [19].

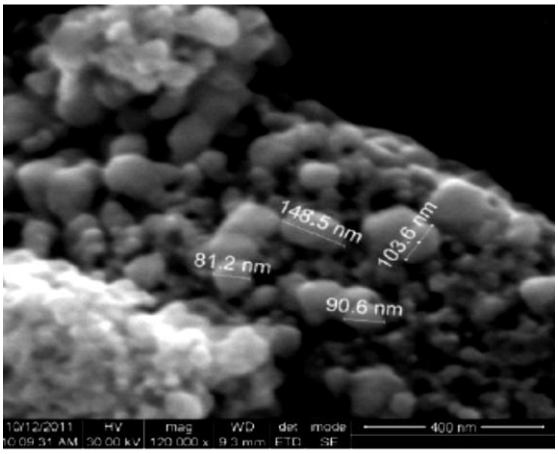

Fig. 10 – SEM image of silver nano particles, using Syzygium aromaticum extract as reducing and capping agent [19]

In 2012 Yi et al. developed a chemical reduction method by seed-mediated method in the presence of trisodium citrate and poly (vinyl pyrrolidone) at room temperature. In this work PVP molecules were used as capping agent and the result was formation of silver nano particles with plate shape morphology (Fig. 11) [21].

The difference approach in this method of green synthesizing was that, with preparing the silver seeds before adding all the components, the 2dimentional particles were produced conveniently [21]. (Fig.12)

In 2013 Bapat et al. introduced Artocarpus heterophyllus Lam. seed extract as a reducing agent for green synthesis of silver nano particles in water medium. The result of this eco-friendly method was nano particles that had irregular shapes and morphologies with semi wide distribution in particle diameters [22].

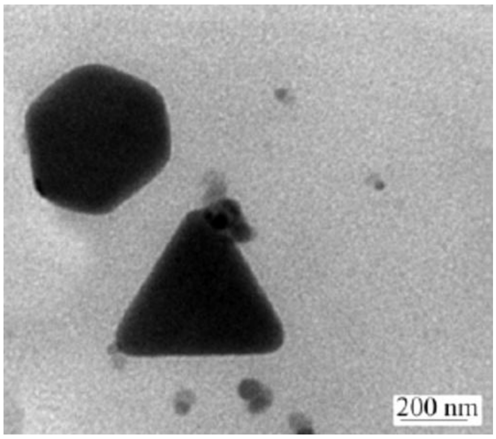

Fig. 11 – TEM image of silver nano plates [21]

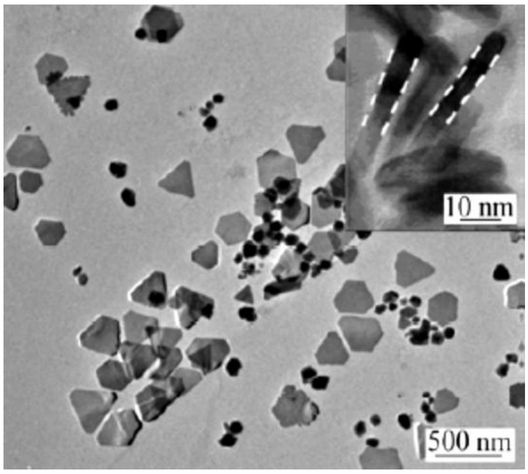

Fig. 12 – TEM image of Silver nanoplates, with average thickness about 5 nm and average tunable size from 40 to 500 nm [21]

This research indicates that the variety of natural compounds that are present in plant extracts can cause a wide distribution in particle diameters and irregularity in particle morphologies as illustrated in Fig.13 [22].

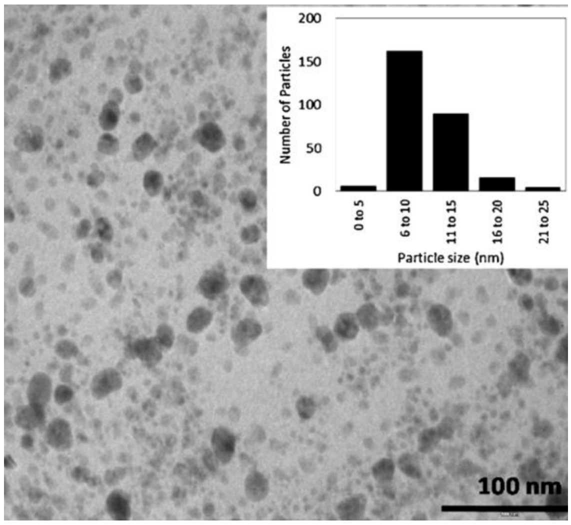

Fig. 13 – TEM image of Silver nano particles, synthesized using Artocarpus heterophyllus Lam. seed extract as a reducing agent, and their diameters [22]

