

# Evaluation of Metal Nanoparticle Synthesis Methods: Green Chemistry and Catalytic Approaches

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## Article Info

Journal of Computational Intelligence in Materials Science (<https://anapub.co.ke/journals/jcims/jcims.html>)

Doi: <https://doi.org/10.53759/832X/JCIMS202402014>.

Received 10 September 2024; Revised from 02 November 2024; Accepted 12 December 2024.

Available online 26 December 2024.

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**Abstract** – One of the twelve tenets of Green Chemistry that has shown its worth over and over again is catalysis. When it comes to creating and developing novel chemical processes, "green chemistry" prioritizes hazard reduction as the primary performance metric, with the goal of eliminating or drastically reducing the usage or synthesis of hazardous compounds throughout the whole process. Nanocatalysis, thanks to its high activity, selectivity, and productivity, has emerged as a new scientific discipline in recent years. Nanocatalysts are distinguished from bulk materials by their unusual characteristics, which are the result of structural and electrical changes brought about by their nanoscale size, shape, and extraordinarily high surface area to volume ratio. Electronics and the creation of composite materials are only two examples of the many applications for nanoparticles. Among them, metal nanoparticles stand out owing to their diversified selectivity, surface area, morphological flexibility, and exceptional catalytic activities. In this article, we will provide an evaluation of the different ways that metal nanoparticles may be synthesized, focusing on eco-friendly methods. The industrialization of the enhanced metal nanostructures as effectual catalysts are also covered, and the catalytic effectiveness of the most utilized metal nanoparticles is examined.

**Keywords** – Green Chemistry, Metal Nanoparticles, Nanocatalysts, Nanotechnology, Mechanochemical Processing.

## I. INTRODUCTION

With environmental issues worsening at an alarming rate, it is more important than ever to develop effective ways to stop more damage to the planet. In particular, methods that minimize costs and have a minimal impact on the environment are being prioritized. In contrast, multifunctional materials for nanoscale future technologies have advanced rapidly thanks to the revolution in nanotechnology and materials science. Research in green chemistry for the nano-sized particles synthesis provides a promising foundation for the creation of environmentally friendly, cost-effective, recyclable, and long-lasting materials for use in a wide variety of industries [1]. When used in an experiment, catalysts reduce the activation energy, allowing the reaction to proceed to completion without the need for additional energy—a resource that has lately become more valuable. This means that the reactions would be more productive under milder circumstances, such as low temperatures and pressures. This has the dual benefit of increasing efficiency and reducing expenses significantly. With their superior surface area, durability, and stability, nanocatalysts produced from nanoparticles (NPs) stand out among a broad spectrum of catalysts. The employment of distinct capping and stabilizing agents, such as ligands (amines, phosphines, thiols), ammonium salts (surfactants), polymers (block-copolymers, polyvinyl pyrrolidone, polyvinyl alcohols), ions, dendrimers (polyamidoamine), and polyoxoanions, among others, allow for nanoparticle synthesis process identified in **Fig 1**.

From basic laboratory research to industrial chemical processes, catalysis is at the center of innumerable procedures. Using catalytic reagents allows for a reduction in the required temperature for a transformation, a decrease in the amount of waste generated from the reaction, and an increase in the reaction's selectivity, all of which contribute to the development of a more environmentally friendly technology. Assaf et al. [2] outlined a set of twelve guiding principles in 1998, which form the foundation of the field of "green chemistry." These principles aim to minimize or eliminate the use of chemicals and chemical processes that have a detrimental effect on the environment. Building the best possible catalysts is a key topic in green chemistry. Under these standards, catalytic reagents (those that are as selective as feasible) should be preferred above stoichiometric ones. Catalytic reagents need just trace quantities to carry out a reaction repeatedly,

whereas stoichiometric reagents require large amounts and may only be employed once. All of green chemistry's twelve tenets revolve on this idea of mimicking nature's processes [3].

Using microbes and/or enzymes to perform environmentally secure processes is clearly possible because to the clear cues provided by nature. Humans rely on a wide range of value-added goods, including pharmaceuticals, specialty chemicals, polymers, fibers, fuels, paints, and lubricants, and many of them would not be possible without the use of catalyst. Catalysis provides the mechanism for chemical reactions, allowing for the economically feasible production of useful substances. Catalysts provide for more cost-effective, environmentally friendly, and long-term production methods. Softer catalysts such as phase transfer zeolites, catalysts, e.g., crown ethers, are employed in industrial settings than heavy metal catalysts, which are often not recoverable from the system. Enzymes catalysis is the most effective and environmentally friendly kind of catalysis in nature, beating out the other two well-known types, heterogeneous and homogeneous catalysis. There are advantages and disadvantages to both heterogeneous and homogeneous catalysis, which is why a novel catalytic system is desperately needed; ideally, it would be active such as homogeneous catalysis and also be readily detectable like a heterogeneous catalyst.

