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Review

Green Synthesis of Metal Oxide Nanoparticles Using Plant Extracts with Emphasis on Vigna unguiculata (Cowpea): A Review

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Abstract:

The green synthesis of metal oxide nanoparticles is received increasing attention due to its offer more environmentally safe alternative compared to conventional chemical methods, with many promising applications. This review focuses on usage of Vigna unguiculata (cowpea) in biosynthesis of metal oxide nanoparticles by showing its role as sustainable and low-cost reducing and stabilizing agent. The synthesis procedure is described, with emphasis on function of plant phytochemicals which help in the formation of nanoparticles. Different characterization methods are discussed, like field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and UV–Vis spectroscopy, to identify structure, morphology, and chemical nature of the nanoparticles. The review also considers the challenges associated with scaling up green synthesis processes and suggests future research directions to improve practical applications. By addressing these aspects, this review aims to provide a better understanding of the synthesis mechanisms, key properties, and real-world applications of metal oxide nanoparticles produced using Vigna unguiculata, thereby supporting the growing field of green nanotechnology.

Keywords: Metal Oxide 2; Green Synthesis 3; Cowpea Seed 4; Nanoscale and 5; Eco-Friendly NPs.

1. Introduction

Nanomaterials become very important component in modern science and technology because of their unique physical, chemical and mechanical properties, which are much different comparing to bulk materials. With their sizes in nanoscale range (1–100 nm), these materials show better electrical conductivity, optical behavior, mechanical hardness, and catalytic activities. These make them very crucial for many areas like electronics, energy storing, medical applications, and environment sciences. Due to their high surface area, quantum effects, and the possibility to control properties by changing the shape and size of particles, nanomaterials have opened new applications like drug delivery, catalysis, water treatment, sensors, and renewable energy systems.

Nanomaterials can be prepared through different synthesis methods; each one has certain advantages for specific applications. Normally, these methods divided into two main types: top-down and bottom-up. The top-down

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approaches, such as mechanical milling and lithography, involve breaking larger materials into nano-sized parts, which give good controlling on size and morphology. In opposite, the bottom-up strategies such as sol-gel method, chemical vapor deposition, and also hydrothermal synthesis [1], are forming nanostructures from molecular or even atomic scale, which makes possible to design more complex structures having specific functions.

The synthesis of nanomaterials by chemical-based methods is often facing several serious drawbacks, especially due to application of toxic chemicals and harmful solvents that may cause danger to human health and also the environment. These processes often result in formation of toxic byproducts and need careful disposal, which is increasing the environmental load. Because of these reasons, there is a rising focus toward green synthesis methods that are using natural materials and less harmful substances. Green synthesis is eco-friendly techniques not only reducing environmental pollution, but also improving the safety in laboratory environment. Through the use of biological origins, like plants or microorganisms [2], researchers can able to produce nanomaterials with a more sustainable and secure approach. This development is reflecting the broader movement in material science for more ethical and responsible innovations. Within these green methods, the synthesis that mediated by plant extracts give very promising alternative, since it minimizes the harmful impact on ecosystem.

Vigna unguiculata, known commonly as cowpea, is annual legume which cultivated for its young pods and mature seeds. It is a warm-climate crop with good tolerance to dry conditions and high temperature [3]. The seeds of cowpea contain high level of protein, fiber, and other nutrients, so they are important food source for human and animal diets [4]. Cowpea seeds act as reducing, capping, and stabilizing agents, allowing fast synthesis of metal and metal oxide nanoparticles [5].

Metallic nanoparticles can be synthesized by using either constructive or destructive chemical methods. The usage of metal precursor is essential for obtaining pure metal nanoparticle with correct structure. The unique optical and electrical property of these nanoparticles is mainly because of their surface plasmon resonance phenomena [1]. Metallic nanoparticles can be synthesized using either **top-down (destructive)** or **bottom-up (constructive)** approaches. The use of an appropriate metal precursor is essential for obtaining nanoparticles with high purity and controlled crystal structure. The unique optical and electrical properties of metallic nanoparticles arise primarily from surface plasmon resonance (SPR), which results from the collective oscillation of conduction electrons in response to incident light[2].

