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GREEN NANOTECHNOLOGY AND NANOPARTICLES: AN ECO-FRIENDLY APPROACH

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ABSTRACT: The field of nanotechnology is one of the notable active analysis areas in modern material science. Recent advances in Nanoscience and nanotechnology have led to the development of nanoparticles, which ultimately decrease potential health and environment hazards. Interest in developing environmentally friendly procedures for the synthesis of metallic nanoparticles has been increased. The purpose is to minimize the negative impact of synthetic procedures, their accompanying chemicals, and derivative compounds. Nanoparticles produced by green technology are more superior when compared to those manufactured with physical and chemical methods based on it eliminates the use of most expensive chemicals and also use less energy along with formation of environmental byproducts. In the synthesis of metallic nanoparticles, natural resources have been used. The exploitation of different biomaterials for the synthesis of nanoparticles is considered a valuable approach in green nanotechnology. This review provides an overview of the mechanisms of green synthesis of metallic nanoparticles and their application.

INTRODUCTION: There have been enormous advancements in the arena of Nanotechnology within the recent years related to the green synthesis of nanoparticles using plant extracts, microorganisms and human genes. Green nanotechnology means the application of green chemistry and green engineering principles in the field of Nanotechnology. Nanoparticles can be synthesized using a variety of methods such as physical method, chemical method, biological method and hybrid method¹⁻³. The production of nanoparticles through conventional (physical and chemical) methods results in toxic by-products that are environmental hazards.

Additionally, these products cannot be used in medicine due to health-related issues⁴. Conventional methods can be used to produce nanoparticles in large quantities with defined sizes and shapes in a shorter period of time; however, these techniques are complicated, costly and outdated.

In recent years, there has been growing interest in the synthesis of environmentally friendly nanoparticles that do not produce toxic waste^{5, 6}. This can only be achieved through biological nature using biotechnological tools that are considered safe and ecologically good for fabrication as an alternative to conventional methods. Green nanotechnology is synthesizing the nanoparticles or nanomaterials using biological routes, as shown in **Fig. 1**, such as microorganisms, plants, viruses, or their by-products such as proteins and lipids. Nanoparticles produced by green technology are far superior to those manufactured with physical and chemical methods based on it eliminates the use of

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expensive Chemicals, consumes less energy and generates environmental friendly by-products⁷.

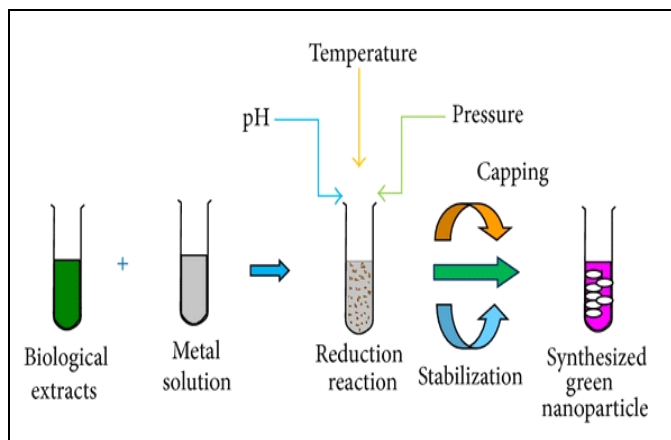


FIG. 1: BIOLOGICAL SYNTHESIS OF METAL NANOPARTICLES

Approaches for the Synthesis of Nanoparticles: Metal particle synthesis typically takes place in one of two ways: top-down or bottom-up, as shown in Fig. 2. The top-down approach uses an external force to pressure bulk materials, eventually causing these materials to break down into smaller components by means of mechanical, chemical, or some other energy sources. A bottom-up approach takes place in a reverse tactic, growing precursor particle size by using chemical reactions to combine atomic or molecular species. It should be noted that the top-down approach is considered to be a physical method while the bottom-up approach is chemical, although both approaches can be applied in a range of states, including liquid, solid, gas, supercritical fluids, or vacuum⁸.