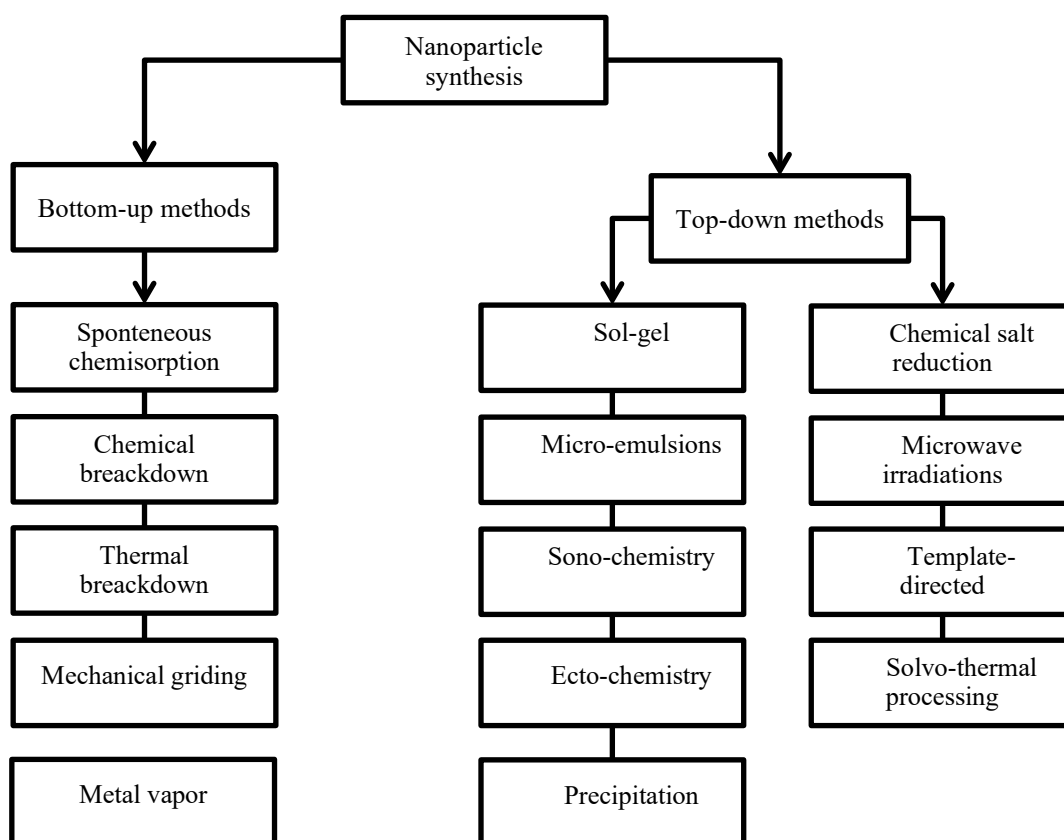


Fig 1. Methods for preparing nanoparticles

According to Wang et al. [4], there are benefits to both heterogeneous and homogeneous catalytic systems, and nanocatalysts provide a middle ground. One advantage of using a nanocatalytic system is that it enables very efficient chemical transformations with high selectivity and high yields of valuable products that can be easily separated from the catalyst and recovered. Most importantly, a catalyst must be capable of being recovered from the system in order to be considered for use in green chemical production processes [5]. Nanoparticles' small size and large surface area allow for much closer interaction between the reactants and the catalyst (Similar phenomena to homogeneous catalysis have been seen). This behavior is similar to heterogeneous catalysis because the catalyst is insoluble in the reaction solvent, making it easy to isolate the catalyst from the reaction mixture.

Catalysts at the nanoscale allow for better interaction between the reactant and the catalysts since their active surfaces are more exposed than those of bulk catalysts [6]. A bigger area for interactions to occur at a catalytic site results in a quicker speed of reaction and, thus, increased catalytic activity. As the surface area increases, so does the number of reactive sites, which in turn speeds up and improves the efficiency of the reaction. Another advantage is that the catalysts are hydrophobic in the reaction media, which makes it much easier to separate and recycle the nanocatalysts. Despite these advantages, however, very little research has been conducted in this field because of the difficulties associated in isolating the catalysts from the end product. Catalysts are used in many branches of research and technology due to their appealing properties. In recent years, nanoparticles made of metals have been recognized for their usefulness in a variety of catalytic

applications. Several different applications may be found for metal nanoparticles, including improving the thermal endurance of nanofluids and creating magnetic materials.

This paper provides an evaluation of the different ways that metal nanoparticles may be synthesized, focusing on eco-friendly methods. The rest of the paper is organized as follows: Section II focuses on a discussion about metal nanoparticles, providing a graphical depiction of the number of articles dealing with the extent of green catalysts. Section III is about the synthesis of metal nanoparticles where a discussion of mechanochemical processing to the synthesis of nanoparticles, and Nano-catalysts is provided. Section IV focuses on the application of metal nanoparticles in catalysis. Lastly, Section V draws final remarks to the paper.

## II. METAL NANOPARTICLES

Nanoparticles, often called ultrafine particles, are typically defined as having sizes between 1 and 100 nm. This class includes fibers and tubes with a diameter of 100 nm or less in a single dimension; however the term is often used to denote the particles that have a size greater than 500 nm. Metal particles less than 1 nm should more accurately be called atom clusters. Nanoparticles are distinguished from the microparticles that range from 1 nm to 1000 nm), "fine particles" (100nm to 2500 nm), and "coarse particles" (more than 2500 nm) by their colloidal features and ultrafast optical features or electrical properties (range from 2500 nm to 10,000 nm). Colloidal particles, on the other hand, are assumed to settle because they are less susceptible to the Brownian motion and have a size range of 1 to 1000 nm.