Metal oxide nanomaterials having specific structural characteristics which make them highly useful in various field such as physical, chemical, and materials sciences. They are engineered to have dense structure, and they play important role in many areas of advanced nanotechnology. Their chemical and physical features are responsible for influence on their electrical, optical and also mechanical behaviors. Because of these advantages, they are suitable for, fluorescence sensor, solar energy systems, the biomedical field, and energy storage technologies like supercapacitors [7–11].

In this review article, we discuss green synthesis of metal oxide nanoparticles using Vigna unguiculata. This method takes advantage from the plant's natural biochemical compounds, which help to reduce metal ions and stabilize formed nanoparticles by action of phytochemicals. Using Vigna unguiculata has many benefits, such as decreasing need for toxic reagents and solvents, thus making the procedure eco-friendlier. Also, the nanoparticles obtained by this method usually show better biocompatibility, which useful in applications like medicine, environmental treatment, and electronic devices. By showing efficiency of this green synthesis, we want to highlight its capability to replace traditional chemical methods and support more sustainable material production. At final part of review, we also discuss some limitations of using Vigna unguiculata in nanoparticle formation and give suggestions how to overcome such issues.

2. Metal Oxide Nanoparticles

Metal oxide nanoparticles have been receiving considerable attention in recent years due to their promising physicochemical characteristics, especially their high surface-to-volume ratio and elevated reactivity. Among the frequently investigated types are zinc oxide (ZnO), titanium dioxide (TiO_2), iron oxide (Fe_2O_3), and lead oxide nanostructures (PbO NSs), each demonstrating certain beneficial properties tailored for targeted applications [12–14]. In recent experimental investigations, metal oxide nanoparticles have demonstrated considerable potential in enhancing catalytic activity during various chemical transformation reactions, particularly by improving reaction kinetics and lowering activation energies [15]. Moreover, their integration with the semiconductor-based systems was reported to have significant influence on the electrical performances, including the efficiency of charge transport and also the stability under operation conditions. These results are highlighting the important role of nanoscale features in affecting the characteristics of device. In biomedical field, increasing studies has been using such nanoparticles for the aim of targeted drug delivery and molecular imaging, because of their high biocompatibility and tunable size-dependent physiochemical property[3]. Their customizing nature allows researchers to adjust size, shape, and surface properties, thus enhance their functionality. However, although they are seeming very promising, but still, there is concerns exist about their toxicity and impact on environment, which it highlights the needing for developing more sustainable methods of producing.

An oxide is a chemical compound which containing at least one oxygen atom binded with another element, or sometimes it can be di-anion form of diatomic oxygen molecule. For example, MeO is known as anion of oxygen in gaseous phase where oxygen shows oxidation state of minus two. The MeO-type compounds can be divided depends on how many atoms they have or also based on oxidation states of the metals involved, Table 1 illustrates the commonly synthesized Metal Nanoparticles using Cowpea Extract[4]. Their structure generally consists of many arrays of different arrays, ranging from individual molecules to polymeric or crystalline forms. The reactivity of a metal surface toward oxygen (O_2) is often related with adsorption strength of O, the tendency for oxidation, and heat release during metal oxide formation. Periodic patterns can be explained by considering the attractive and repulsive interactions with d-band. Inert metals often possessing a single d-band which is having low energy and considerable spatial overlapping. The surfaces that are more exposed or having uncompleted bonding sites tend to be more reactive with oxygen or other reactive species [16]. In the recent years, significant progresses have been made for understanding the molecular structures of metal oxide species that located on surface of material and also on the catalytic active site.

Table 1. Commonly Synthesized Metal Nanoparticles Using Vigna unguiculata (Cowpea) Extract

Metal Nanoparticle	Plant Part Used	Typical Synthesis Role of Extract	Approximate Size Range (nm)	Main Applications
Silver (Ag NPs)	**Leaf extract**	**Reducing and stabilizing agent**	**10–50 nm**	**Antibacterial, antimicrobial, catalytic reduction (e.g., p-nitrophenol), antioxidant activity**
Gold (Au NPs)	**Leaf extract**	**Bioreduction and capping agent**	**15–60 nm**	**Biomedical applications, biosensing, antioxidant activity**
Copper (Cu NPs)	**Seed or leaf extract**	**Reduction of Cu^{2+} ions and stabilization**	**20–80 nm**	**Antibacterial activity, catalytic applications**
Iron (Fe NPs)	**Leaf extract**	**Phytochemicals act as reducing agents**	**10–100 nm**	**Environmental remediation, adsorption of pollutants**
Nickel (Ni NPs)	**Leaf extract**	**Green reduction and surface stabilization**	**30–90 nm**	**Catalysis, antimicrobial applications**