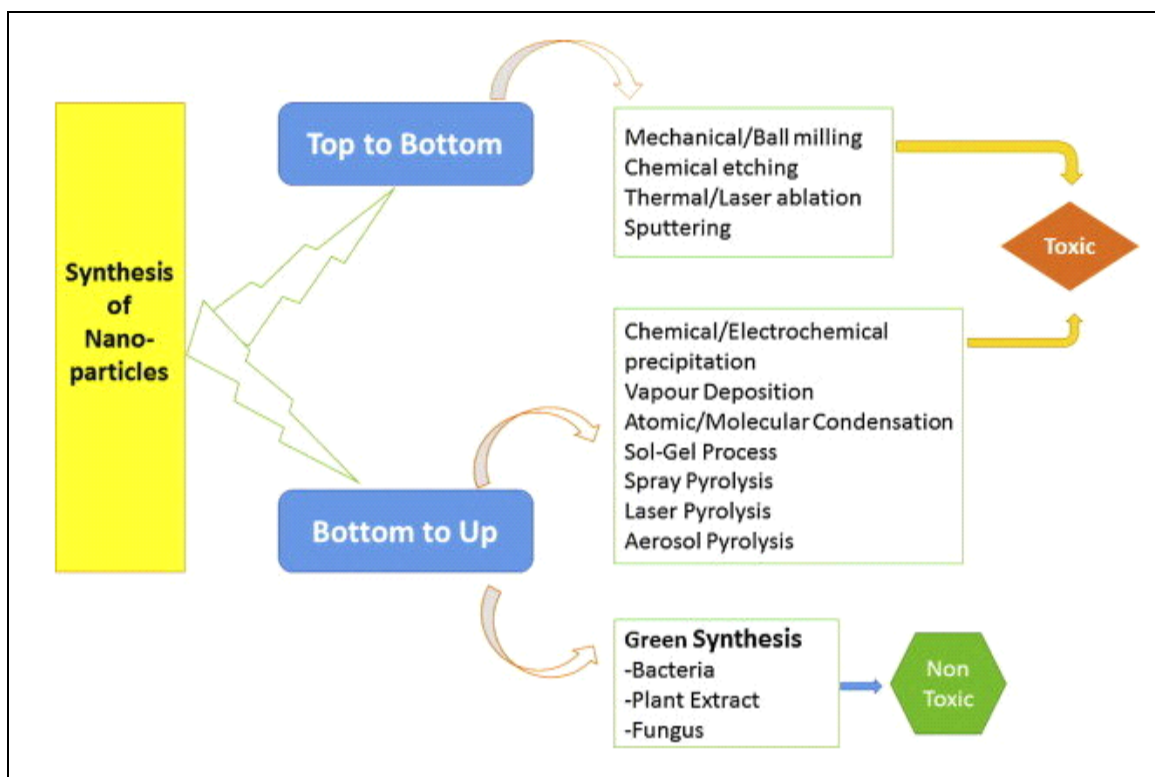


FIG. 2: DIFFERENT APPROACHES FOR SYNTHESIS OF METAL NANOPARTICLES

Green Synthesis of Metal Nanoparticles:

1. Micro-organisms Based Mechanism: There are different mechanisms for the formation of nanoparticles using different microorganisms. First metallic ions are captured on the surface or inside the microbial cells, and then these arrested metal ions are reduced into metal nanoparticles by the action of enzymes. The two key aspects in the biosynthesis of nanoparticles are NADH (Nicotinamide Adenine Dinucleotide) and NADH-dependent nitrate reductase. Nonetheless,

The bioreduction mechanisms associated with the production of metal salts and the resulting metal nanoparticles formed by microorganisms remain unexplored⁹.

- **Bacteria:** Bacterial species have been widely utilized for commercial biotechnological applications such as bioremediation, genetic engineering, and bioleaching. Bacteria possess the ability to reduce metal ions and are momentous candidates in nanoparticles preparation.