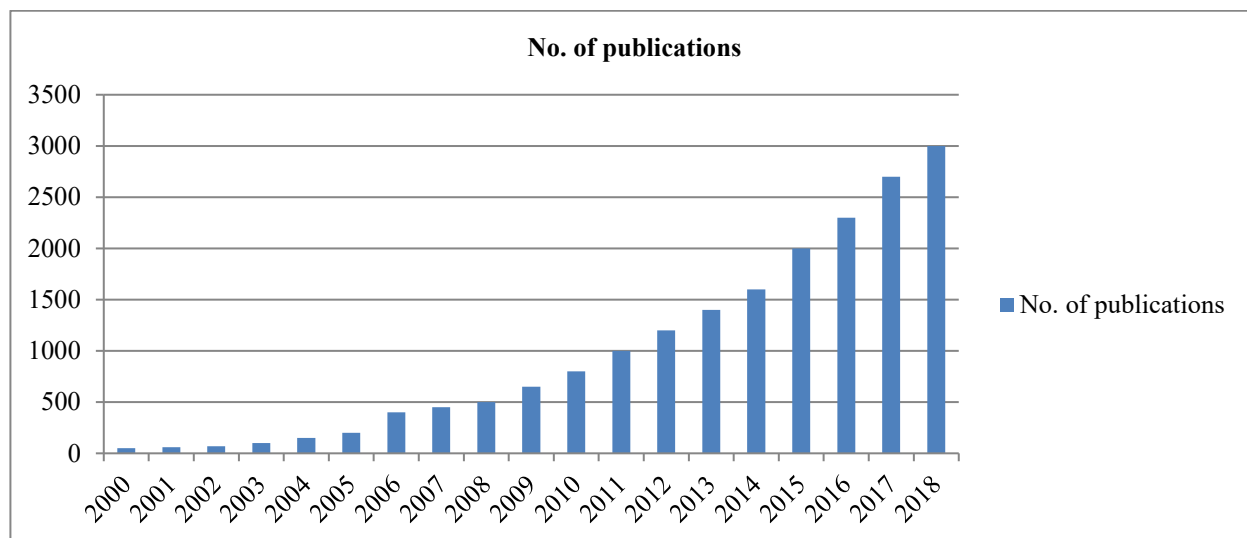
Due to their small size, nanoparticles can only be seen using optical microscopes or electron microscopes integrated with lasers. While larger particles in suspensions tend to disperse all or some light affecting them, nanoparticle suspensions in transparent fluids may also be transparent. Nanoparticles are so tiny that they may go through typical fibers, e.g., ceramic candles, rendering liquids separation challenging. Due to this, nanofiltration techniques must be used. Nanoparticles often display remarkably different properties than larger, similarly sized particles of similar substances. As the normal atom has size ranging from 0.15 nm to 0.6 nm, many materials composing nanoparticles are found within some atomic diameters of its sizing surface. Hence, it is possible that the top layer's attributes will take priority over the bulky components. This effect is enhanced for nanoparticles, which have been dispersed in liquids with distinct composition, since the interaction between the interface materials become more significant. As a result of nanoparticles being so common, scientists from a wide range of disciplines are interested in studying them. This includes the chemical, physical, geological, and biological sciences. Often, their activities defy description at the bulk material or the atomic or molecular scale. Although they do contribute to air pollution, they are also necessary components of many modern conveniences. Nanotechnology may be used to create custom-made nanoparticles.

Although the concentration of point defects in nanoparticles is often lower than in bulk materials, a wide range of dislocations may still be seen using a high-resolution electron microscope [7]. Due to dislocation mechanics and surface structure variations, nanoparticles' mechanical properties deviate from those of the bulk materials. Most nanoparticles comprising of non-spherical geometric properties (such as rods, prisms and cubes) exhibit shape- and size-dependent physical and chemical features (anisotropy). These non-spherical nanoparticles of metals like Silver (Ag), Gold (Au) and Platinum (Pt) are finding use in many different areas due to their exceptional optical properties. Colloidal solutions made using non-spherical nanoprisms have larger effectual deeper colors, and cross-sections. By adjusting the particle's geometry, resonance frequencies may be changed, allowing for use in a wide variety of fields, including nanotechnology, biomolecular assays, trace metal detection, and molecular labeling. Anisotropic nanoparticles respond differently to polarized and unpolarized light in a number of ways, including absorption behavior and particle orientation.

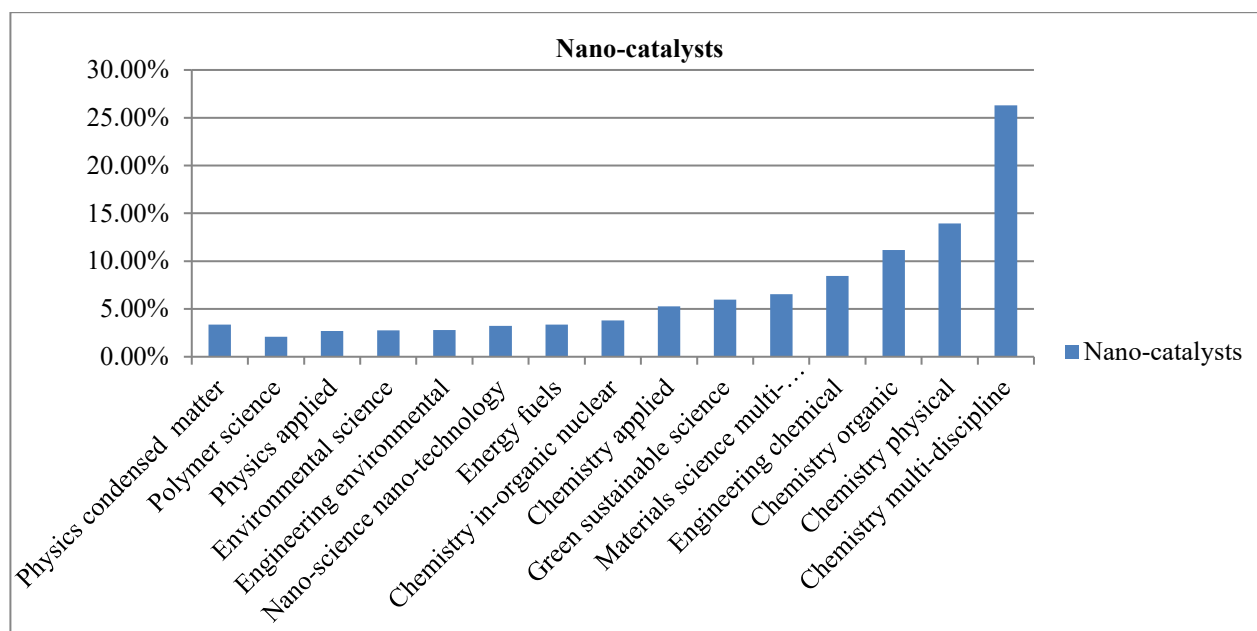
Many diagnostic and therapeutic methods include the use of metallic NPs [8]. Quantum dots, gold NPs and magnetic NPs are just a few examples of metallic NPs that find therapeutic use as drug delivery carriers or bioimaging agents. Metallic NPs are effective carriers because of their physiochemical characteristics, high reactivity, high stability, photothermal, and plasmonic capabilities. Hence, plasmonic NPs, such as gold NPs, have been employed in photothermal treatment to eradicate brain tumor cells. Bioimaging applications have made use of magnetic iron NPs and quantum dots. For these reasons, certain metallic NPs have found utility in the field of theranostics, where they may serve both therapeutic and diagnostic purposes. To treat neurological disorders, scientists have modified engineered metal NPs by synthesizing them with specific surface changes that change their size, shape, and the presence of ligands. Small enough to pass across the BBB, these designed metallic NPs may be modified with ligands to selectively target disease-associated cells. Translocation of transferrin-conjugated nanoparticles across the blood-brain barrier (BBB) and their efficacy in the management of glioblastoma have both been reported recently. Magnetoferritin, a form of ferritin linked to iron oxide magnetic Nanoparticles, has been shown to pass the blood-brain barrier and may be useful in the treatment of brain tumors.