2.1 Doped and Undoped Metal Oxide Nanoparticles

The various applications and tunable features of doped and undoped (MONPs) metal oxide nanoparticles have made them a central topic in materials science. Doping is intentional introduction of impurity into material to modify its electrical and optical features. Nevertheless, producing doped MONPs is more challenging than undoped type, because it needs precise controlling of doping scheme to ensure obtaining intended features. However, the ability to adjust MONPs' characteristics by doping has resulted in remarkable advances in areas such as renewable energy, environmental cleanup [5], and electronics [5,6].

Electron doping of metal oxides provide enhanced optical, electrical, also the catalytic properties [7,8]. The primary process supporting this feature tuning is to exert control over doping that modifies electron transport properties by modifying the crystalline structure of the pure Metal Oxide NP [9,10]. Such modifications cause a reduction or enlargement of the band gap, leading to a change in the spatial position of conduction band. TiO2, a widely used photocatalyst, exhibits a decrease in band gap when doped with non-metals (such as: nitrogen, carbon, sulfur), transition metals (such as Ni, Cu, Pt, Fe, Cr), or noble metals (such as Au, Pt, and Ag) [11]. Although undoped TiO2 exhibits photoactivity only in the ultraviolet (UV) region, the process of doping-induced band gap narrowing allows it to be photocatalytic and produce (ROS) reactive oxygen species when exposed to visible light. As shown in **Table 2** doped Metal and Metal Oxide Nanoparticles Synthesized using Cowpea Extract[12]. This phenomenon arises from alterations in lattice characteristics or the presence of dopants that function as electron traps, therefore inhibiting charge recombination The presence of doping in Mn-doped ZnO and Sn-doped In_2O_3 might cause shifts in the conduction band edge, resulting in an increased production of reactive oxygen species (ROS) compared to the counterparts that are not doped. Biosynthesis of the (Al) aluminum doped and undoped (pure) (ZnO) zinc oxide nanoparticles (NPs) for the applicability of dye degradation capability [2]. The alterations are ascribed to the disruption of the lattice arrangement of the original metal oxides, such as tin in tin-doped indium oxide (In_2O_3). The extent of these alterations is contingent upon the level of doping and the arrangement of dopants [10,13–15].

Table 2. Doped Metal / Metal Oxide Nanoparticles Synthesized Using Vigna unguiculata (Cowpea) Extract

Nanoparticle System	Dopant(s)	Plant Part Used	Role of Cowpea Extract	Approx. Size (nm)	Reported Applications
NiO NPs	Mn-doped NiO	Seed extract	Reducing, capping, stabilizing agent	20–60	Photocatalytic degradation, optical enhancement
ZnO NPs	Ag-doped ZnO	Leaf extract	Bioreduction and surface functionalization	25–70	Antibacterial, enhanced photocatalysis
ZnO NPs	Fe-doped ZnO	Leaf extract	Controls nucleation and growth	30–80	Visible-light photocatalysis, dye degradation
CuO NPs	Co-doped CuO	Leaf extract	Stabilization and morphology control	20–90	Catalysis, antimicrobial activity
TiO_2 NPs	Fe-doped TiO_2	Leaf extract	Enhances dispersion and defect formation	15–50	Environmental remediation, photocatalysis

3. Methods for Preparation of Nanoparticles

Green synthesis approaches for metal oxide nanoparticles (MONPs) encompass a variety of methods, each contributing to the unique properties and applications of these materials, as shown in **Figure 1**. Chemical methods such as sol-gel, hydrothermal, sonochemical, solvothermal, electrochemical, microwave, co-precipitation, and microemulsion techniques are employed to produce MONPs with specific characteristics. Physical methods, including inert gas condensation, laser ablation, high-energy ball milling, and physical vapor deposition, further enhance the properties and morphologies of MONPs. Biological methods leverage plant-mediated and microbe-mediated processes to synthesize nanoparticles in an environmentally friendly manner, adhering to the principles of green chemistry. These synthesis techniques, ranging from utilizing simple precursors and environmentally friendly processes to high-pressure and high-temperature conditions, enable the synthesis of nanoparticles with tailored properties for applications in mechanics, optics, electronics, biology, and energy storage. The integration of these methods facilitates the development of advanced nanodevices and a deeper understanding of dimensional systems.