For the preparation of metallic and other novel nano-particles, a variety of bacterial species are utilized. Prokaryotic bacteria and action mycetes have been broadly employed for synthesizing metal/metal oxide nanoparticles. The bacterial synthesis of nanoparticles has been adopted due to the relative ease of manipulating the bacteria. Some examples of bacterial strains that have been extensively exploited for the synthesis of bio-reduced silver nanoparticles with distinct size / shape morphologies include: *Escherichia coli*, *Lactobacillus casei*, *Bacillus cereus*, *Aeromonas* sp. SH10 *Phaeocystis antarctica*, *Pseudomonas*

proteolytica, *Bacillus amyloliquefaciens*, *Bacillus indicus*, *Bacillus cecembensis*, *Enterobacter cloacae*, *Geobacter* spp., *Arthrobacter gangotriensis*, *Corynebacterium* sp. SH09, and *Shewanella oneidensis*. Likewise, for the preparation of gold nanoparticles, several bacterial species (such as *Bacillus megaterium* D01, *Desulfovibrio desulfuricans*, *E. coli* DH5a, *Bacillus subtilis* 168, *Shewanella alga*, *Rhodopseudomonas capsulate* and *Plectonema boryanum* UTEX 485) have been extensively used. Information on the size, morphology, and applications of various nanoparticles is summarized in **Table 1**.

TABLE 1: SYNTHESIS OF METALLIC NPS FROM VAR

S. no.	Species	Nanoparticles	Size (nm)	Morphology	Application	Reference
1	<i>Bacillus cereus</i>	Silver	20-40	Spherical	Anti- bacterial activity	10
2	<i>Pseudomonas proteolytica</i> , <i>Bacillus cecembensis</i>	silver	6-13	Spherical	Anti -bacterial activity	11
3	<i>Lactobacillus casei</i>	Silver	20-50	Spherical	Drug delivery, cancer treatment, bio labeling	12
4	<i>Klebsiella pneumonia</i> , <i>Escherichia coli</i> , <i>Enterobacter cloacae</i>	Silver	28-122	Spherical	Optic receptors, anti -microbial agent	13
5	<i>Bacillus indicus</i>	Silver	-	-	Anti -microbial agent	14
6	<i>Plectonema boryanum</i> UTEX 485	Gold	10-25	Cubic, octahedral	-	15
7	<i>Bacillus subtilis</i> 168	Gold	5-50	Hexagonal, octahedral	-	16
8	<i>Bacillus megaterium</i> D01	Gold	<25	Spherical	Catalysis, bio-sensing	17
9	<i>Shewanella alga</i>	Gold	10-20	Triangular	-	18
10	<i>E. coli</i> DH 5a	Gold	8-25	Spherical	Direct electrochemistry of hemoglobin	19
11	<i>Desulfovibrio desulfuricans</i>	Gold	20-50	Spherical	Catalysis	20
12	<i>Rhodopseudomonas capsulate</i>	Gold	10-20	Triangular	Cancer hyperthermia	21
13	<i>Magnetospirillum magneto-Tactium</i>	Iron oxide	47	-	-	22
14	<i>Aquaspirillum magnetotacti- Cum</i>	Iron oxide	40-50	Octahedral prism	-	23
15	<i>Shewanella oneidensis</i>	Uranium oxide	1-5	-	-	24
16	<i>Klebsiella aerogenes</i>	Cadmium sulphide	20-200	-	-	25
17	<i>E. coli</i>	Cadmium sulphide	2-5	Wurtzite structure	Fluorescent labels	26
18	<i>Rhizopus nigricans</i>	Silver	35-40	Round	Bactericidal, catalysis	27
19	<i>Aspergillus niger</i>	Silver	20	Spherical	Anti-bacterial agent	28
20	<i>Verticillium luteoalbum</i>	Gold	<10	Triangular, hexagonal	Optics, sensor, coatings	29
21	<i>Aspergillus terreus</i>	Zinc oxide	8	Spherical	Catalysis, bio-sensing, drug delivery, diagnostics	30
22	<i>Aspergillus flavus</i> TFR7	Titanium dioxide	12-15	Spherical	Plant nutrient fertilizer	31
23	MKY3	Silver	2-5	Hexagonal	Coatings for solar energy absorption	32
24	<i>Saccharimycetes cerevisiae</i>	Gold, silver	4-15	spherical	Catalysis	33

• **Fungi:** Fungi-mediated biosynthesis of metal/metal oxide nanoparticles is also a very efficient process for the generation of mono-dispersed nanoparticles with well-defined morphologies. They act as better biological agents for the preparation of metal and metal oxide nanoparticles, due to the presence of a variety of intracellular enzyme. Competent fungi can synthesize larger amounts of nanoparticles compared to bacteria. Moreover, fungi have many merits over other organisms due to the presence of enzymes/proteins/reducing components on their cell surfaces. The probable mechanism for the formation of the metallic nanoparticles is enzymatic reduction (reductase) in the cell wall or inside the fungal cell. Many fungal species are used to synthesize metal/metal oxide nanoparticles like

silver, gold, titanium dioxide and zinc oxide, as discussed in **Table 1**.