Metal nanoparticles are synthesized from organic and inorganic components that are mixed with different metals on a nanometer (1-100 nm) scale. They include everything from semiconductors to alkali metals. Metal nanoparticles are often employed as green catalysts because they have a high ratio of surface area to volume when contrasted to the bulk material. This encourages the formation of solid bonds, which in turn makes it easier for reactants to attach to metal sites and for chemical reactions to proceed quickly. Along with nanoparticles, layered transition metal dichalcogenides (TMDs) were discovered to function as rare metals. The elements molybdenum (Mo), tungsten (W), selenium (Se), boron (B), and tellurium (Te) are all examples of transition metal dichalcogenides (TMDs) [9]. TMDs are of significant interest precisely

because of their unique features such as their superior optical and electrical capabilities and huge energy density. **Fig 2** depicts the rise in the number of articles dealing with the extent of green catalysts in **Fig 3** and metallic nanoparticles, demonstrating their increasing significance in many research areas.



**Fig 2.** Quantitative analysis of articles from 2000-2018



**Fig 3.** The extent of green catalysts

Similar attention has been focused on metal nanoparticles because of their unique characteristics and increased catalytic activity. Furthermore, investigations in this area have garnered a lot of interest and are providing food for thought in the design of cutting-edge catalysts for use in both basic research and practical applications in industry. Metal nanoparticles, due to their adaptability and relatively low cost to synthesize, are poised to become ubiquitous in future technology. The promising catalytic activity and simple scalability of metal nanoparticles are at the heart of their meteoric rise in popularity. High surface areas and finely controllable porosities are desirable characteristics in a catalytic support material. To further enhance the catalytic characteristics, the electric charge fosters a synergetic interaction. Due to their one-of-a-kind properties, metal nanoparticles have found increasing use in fields including optics, medicine, technology, and biomedicine. Nonetheless, surface contamination, the elimination of capping components, and aggregation of particles are examples of the most encountered issues. The major use of metal nanoparticles stem from their high boiling and melting points, high mechanical and thermal thermodynamic stability, high electrical thermodynamic properties, potent optical and magnetic properties, and low densities. The temperature stability of metal nanoparticles has a considerable influence on their usability. The discovery by Xu et al. [10] that amorphous silicon (a-Si) doped silver nanoparticles is more thermally stable opens up new applications for these particles.

### III. SYNTHESIS OF METAL NANOPARTICLES

#### *Mechanochemical Processing to the Nanoparticle Synthesis*

Nanoparticle production techniques are often divided into two categories: top-down and bottom-up (see **Fig 1**). Ultrafine powders are typically made by grinding down bulk raw materials into tiny particles, either in liquid medium, solid diluent, or air medium and top-down procedures are an extension of these conventional processes. The formation of nanoparticles from smaller components like atoms or molecules in a gas, solid or liquid medium is identified as a bottom-up technique. One example of a bottom-up strategy for synthesizing nanoparticles is mechanochemical processing.

The term "mechanochemical processing" is sometimes used interchangeably with "mechanical pulverisation" (top-down technique). In order to produce metallic nanoparticles, for example, one method is grinding the precursor components into a fine powder using a solid matrix, then heating the powder to transform it into metal oxides. Therefore, unless it results in chemical alterations in the precursor nanoparticles, milling is not a mechanical alloying process. The grinding action inherent in mechanochemical processing also lends credence to the misconception that it is a top-down method. When it comes to mechanochemical processing, grinding is solely engaged in the pulverization of raw reactant materials. Mechano-chemical processing relies on the application of mechanical energy to raw materials in order to trigger chemical reactions.

Reactant materials undergo repeated deformation, fracturing, and welding during ball or powder collision events. This ultimately results in the reactant components forming a nanoscale composite structure. Grain boundaries between adjacent reactant phases in the nanocomposite structure serve as the sites of initiation for chemical reactions. These three characteristics of reaction kinetics are especially impacted by this circumstance. To begin, reactant atoms can only go a short distance before being halted by the smaller grain sizes seen at the nanoscale. Second, the reactant nanocomposite has high leftover energy as radicals or structural flaws, which lowers the reaction threshold energy. Last but not least, new reaction surfaces are created when raw materials are continuously welded and cracked, creating new reactions. Mechanochemical processing allows for the induction of chemical processes that normally need high temperatures and extended heat treatment to take place at or near room temperature. If a chemical reaction does not complete itself during milling, it may be able to do so with post-milling thermal management at lower temperatures since the reactor threshold energy is significantly minimize during the process of mechanical alloying.

#### *Limitations and Advantages of Mechanochemical Nanoparticle Synthesis*

Zhu et al. [11] appreciate mechanochemical synthesis for the environmental benefits it is thought to provide. Making metal-oxide nanoparticles by mechanochemical processing offers potential for reducing our ecological footprint<sup>8,9</sup> since it does not need the use of organic solvents or high temperatures. Although various liquid-stage synthesis approaches employ solvents, vapour-stage syntheses employ organic precursors. Because to the quick reaction rate, it may be difficult to properly regulate the particle size distribution in water-based liquid-phase synthesis without the application of surfactants<sup>1</sup>. However, it is plausible that high-energy ball milling needs a lot of juice to get the job done. To evaluate the relative environmental advantages of different bottom-up techniques to producing metal-oxide nano-particles, a comprehensive life-cycle analysis is advised. Whereas standard solution approaches have a high E-factors and higher process mass capacity, organometallic specie mechano-synthesis has been considered to have a lower E-factor and reduced mass intensity.