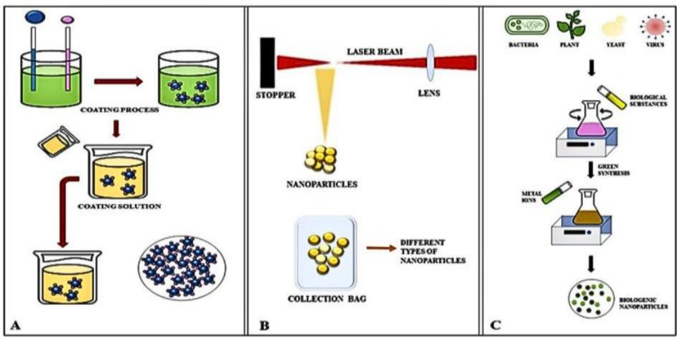

Figure 1. Methods of preparation of Nanoparticles (A) Chemical synthesis (B) Physical Synthesis (C) Biological Synthesis [16].

The present review focuses on biological synthesis methods, specifically plants, due to their eco-compatibility, resource efficiency, and alignment with sustainable synthesis principles.

3.1 Biological Synthesis of Nanoparticles Using Plants

Plant-mediated green synthesis approaches utilize various plant components, including seeds, fruits, calluses, barks, stems, flowers, and leaves, to produce metal and metal oxide nanoparticles with diverse sizes and forms [17]. Metabolites present in plant extracts serve as stabilizing and reducing agents in the formation of metallic nanoparticles [18].A remarkable capacity to convert metal salts into nanoparticles is demonstrated by plants, illustrated in **Figure 2**. Which are constituted of biomolecules such as proteins, coenzymes, and carbohydrates.

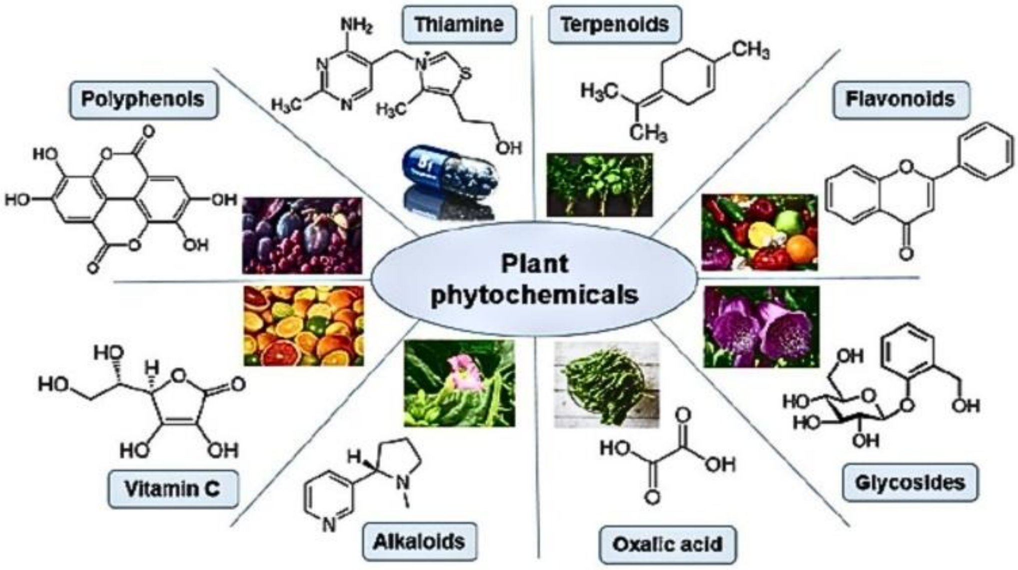

Figure 2. Plant phytochemicals [19].