2. Plant Extract Based Mechanism: For a long time, it has been known that plants have the potential for biological reduction of metallic ions and hyper-accumulation. Because of such remarkable properties, plants have been considered a more environmentally friendly biological method for synthesis of metallic nanoparticles, and also useful for detoxification applications. Plant extracts contain various bioactive, such as alkaloids, proteins, phenolic acids, sugars, terpenoids and polyphenols, which have been found to have an important role in first reducing and then stabilizing the metallic ions, as shown in **Fig. 3**.

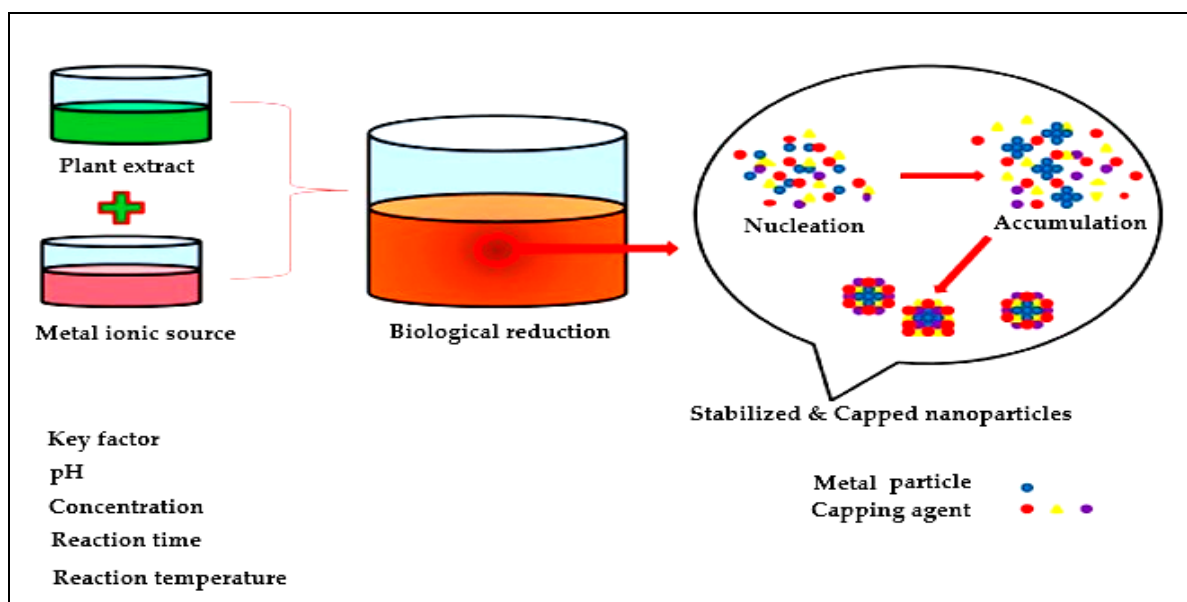


FIG. 3: BIOSYNTHESIS OF NANOPARTICLES USING PLANT EXTRACT

The shape and size of nanoparticles mainly depend on the variation in composition and concentration of active biomolecules of different plants, and their interaction with the aqueous metal ions. Especially in the chemical and biological synthesis of nanoparticles, the aqueous metal ion precursors from metal salts are reduced, which results in a colour change of the reaction mixture and provides a quantitative indication of nanoparticle formation. More importantly, the nanoparticles synthesized from reducing agents may show general toxicity, engendering serious concern for developing environmentally friendly processes. The process of the formation of nanoparticles begins by mixing a metal-salt solution with a sample of plant extract.

During the synthesis of nanoparticles, biochemical reduction of the salt solution starts immediately and the change in colour of the reaction mixture indicates the formation of nanoparticles.