In 2013 Saravanan et al. produced silver nanoparticles with another green synthesizing method by using leaf extract of Mimusops elengi, Linn. at room temperature. The reason for using this plant extract was because leaf of Mimusops elengi, L. appeared to be a potential source of hydrocarbons. It has been reported that the leaves contain various organic compounds such as alkaloids, flavonoids, tannins, terpenoids, steroids, glycosides and benzenoids, which are water soluble compounds present in the aqueous extract. As a result these compounds act as efficient stabilizing agents during reduction of silver ions [23].

Fig.14 shows the SEM image of the spherical silver nano particles that were produced by this leaf extract.

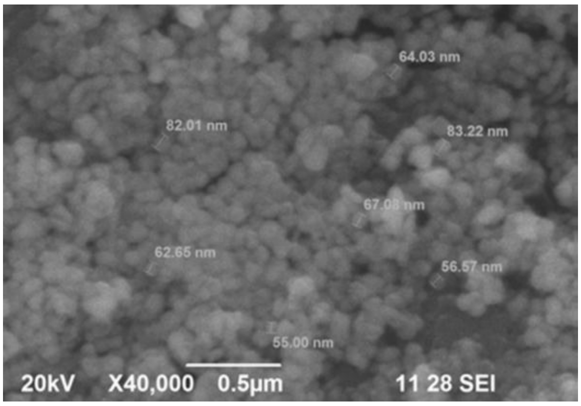

Fig. 14 – SEM image of Silver nano particles, synthesized using leaf extract of Mimusops elengi, Linn. as an stabilizer [23].

In 2013 Kannan et al. reported an inexpensive and reproducible method for the large scale synthesis of silver nano particles by reduction process using flower extract of Millingtonia hortensis. This flower extract, which can act both as reducing and stabilizing agent [24].

Silver nano particles with diameters in the range of 10–40nm using the broth of flower as reducing agent and capping agent, were synthesized (Fig.15). It was understood that the flower extract can reduce the silver salt solution and also hindering the particle growth. This green chemistry approach toward the synthesis of silver nano particles has many advantages such as, ease with which the process can be scaled up, economic viability, etc. The reduction of silver ions and stabilization of the silver nano particles happened through the participation of flower compounds like proteins and metabolites [24].

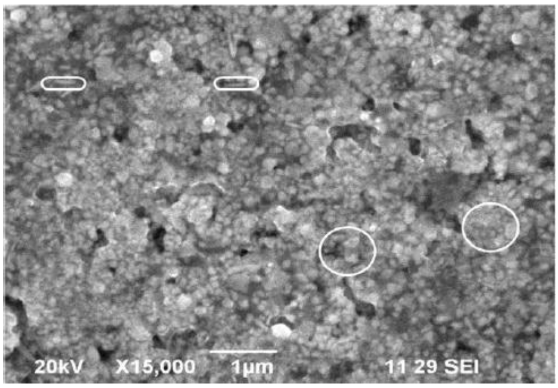

Fig. 15 – sEM image of Silver nano particles, synthesized using Millingtonia hortensis [24].

4. CONCLUSION

Both chemical and physical methods have been used to prepare metal nano particles. Chemical reduction is the most common method because of its convenience. Control over the growth of metal nano particles is required to obtain nano particles of small size with different shapes. It is well known that silver nano particles can be produced by chemical reaction at low cost and in high yield [25].

Natural sources have the potential to reduce metal ion into metal nanoparticles [26]. Silver nano particles were used in various applications such as catalytic, electrical conducting [27–30] and antimicrobialactivity [31-32].

The size, shape and surface morphology of nanoparticles plays a vital role in controlling the physical and chemical properties. The synthesis of metal nanoparticles by chemical reduction method was often performed in the presence of stabilizing agent to prevent the unwanted agglomeration of colloids. Furthermore, the chemically synthesized metal nanoparticles are expensive, hazardous to environment and require high energy consumption. Biological approaches using plant extracts for metal nanoparticles synthesis have been suggested as valuable alternative tool towards chemical methods.

It is understood that the variety of natural compounds that are present in plant extracts can cause irregularity in particle morphologies and shapes and in case of spherical particles wide distributions in particle diameters.

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