In order to regulate pH, concentration, reaction duration, and temperature, the plant extract material is combined with a metal precursor solution and stirred with a magnetic stirrer [20]. Bioreduction is a complex process where plant compounds act as reducing agents, giving electrons to metal ions, thus reducing them to pure metal. The process includes a growth stage where small particles merge to form larger nanoparticles. Plant extract stabilizes the nanoparticles in the last phase, affecting their energetic stability and desirable shape. In addition, a capping agent is used to prevent excessive growth and to preserve nanoscale dimension. This synthesis schema, shown in Figure 3, considers various factors [32, 33].

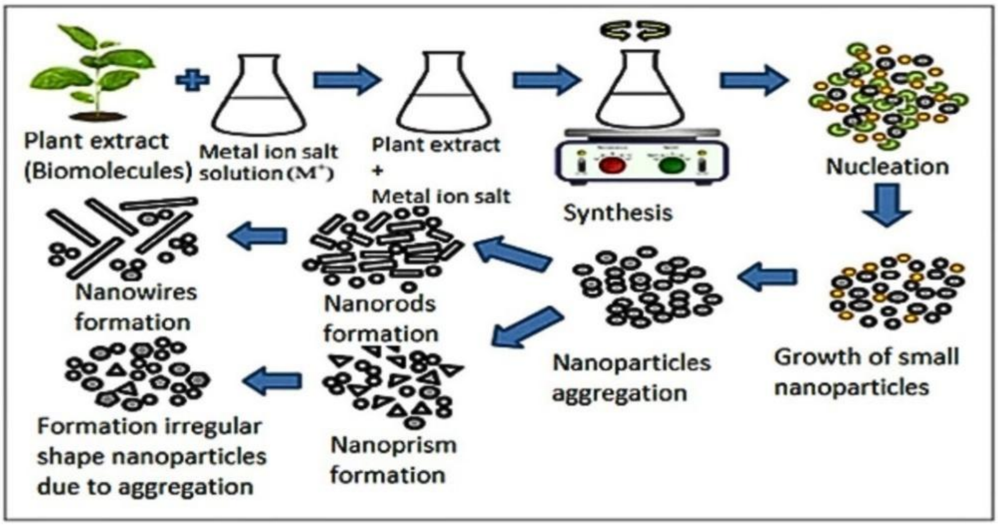

Figure 3. General mechanism for metal and metal oxide nanoparticles synthesis by plant source [21].

Compared to microbial-based synthesis, nanoparticles produced using plant and plant extract are showing greater stability and shorter reaction times [18][22]. This review analyses the synthesis process using Vigna unguiculata (L.) Walp. (cowpea) extract components through a sustainable and eco-friendly method known as green synthesis.

3.1.1 Vigna Unguiculata (Cowpea)

Vigna Unguiculata (L) Walp is a member of the Fabaceae family the Taxonomical classification illustrated in Table **3**. Cowpea is the common name for this plant. Figure 4, Table 4 shows the names of Vigna unguiculata in different languages. Its primary distribution is in India, China, Africa, and Central America. Vigna Unguiculata (L) Walp has attracted significant attention in phytochemical and Ayurvedic research because of its exceptional therapeutic properties [23]. This review aims to compile information on the phytochemical components, synthesis of nanoparticles utilizing cowpea extract, characterization, and uses of these nanoparticles.

Figure 4. Vigna unguiculata (Cowpea) plant parts.

Table 3. Cowpea taxonomical classification.

Taxonomic Level	Classification
Kingdom	**Plantae**
Division	**Angiosperm**
Class	**Eudicots**
Subclass	**Rosids**
Order	**Fabales**
Family	**Fabaceae**
Genus	**Vigna**
Species	**Unguiculata**

Table 4. Different Vigna unguiculata names in world various languages [24]