Nanoparticles composed of a lower intensity of aggregation may be produced using mechanochemical techniques, which is still another advantage of these technologies. This is due to the fact that a solidified byproduct matrix establishes a physical obstruction between nanoparticles during the growth phase. The deficiency of solidified physical obstruction between nanoparticles during the growth phase of vapour- or liquid-phase generated nanoparticles may result to the agglomeration of particles. By utilizing liquid-stage synthesis processes, micelles and surfactants could be employed to minimize particle agglomeration, but this restricts how the nanoparticles' surfaces can be handled in the end product. Because particle aggregation is inhibited by the lack of a solidified barrier, synthesis in vapour or liquid phase should be carried out at very dilute conditions to get a high yield.

Moreover, mechanochemical synthesis has the potential to manufacture nanoparticles with uniform size and shape, and it is simple to implement and scale up [12]. Nevertheless, a homogeneity issue arises when liquid-phase activities are accelerated since the reactor environment is typically large compared to a beaker. The disadvantages of mechanochemical synthesis in compared to other methods are as follows:

- a) The by-product phase may introduce contamination, either from the milling balls or the milling containers;
- b) The final product can have poor crystallinity as a result of residual issues and amorphization stimulated by mechanical energy data. In contrast, the vapour-phase synthesising has the potential to produce ultra-pure metal-oxide nanoparticles. Nevertheless, vapour-phase synthesis enables the metal-oxide nanoparticles production with exceptional crystallinity because of the high temperature needed. Contaminants migration or particle agglomeration from the by-product stage into nanoparticles<sup>1</sup> are two potential side effects of post-milling annealing, which may improve the crystallinity of mechanochemically produced particles.
- c) The creation of byproducts that is difficult to isolate, such as extremely soluble metal oxides that dissolve in cleaning solutions. Due to the fact that  $B_2O_3$  is soluble in water and various organic solvents, the elimination

of a by-product stage should instead depend on re-routing or other physical processes rather than a washing process<sup>60</sup>.

### Synthesis of Different Nanocatalysts

It is crucial to investigate the toxicity of various nanocatalysts and the processes used to create them. It has been noted that factors such as particle size, surface chemistry, and shape affect metallic nanoparticles' toxicological and biological activity. In the recycling process, solubility levels and chemical make-up also matter a lot. Metal nanoparticles may be created using a number of techniques, each of which is tailored for a particular outcome and set of applications. Nonetheless, there are two main classifications of synthesis: chemical and physical. Examples of the physical strategy integrate FSP (flame spray pyrolysis), spray pyrolysis, unique machining, and electrospray. For example, the FSP method is ideal for industrial-scale synthesis of metal nanoparticles. In this method, metal salts are dissolved in water and sprayed onto a flame in the form of a fine mist. Metal salts condense into drops, and the resulting compounds are oxides of those metals. Oxides clump together, then the nanoparticles develop, and they are eventually collected. Spray pyrolysis starts when nanoparticles of a solution are subjected to high temperatures.

When the droplets as well as the precipitated solvent have evaporated, the precipitate is annealed, and the metallic nanoparticles are created. In addition to traditional physical methods, scientists have also experimented with a number of chemical methods for synthesizing metallic nanoparticles. Using biomaterials that are enzymatically active is a common approach. One such example is the synthesis of cadmium sulfide (CdS) metallic nanostructures from *Fusarium oxysporum*, which was described by Li et al. [13]. Creation of metal nanoparticles is a byproduct of the biological process of biomineralization, in which elements from the surrounding environment are transformed into useful compounds. The hot-injection method has obtained considerable attention as of late because of how effective it is. Despite its primary usage in nanocrystal development, the hot-injection synthesization approach displays the capacity to make more unvarying nanocrystals, offering methods to manufacture metallic nanoparticles evenly. Among the several well-known chemical procedures for producing uniformly sized gold nanoparticles, J. Turkevich's Turkevich method stands out.

The overall procedure is first reducing citrate at 100 C, then combining the reduced citrate with a gold hydrochlorate solution. Various particle sizes with controllable characteristics were achieved by adjusting the concentration of a citrate solution. The rapid nucleation process that characterizes this strategy essentially depletes the available gold ions. Particle size is also heavily influenced by temperature (i.e., the nucleation process is somewhat slow and hence the size distribution is rather wide at low temperatures). According to Qi and Wang [14], metallic nanoparticle size steadily decreased as the intensity of the surface-plasmon resonance rose. The dimension of gold nanoparticles shrunk as a consequence of maturation in the gastrointestinal system, and additional mono-dispersed nanoparticles were produced, based on the reverse Ostwald development model of evolution. Synthesized metal nanoparticles' characteristics may be modified more precisely using this method.

Also, a number of techniques were described, including substituting citrate buffers for citrate concentrations to control particle size and adding ethylene diamine tetra acetic acid to control the uniformity of the nanoparticles' shape. Many alternative environmentally friendly methods have been developed to produce metal nanoparticles in addition to the ones already listed. For instance, Vitamin B1 was used in a room-temperature process to generate palladium-based nanoparticles with varying morphologies. The manufacture of a silica nanocatalyst with a platinum (Pt) metal core was described by Huang and Tu [15]. High-temperature catalytic processes including ethylene hydrogenation and carbon monoxide oxidation were carried out with the help of the created nanocatalyst. Due to their lower toxicity and biodegradability, metal nanoparticles based on gold, copper, and iron have been the subject of much research. **Table 1** provides a summary of the many different types of current catalysts and the processes they are used for.