During synthesis, initially there is an activation period process in which metal ions are converted to zero-valent state from their mono or divalent oxidation states, so that the nucleation of such reduced metal atoms takes place. Furthermore, the process of nanoparticle synthesis is followed by the integration of smaller neighboring particles to form larger nanoparticles, which are thermodynamically stable, and, subsequently, the metal ions are reduced biologically.

In this way, growth progresses and nanoparticles aggregate to form a variety of shapes such as spheres, cubes, triangles, rods, wires, hexagons, and pentagons. In the final stage of the process, the ability of plant extract to stabilize the nanoparticle finally determines its stable morphology. Significantly, the quality, size, and morphology of the nanoparticles are influenced by properties of the plant extracts; mainly its concentration, reaction time, metal salt concentration, reaction solution pH, and temperature ³.

Applications:

1. Anti-microbial Activity: Various studies have been carried out to ameliorate antimicrobial functions because of the growing microbial resistance towards common antiseptic and antibiotics. According to in vitro antimicrobial studies, the metallic nanoparticles effectively obstruct several microbial species.

The antimicrobial effectiveness of the metallic nanoparticles depends upon two important parameters like material employed for the synthesis of the nanoparticles and the particle size of the metal nanoparticle. Silver nanoparticles are the most admired inorganic nanoparticles, and they are utilized as efficient antimicrobial, antifungal, antiviral and anti-inflammatory agents. The antimicrobial potential of silver nanoparticles can be described in the following ways:

- a) Denaturation of the bacterial outer membrane.
- b) Generation of pits/gaps in the bacterial membrane leading to fragmentation of the cell membrane.
- c) Interactions between silver nanoparticles and disulphide or sulfhydryl groups of enzymes which disrupt the metabolic processes and leads to death ⁹.

TABLE 2: GREEN SYNTHESIS OF METALLIC NPS FROM VARIOUS PLANT EXTRACTS

S. no.	Species	Nanoparticle	Size (nm)	Morphology	Applications	Reference
1	<i>Aloe barbadensis</i> Miller (Aloe vera)	Gold & silver	10-30	Spherical, triangular	Cancer hyperthermia	35
2	<i>Aloe barbadensis</i> Miller (Aloe vera)	Indium oxide	5-50	Spherical	Solar cells, gas sensors	36
3	<i>Acalypha indica</i>	silver	20-30	Spherical	Anti-bacterial activity	37
4	Apiinextracted from henna leaves	Silver & gold	39	Spherical, triangular	Cancer hyperthermia, IR-absorbing optic coating	38
5	<i>Avena sativa</i> (oat)	gold	5-20	Rod-shaped	-	39
6	<i>Azadirachta indica</i> (neem)	Gold, Silver & silver-gold alloys	5-35, 50-100	Spherical, triangular, hexagonal	Remediation of toxic metals	40
7	<i>Camellia sinensis</i> (black tea leaf extracts)	Gold & silver	20	Spherical, prism	Catalyst, sensors	41
8	<i>Brassica juncea</i> (mustard)	Silver	2-35	Spherical	-	42
9	<i>Cinnamomum camphora</i> (camphor tree)	Gold & silver	55-80	Triangular, spherical	-	43
10	<i>Carica papaya</i> (papaya)	Silver	60-80	Spherical	-	44
11	<i>Citrus limon</i> (lemon)	Silver	<50	Spherical	-	45
12	<i>Coriandrum sativum</i> (coriander)	Gold	6.75-57.91	Spherical, triangular, decahedral	Drug delivery, tissue/tumor imaging	46
13	<i>Cymbopogon flexuosus</i> (lemongrass)	Gold	200-500	Spherical, triangular	IR-absorbing optics coating	47
14	<i>Cycas sp.</i> (cycas)	Silver	2-6	Spherical	-	48
15	<i>Diospyros kaki</i> (persimmon)	Bimetallic gold & silver	50-500	Cubic	-	49
16	<i>Emblica officinalis</i> (Indian Gooseberry)	Gold & silver	10-20 & 15-15	-	-	50
17	<i>Eucalyptus citriodora</i> (neelagiri)	Silver	20	Spherical	Anti-bacterial activity	51
18	<i>Eucalyptus hybrid</i>	Silver	50-150	Crystalline,	-	52