Language	Names
Kurdish	لوبيك
Arabic	اللوبياء
Bengali	**Ghangra, Kulattha, Kalaya, Barbati**
English	**Cowpea, Black-eye pea, Horse gram, Asparagus bean, Cajjang, Cajjang cowpea, Chinese long bean, Clay pea, Cream pea, Crowder pea, Pea bean, Purple-Hull pea, Southern pea, Sow pea, Yard-Long bean**
French	**Dolique asperge, Dolique mongette, Haricot asperge, Haricot indigène, Niébé, Pois à vaches**
Ghana	**Adua, Ayi, Tipielega, Tuya, Ssau**
Gujrati	**Kalathi, Kulathi**
Hindi	**Lobia, Kulathi, Kurathi**
Indonesian	**Kacang bol, Kacang merah, Kacang toonggak, Kacang béngkok**
Kamada	**Alasabde, Alasund, Huruli, Hurali**
Kashmiri	**Kath**
Malayalam	**Mudrna**
Marathi	**Alasunda, Chavali**
Nigeria	**Wake, Ezo, Nyebbe, Ngalo, Azzo, Dijok, Alev, Arebe, Lubia, Mongo, Ewa, Akedi, Akoti**
Portuguese	**Feijão-espargo, Feijão-fradinho**
Punjabi	**Lodhar**
Sanskrit	**Mahamasah, Rajamasah, Khalva, Vardhipatraka**
Spanish	**Costeño, Frijol de costa, Judía cajjang, Judía espárrago, Rabiza**
Swahili	**Kunde**
Tamil	**Kaattuulundu, Karamani**
Telugu	**Alasandalu, Kararamanulu**
Urdu	**Gawara, Gawar ka beej**

3.1.2 Plant Morphology

This plant is an herbaceous annual that has twining stems that can vary in their erectness and bushiness. As shown in Figure 4, the leaves are trifoliate, with petioles of 2.5 to 12.5cm in length. The central leaflet is hastate in shape, measuring 2.5 to 12 cm in length. It has a smooth texture, whereas the lateral leaflets are uneven in shape. The flowers are arranged in axillary racemes, which are elongated clusters, and are supported by stalks that measure 15 to 30 cm in length. The pod is pendulous, smooth, and is 10 to 23 cm in length. It has a strong curving beak and contains 10 to 15 seeds. The seeds range in length from 4 to 8 mm and in width from 3 to 4 mm, exhibiting variation in both size and color.

3.1.3 Chemical Constituents

Vigna Unguiculata typically consist of proteins (20.5-31.7%), carbohydrates (56-67%), fats (1.14-3.03%), minerals, vitamins, soluble and insoluble dietary fibers. They also contain different amounts of glycosides, alkaloids, tannins, flavonoids, polyphenols, Vignali, saponins, and soyasaponin B, which is a type of triterpenoid from the oleanane series. In addition to saponin-cycloartenol, stigmasterol, sitosterol β-D-glycosides, and oleanolic acid acetate [23].

3.2 Nanoparticle Synthesis Using Different Parts Extract of Vigna Unguiculata (Cowpea)

3.2.1 Seed Extract

Seeds offer researchers a cost-effective alternative to conventional biological methods due to their low maintenance costs, ability to be grown independently for biomass, and the presence of a diverse array of phytochemicals that can be employed as reducing and capping agents as shown in **Figure 5** different parts of Vigna unguiculata been used to prepare NPs. Consequently, the synthesis of magnetic nanoparticles (MNPs) is considered to be effective when using sustainable green synthesis methodologies.

Figure 5. Different parts of Vigna unguiculata beans used to prepare NPs.

Titanium dioxide nanoparticles are synthesized by using extract derived from Vigna unguiculata seeds. A solution with 0.1 mM of titanium precursor was mixed with cowpea seed extract for producing the nanoparticles. The nanoparticles having oval shape, which are produced by biological synthesis, was showing good efficacy against several clinical pathogens. The signal observed at 418 cm^{-1} is confirming the successful formation of the TiO_2 nanoparticles. The TiO_2 nanoparticles exhibited strong antioxidant activity and demonstrated cytotoxic effects on MG63 osteosarcoma cell lines [25].