**Table 1.** Types of current catalysts and the processes

| Metal Nanoparticles   | Catalysts  |
|---|--|
| <b>Metal Nanoparticles</b>  | The manufacture of single-walled nanotubes may benefit from the catalytic characteristics of metallic nanoparticles.   |
| <b>Mesoporous Carbon Nitrides and N-doped Carbons Contain Metal Nanoparticles</b> | Carbon nitrides and nanoporous N-doped carbons contained in Mott-Schottky heterostructures with metal nanoparticles at their surfaces may serve as effective catalysts.                          |
| <b>Antimony–Vanadium Oxide Catalysts</b>  | The catalysts that are created are selective for the synthesis of acrylonitrile.   |
| <b>Cerium Oxide Nanostructures</b>  | Due to their catalytic nature, the nanostructures have different possible applications in the clinical sector  |
| <b>Titanium Carbide Nanoparticles</b>   | Bioethanol electrooxidation in acidic environments is facilitated by platinum catalysts that may be supported by such nanoparticles.   |
| <b>Strontium-Doped Zinc Oxide Nanoparticles</b>                                   | Sol-gel synthesis allows for the production of these nanoparticles, which have been shown to have effective photocatalytic activity for the elimination of methylene blue in laboratory testing. |

|   |   |
|---|---|
| <b>Calcium Oxide Nanoparticles</b>                                    | When pyridines are added to an aqueous ethanol media containing calcium oxide nanoparticles, a catalytic reaction occurs.   |
| <b>Silver Nanoparticles</b>   | In anaerobic circumstances, silver nanoparticles are chemically stable and have no negative impact on bacteria.   |
| <b>Zinc Oxide Nanoparticles</b>                                       | Catalytic development of nanoparticles into semi-conducting zinc oxide nanowires allows for the examination of their photoluminescence characteristics.   |
| <b>Imidazolium Metal Nanoparticles</b>                                | Imidazolium ionic solutions containing metal nanoparticles have interesting catalytic characteristics.  |
| <b>Dendrimer-Encapsulated Metal Nanoparticles</b>                     | Metal nanoparticles employed as catalysts may have their location and other characteristics manipulated with the use of dendrimers.   |
| <b>Silica Vanadium Oxide Nanoparticles</b>                            | Exhibit oxidation-testable catalytic capabilities on both unsaturated and saturated hydrocarbons  |
| <b>Silica Titanium Oxide Nanoparticles</b>                            | demonstrate oxidation testing potential for both unsaturated and saturated hydrocarbons, indicating catalytic characteristics   |
| <b>Elemental Sulfur Nanoparticles</b>                                 | Elemental sulfur nanocrystals were applied to chromium (VI), which triggered a catalytic sulfide reaction.  |
| <b>Gold Nanoparticles</b>   | An effective catalyst for the elimination of nitro compounds in an aqueous medium may be made by depositing gold nanoparticles on top of nanocrystals magnesium oxide. When gold nanoparticles are present, carbon monoxide (CO) may be oxidized catalytically. |
| <b>Palladium Nanoparticles</b>  | Using palladium nanomaterials synthesized by oleylamine-mediated synthesis, formic acid may be oxidized catalytically.  |
| <b>Iridium Oxide Nanoparticles</b>                                    | Iridium oxide nanomaterials with strong electrocatalysts without ligands. Reusable catalysts for the bilayered hydroxylation of olefins in a moderate reaction environment in room temperature 3-methylimidazolium 1-n-butyl hexafluorophosphate electrolyte.   |
| <b>Titanium Dioxide Nanoparticles</b>                                 | Titanium dioxide (TiO <sub>2</sub> ) that has been treated with carbon may be utilized for photocatalysis under sunlight. The photocatalytic activity of TiO <sub>2</sub> nanoparticles was tested using an intermediate mercury UV lamp.                       |
| <b>Cuprous Oxide Nanoparticles</b>                                    | Electrocatalyst for optimal oxygen reduction reaction (ORR) using cuprous oxide particles maintained on RGO (reduced graphene oxide).   |
| <b>Tungsten Oxide Nanoparticles</b>                                   | Atomic layer breakdown of tungsten oxide (WO <sub>3</sub> ) in combination with an oxygen generating catalyst yields hetero-nanostructured photoanode.  |
| <b>Silver Nanoflakes</b>  | Catalytic decomposition of tryptophan using silver nanoflakes supported on molybdenum sulphide (MoS <sub>2</sub> ) sheets.  |
| <b>Tin Oxide Nanoparticles</b>  | Organic compound photodegradation and reduction catalysts   |
| <b>Zirconia Nanoparticles</b>   | Catalysts for aqueous precipitation, solgel synthesizing, hydrothermal synthesis, and thermal decompositions  |
| <b>Nano-sized magnetic particles of iron oxide</b>                    | Chemical component oxidation by catalysis of phenol and acetonitrile (Fe <sub>3</sub> O <sub>4</sub> )  |
| <b>Cobalt Oxide Nanocrystals</b>                                      | Catalytic systems for chlor-alkali electrolytic systems comprised of cobalt oxide nanoparticles and carbon nanofibers   |
| <b>Nanoparticles of platinum-antimony tin oxide</b>                   | Methanol direct fuel cells using oxygen reduction process catalyzed at the cathode  |
| <b>Nanoparticle Bimetallic Chalcogenide of Molybdenum and Bismuth</b> | Transformation of Carbon Dioxide into Methanol  |

In the fields of chemistry and materials science, creating sustainable catalysts that are both durable and recyclable is seen as a major issue. The use of metal nanoparticles in this field is growing, making familiarity with their efficacy more important. Catalytic materials are essential, and their development is crucial for reducing waste disposal. Green catalysts are recyclable and environmentally benign. Catalysts have been broadly categorized as homogeneous, heterogeneous, and biocatalytic. When both the reagent and the catalysts are in the same stage or physical condition, we say that the reaction is homogeneous. In many manufacturing procedures, both the products and reactants exist in one phase (liquid or gaseous), hence homogeneous catalysts are often utilized.

By contrast, heterogeneous catalysts are those that exist in a phase other than that of the reactants. Solid catalysts are common, and they typically work best with fluid or gaseous reactants. It is generally agreed that heterogeneous catalysts outperform homogeneous catalysts in terms of activity, efficiency, and selectivity. This is because additional active sites

for the reactions may be made available owing to the metal nanoparticle catalysts' uniform distribution throughout the reactants. Nevertheless, since catalysts might be found dispersed homogeneously in the reaction mixture, it is more difficult to isolate individual catalysts once reactions are complete. In heterogeneous catalysts, highly active sites that reduce energy by adsorption of reactant monomers on their surface are often formed by coating the catalyst with metallic elements and their derivatives. Chemical and energy transformations are not possible without the use of heterogeneous catalysts, which have been pivotal in the pharmaceutical industry for decades.