19	<i>Garcinia mangostana</i> (mangosteen)	Silver	35	spherical Spherical	Anti-microbial agent	53
20	<i>Gardenia jasminoides Ellis</i> (gardenia)	palladium	3-5	-	Nano catalyst	54
21	<i>Medicago sativa</i> (alfalfa)	Iron oxide	2-10	crystalline	Cancer hyperthermia, drug delivery	55
22	<i>Sedum alfredii</i> Hance	Zinc oxide	53.7	Hexagonal, wurtzite	Nano electronics	56
23	<i>Ocimum sanctum</i> (tulsi; leaf extract)	Gold & silver	30 & 10-20	Crystalline, hexagonal, triangular & spherical	Bio-labeling & bio-sensors	57
24	<i>Pear fruit extract</i>	Gold	200-500	Triangular, hexagonal	Catalyst, bio-sensors	58
25	<i>Terminalia catappa</i> (almond)	Gold	10-35	Spherical	Biomedical field	59

2. Catalytic Activity: Metal nanoparticles play a notable role in catalysis application. Specifically, metal nanoparticles with high surface area and more active sites promote faster reactions and increase product yield.

These particles can be broadly divided into two main groups: noble-metal (Au, Pt, Ag, etc.) - supported metal nanoparticles and non-noble-metal (Fe, Cu, Ni, Co, etc.)-based nanoparticles **Table 3**.

TABLE 3: VARIOUS METAL NANOPARTICLES SYNTHESIZED AND THEIR CATALYTIC PROPERTIES ⁶⁰⁻⁸⁸

S. no.	Metal Nanoparticles	Catalysts
1	Molybdenum–Bismuth Bimetallic Chalcogenide Nanoparticles	CO ₂ to Methanol
2	Platinum–Antimony Tin Oxide Nanoparticles	Cathode catalysis for direct methanol fuel cells via an oxygen reduction reaction (ORR)
3	Cobalt Oxide Nanocrystals	Cobalt Oxide Nanocrystals with CoO nanocrystals coupled with carbon nanotubes as catalysts for chlor–alkali electrolysis systems
4	Iron Oxide Magnetic Nanoparticles	Catalytic oxidation of phenolic and aniline chemical compounds (Fe ₃ O ₄)
5	Zirconia Nanoparticles	Catalysts for sol–gel synthesis, aqueous precipitation, thermal decomposition, and hydrothermal synthesis
6	Tin Oxide Nanoparticles	Catalysts for the reduction and photo degradation of organic compounds
7	Silver Nano flakes	Silver Nano flakes on molybdenum sulfide (MoS ₂) films for the catalytic oxidation of tryptophan
8	Tungsten Oxide Nanoparticles	Hetero-nanostructured photo electrodes synthesized via the atomic layer decomposition of tungsten oxide (WO ₃) combined with an oxygen evolving catalyst
9	Cuprous Oxide Nanoparticles	Cuprous oxide nanoparticles on reduced graphene oxide (RGO) for usage as an efficient electro catalyst in ORR
10	Titanium Dioxide Nanoparticles	Carbon modified titanium dioxide (TiO ₂) can be used in daylight photo catalysis. TiO ₂ nanoparticles and photo catalytic performance measured under a medium-pressure mercury UV lamp.
11	Iridium Oxide Nanoparticles	Ligand-free iridium oxide nanoparticles for high electro catalytic activity. Reusable catalyst in 1-n-butyl-3-methylimidazolium hexafluorophosphate room-temperature ionic liquid for the biphasic hydrogenation of olefins under mild reaction conditions.
12	Palladium Nanoparticles	Catalytic formic acid oxidation can take place through the oleylamine-mediated synthesis of palladium nanoparticles
13	Gold Nanoparticles	Gold nanoparticles help to create an active catalyst for the reduction of nitroarenes in an aqueous medium when placed on top of nanocrystalline magnesium oxide. Catalytic CO oxidation can occur under the presence of gold nanoparticles