Elumalai et al. [16] present another method of nanoparticle synthesis i.e. the biological method. The biological technique is favored over the top-down and bottom-up approaches because it is eco-friendly, sustainable, and does not need a greater use of energy. By using a biological method, one may produce nanoparticles with enhanced enzymes, metal salts, and catalytic activity. Hence, the primary goal in biological nanoparticle synthesis is to make efficient use of low-cost inputs and to enable a steady stream of nanoparticle production. Nanoparticles may be easily synthesized from biological sources, leading to consistent particle size and quantity thanks to a straightforward process and simple increase in biomass. There are many different biological ways to nanoparticle manufacturing, but one of the most well-known involves the employment of bacteria. A variety of bacteria, fungus, and algae are used. Most of the living things in our biosphere are bacteria. Bacteria have the capacity to produce different nanoparticles under favorable circumstances like pH, temperature, and pressure. To create nanoparticles, the best species to use are bacteria due to their adaptability to harsh environments and rapid cell division. Several of their resistance mechanisms allow them to procreate and expand even when exposed to high metal concentrations.

Furthermore, bacterial strains that are sensitive to high concentrations of metals may be used. Bioleaching, biomineralization, bioremediation and biocorrosion are just a few of the biological applications for the nanoparticles created by microbes. Other than bacteria, fungus and algae are other viable green sources for manufacturing nanoparticles. Fungi are remarkable in their capacity to synthesize a wide range of bioactive substances with broad potential uses. They're produced readily on a large scale for the creation of nanoparticles with regulated shape and size, and they find widespread usage as reducing and stabilizing agents. Comparable bioactive chemicals, pigments, and proteins may be synthesized by algae, aiding in the elimination of salts and serving as coating material in the manufacturing process.

#### IV. METAL NANOPARTICLES IN CATALYSIS APPLICATION

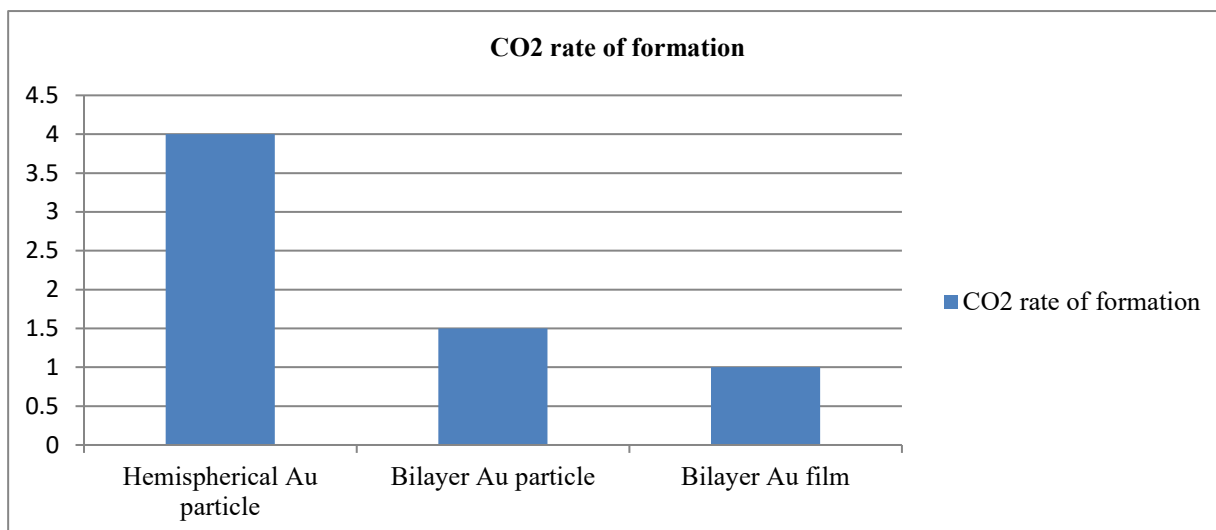
Catalysis applications make significant use of metal nanoparticles. High-surface-area metal nanoparticles with several active sites accelerate processes and boost output. Both noble metals (Au, Ag, Pt, etc.) and non-noble metals (Fe, Co, Ni, Cu, etc.) nanostructures exist, but they are separated by a large middle ground. Enhancements in materials nanotechnology and science during the last two decades have allowed for unprecedented precision in the production of metallic nanoparticles of tunable size, shape, and composition. Moreover, colloidal chemistry's capacity to fine-tune morphology and structure paves the way for more extraordinary ways to create catalysts with increased active sites. These developments connect the gap between the study of particles and their uses as heterogeneous catalysts. The analysis catalytic activity of carbon monoxide (CO) in the aspect of gold nanostructures integrated on the metal oxide by Kuang, X. Wang, and Liu [17] sparked such revolutions. The researchers showed that clusters and nanoparticles with sizes in the sub-nanometer degree (1-3 nm) were critical for CO oxidation catalysis processes and had a major effect on the overall catalytic activity.

After extensive testing of several strategies for adjusting the size of particles by rectifying the calcination temperatures, researchers headed by Pradeep Kumar [18] identified that 3.0 nm nanoparticles were more effectual for CO oxidation. This unexpected result motivated more research into the generation of other metallic Au-based nanostructures, which eventually saw considerable utilization as catalysts in a wide range of catalytic applications. Platinum-supported nanostructures have found broad employment of different applications, such as electrocatalytic oxidation process for fuel cells, because of their excellent miscibility and catalytic activity. In order to provide a reliable catalyst for alcohols oxidation, vitamin precursors, carbon monoxide, etc., platinum (Pt) material has been mounted on a wide range of nanostructures, including metallic particles like iron oxides. Palladium (Pd) is a generally investigated and promising material for making Pd-supported nanoparticles. Catalytically active catalysts for a variety of reactions were produced by supporting metallic Pd on various substrates, including porous carbons, nanomaterials, polymeric materials, etc.

Metal nanoparticles such as Pt, Au, and Pd have shown exceptional activity and selectivity in the mild oxygenation of methyl esters. Recent studies have also shown the efficiency of Pd-supported microporous oxide and other single-atom catalysts for the selective combustion of acylation alcohols. To put this in context, single-atomic Pd-embedded on the micro-porous alumina showed a high frequency of turnover compared to Au nano-structures whereas having inferior level of selectivity. The unpredictability and high price of noble-metal-based catalysts has enhanced the necessity for widely available, less-expensive, and non-toxic electrocatalysts. Non-noble metallic elements such as Ni, Fe and Cu aided nanoparticles have stimulated improved attention due to their vibrant catalytic features and improved availability. As a result of the complex catalytic activities, ecological sustainability, and superior stability, Cu, Fe, and Ni, have all been visualized as potential active stimulators in the heterogeneous catalytic applications. The oxygen-based alcohol esterifications have proved to be catalyzed by one-atom decomposition of Cu, Co, Ni, and Fe, onto N-C (Nitrogen-doped Carbons). Liang et al. [19] argue that N-C performed better, while others claimed that it was less efficient at oxidizing



aliphatic alcohols. In another research effort, Co atoms were dispersed inside a Co-MOF (metal-organic framework) and tested for their ability to preferentially hydroxylate nitro compounds.



**Fig 4.** Carbon monoxide oxidation: how nanoparticle dispersion affects catalytic activity

Researchers in [20] have looked at using metal catalysts based on Co and Ni for electrocatalytic water splitting to generate hydrogen. Nanoparticles made of materials besides cobalt (Co), such as copper (Cu), nickel (Ni), and iron (Fe), have attracted a lot of interest recently. Hydrogenation of alkenes was reported to be catalyzed by sub-nanometric Fe clusters at mild circumstances, with substantially greater efficiency than Fe nanoparticles. Furthermore, it was discovered that the catalytic capabilities of graphene, Carbon Nanotubes (CNTs), 2D materials, and reactivated carbons, might be considerably altered by the introduction of magnetic Fe nanoparticles. Similarly, iron oxide-supported gold clusters have been shown to be effective in oxidizing carbon monoxide (CO). Nonetheless, the responsiveness of distinct Au species remains a matter of some contention. More generally, the catalytic behaviors are significantly impacted by the creation of atomically thin metal clusters. There are several applications for metal-supported nanomaterials, which may be manufactured, such as water dispersion and environmental remediation. Making metallic nanoclusters with a thickness of a few atoms in a controlled manner is still considered as a challenge. Hence, it will become more important to create strong approaches in order to comprehend and enhance catalysis' performance.

In general, several different metal-supported nanoparticles have been fashioned in recent years to investigate their potential catalytic uses in more depth. Overall, it is feasible to synthesize green catalysts, which may help solve the environmental issues associated with current chemical processes and increase the productivity of product manufacturing. In any case, the issue of eco-friendly metal nanoparticle preparation emerges (i.e., precursors, solvents, etc., that are safer for the planet to utilize). Interestingly, several papers have proposed the utilization of bio-extracted bioparticles, such as plant-derived and starch materials, to manufacture metal nanoparticles (Au, Ag, Cu, etc.) that are less harmful to the environment. To create bio-inspired polymer nanocomposites, these metallic nanoparticles are deposited on various substrates, such as proteins and CNTs such as poly-L-lysine, soybeans, etc. Carbon monoxide is oxidized to carbon dioxide in an oxidation process under different Au conditions, as shown in **Fig 4**, which demonstrates the impact of nanoparticle dispersion on the catalytic performance (ToF is a typical representation of catalyst activity shown vertically). As an alternative, metal nanoparticle might be encased in biopolymers like chitosan, viscose, etc. that are occasionally used to filter out chlorine from water.

As with nanoparticles themselves, the substrates that sustain them have a wide range of potential uses. Creating extremely active and selective catalysts using environmentally friendly methods is possible, but we have a long way to go before we can put them into practice. Toxicological information on the produced nanoparticles is another major issue. It has been found that the toxicity of metal nanoparticles like Pd, Rh, and Pt varies depending on a number of different parameters. These factors include particle size, associated ligands, etc. A systematic investigation is still required to painstakingly analyze the biocompatibility and cytotoxicity of these nanoparticles prior to their bulk synthesis and industrialisation, despite the fact that Fe-, Ni-, and Cu-based activated carbons are shown to be less problematic than Rh-, Pd-, Pt-oriented catalysts.

## V. CONCLUSIONS

Catalytic capabilities of nanomaterials, particularly metal nanoparticles, are frequently exploited in the manufacture of nanocatalysts, which are then used to a broad variety of chemical processes to speed up the reactions and improve the yield of the products. When nanocatalysts are manufactured on a large scale, they will cause a revolution in many sectors of the economy, most notably the oil, pharmaceutical, and petrochemical sectors. In this overview, we spoke about the ways to

make metal catalysts and how they may be used in catalysis. Despite the substantial advances, there are still a number of challenges to be overcome, including: developing simple techniques to synthesis large amounts of less homogeneous, toxic, robust nanoparticle with viable surface segments and specificity features; maintaining the catalytic capacities of the nanomaterials intact under complex situations; comprehending the catalytic process mechanics to structure robust catalytic models; and investigating the cytocompatibility of the nanomaterials. Current and potential industrial applications need an immediate assessment of all these challenges. The synthesis and implementation of effective catalysts for a wide range of practical applications is anticipated in the near future despite the presence of several obstacles and the lack of a systematic evaluation of the many processes involved.

#### Data Availability

No data was used to support this study.

#### Conflicts of Interests

The author(s) declare(s) that they have no conflicts of interest.

#### Funding

No funding was received to assist with the preparation of this manuscript.

#### Competing Interests

There are no competing interests.

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