14	Elemental Sulfur Nanoparticles	Catalysis occurred when elemental sulfur nanoparticles were placed on chromium (VI) with a sulfide reaction
15	Silica Titanium Oxide Nanoparticles	Exhibit catalytic properties that can be tested for the oxidation of saturated and unsaturated hydrocarbons
16	Silica Vanadium Oxide Nanoparticles	Exhibit catalytic properties that can be tested for the oxidation of saturated and unsaturated hydrocarbons
17	Dendrimer-Encapsulated Metal Nanoparticles	Dendrimer can be used to control the placement and other properties of metal nanoparticles for their usage as catalysts
18	Imidazolium Metal Nanoparticles	Metal nanoparticles immersed in imidazolium ionic liquids exhibit unique catalytic properties
19	Zinc Oxide Nanoparticles	Semiconducting zinc oxide nanowires made from nanoparticles can be tested for photoluminescence properties through catalytic growth
20	Silver Nanoparticles	Silver nanoparticles can be used as chemically stable nanoparticles with no environmentally harmful effects on microbes under anaerobic conditions
21	Magnesium Oxide Nanoparticles	EXAFS spectroscopy shows that magnesium oxide is a precursor of a type of mononuclear complex of gold that can catalyze ethane hydrogenation
22	Calcium Oxide Nanoparticles	Calcium oxide nanoparticles can be catalyzed with pyridines in an aqueous ethanol medium
23	Strontium-Doped Zinc Oxide Nanoparticles	Can be created with the sol-gel method, and tests showed successful photocatalytic activity of these nanoparticles when removing methylene blue (MB)
24	Titanium Carbide Nanoparticles	Such nanoparticles can support platinum catalysts for methanol electrooxidation in acidic mediums
25	Cerium Oxide Nanoparticles	These nanoparticles with their catalytic properties can be used for a variety of biomedical applications
26	Antimony-Vanadium Oxide Catalysts	Catalysts prepared are selective for acrylonitrile formation
27	Metal Nanoparticles at Mesoporous N-doped Carbons and Carbon Nitrides	Metal nanoparticles at Mesoporous N-doped carbons and carbon nitrides held in Mott-Schottky heterojunctions can function as efficient catalysts
28	Metal Nanoparticles	Catalytic properties of metal nanoparticles can be used in the synthesis of single-walled carbon nanotubes

3. Removal of Pollutant Dyes: Cationic and anionic dyes are a main class of organic pollutants used in various applications. Organic dyes play a very imperative role due to their gigantic demand in paper mills, textiles, plastic, leather, food, printing, and pharmaceutical industries. In textile industries, about 60% of dyes are consumed in the manufacturing process after which 15% of dyes are wasted and are discharged into the hydrosphere, they represent significant source of pollution. Dyes produce undesirable turbidity in the water, which will reduce sunlight penetration and leads to the resistance of photochemical synthesis and biological attacks to marine and aquatic life⁹. The need for hygienic and safe drinking water is increasing day by day. Considering this fact, the use of metal and metal oxide semiconductor nanoparticles for oxidizing toxic pollutants has become of great interest in recent material research fields.

4. Heavy Metal Ion Sensing: Heavy metals (like Ni, Cu, Fe, Cr, Zn, Co, Cd, Pb, Hg) are well known for being pollutants in air, soil and water. There are

innumerable sources of heavy metal pollution such as mining waste, vehicle emissions, natural gas, paper, plastic, coal, and dye industries. Some metals (like lead, copper, cadmium, and mercury ions) show enhanced toxicity potential even at the traces of ppm levels. Therefore, identifying toxic metals in the biological and aquatic environment has become a vital need for proper remedial processes. Due to the tunable size and distance-dependent optical properties of metallic nanoparticles, they have been preferably employed for the detection of heavy metal ions in polluted water systems⁸⁹⁻⁹⁰. The advantages of using metal nanoparticles as colorimetric sensors for heavy metal ions in environmental systems/samples include simplicity, cost, effectiveness and high sensitivity at sub-ppm levels.

CONCLUSION: Green synthesis of metal and metal oxide nanoparticles has been a highly attractive research area over the last decade. The use of nanoparticles in the medical, food, pharmaceutical and agricultural industries has garnered a great deal of interest, with a focus on

development of more convenient methods using green biotechnology tools for production of eco-friendly, non-toxic, and environmentally benign nanoparticles. Numerous kinds of natural resources like plants, bacteria, fungi, yeast and plant extracts have been employed in the synthesis of metallic nanoparticles. Among them, plant extract has been proven to possess high efficiency as stabilizing agent and reducing agent for the synthesis of controlled materials.

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