Silver nanoparticles (AgNPs), a widely used nanomaterial, are commonly used in many industries, from medical devices to water purification. This study presents a new method for preparing AgNPs by using cowpea seed extract. The method is cost-effective, environmentally benign, and reproducible. The resulting AgNPs show long-term stability. Spherical AgNPs are synthesized by combining 10^{-3} M silver nitrate solution with 2.5 or 10 mL of seed extract. The resulting AgNPs have diameters below 70 nm and show maximum UV–vis absorbance at 431 nm. The formation process yielded AgNPs with spherical shape and composition in ratio 2.19 and 1.09%. Observed peaks in extract correspond to carbonyl, amide I, II, III groups, indicating presence of carbohydrate and protein that stabilized AgNPs for 11 months[26].

A study was carried out which synthesized silver, copper and also zinc nanoparticles by using extract from cowpea seed, which shown antimicrobial activity. NPs was analyzed using UV–vis spectrophotometer, showing characteristic peaks appearing at 385 nm, 680 nm and 350 nm respectively. The antimicrobial potential was further confirmed by performing agar well diffusion assay on Muller–Hinton agar medium[27].

The study also investigating the antiglycation property of gold nanoparticles that was synthesized by using extract from Vigna unguiculata seeds. The synthesis process involves reducing of gold ions with bioactive components found inside the seed extract, and result in formation of V-GNPs. The finding is in agreement with former studies which demonstrating the ability of gold nanoparticles to reduce the complications linked to glycation-related diseases. This finding also broadens the possible utilization of V-GNPs in field of nanomedicine[28].

3.2.2 Leaf Extract

Silver nanoparticles (Ag NPs) were synthesized by using the leaf extract of Vigna unguiculates, a legume food crop that grown in tropical and subtropical areas. The leaf extract, which contains high proteins and flavonoids, was helpful to reduce the particle size of Ag NPs because of blue shifting in SPR peaks. The XRD analysis confirming a face-centered cubic structure, with crystallites arranged along the silver crystal directions [41].

Also, cowpea leaf extract has been used in microwave-assisted biosynthesis to produce silver nanoparticles (AgNPs) in eco-friendly way. The optimal power was identified as MEDIUM LOW (364 W) for 4 minutes. The nanoparticles showed better antioxidant activity than water extract. Moreover, they displayed bigger Zone of Inhibition (ZOI) against E. coli compared to S. aureus. This indicate that such AgNPs can act as therapeutic substance in fighting diseases that caused by free radicals [29].

3.2.3 Stem Extract

In this work, silver nanoparticles (AgNPs) were fabricated by using $AgNO_3$ solution with the stem extract of cowpea as reducing agent. The produced nanoparticles were analyzed using UV-Vis spectroscopy, SEM, FTIR, and XRD. The adsorption behavior was strongly influenced by some parameters like dye concentration, contact duration, pH of solution, temperature, and also initial adsorbent level [43].

3.2.4 Starch Extract

This study shown the green synthesis of AgNPs by mixing starch extracted from cowpea with $AgNO_3$, forming nanoparticles that exhibited notable antibacterial effects against different bacteria strains. The cytotoxicity tests showed good tolerance on both noncancerous and cancerous cells, with cell survival more than 50% and a low value of apoptotic index[30].

4. Characterizations of Metal Oxide Nanoparticles

Characterization methods for metal oxide nanoparticles (MONPs) are very important for understanding their properties and usefulness. Fourier Transform Infrared (FTIR) spectroscopy is useful for identifying the functional groups and verifying the nanoparticle creation by absorption peaks analysis. UV-Vis spectroscopy used to measure the optical bandgap and to confirm synthesis via the specific absorbance bands that show reduction was occurred. X-ray Diffraction (XRD) is used for studying crystal structure, phase, and grain size; the Scherrer equation is sometimes used to calculate crystallite size. Scanning Electron Microscopy (SEM) together with Energy Dispersive X-ray (EDX) analysis gives insight into surface morphology and the element composition. Transmission Electron Microscopy (TEM) shows a very detailed image for nanoparticle shape and distribution. In addition, Field Emission SEM (FE-SEM) and Selected Area Electron Diffraction (SAED) are further confirm polycrystalline feature and support elemental mapping. All of these characterizations together help better understanding of MONPs and their potential usage in many fields.

4.1 Factors Affecting Metal Oxide Nanoparticles

Nanoparticles (NPs) are grouped according to many different factors, such as pH, concentration of reactants, time of reaction, and temperature, as demonstrated in Figure 6. The synthesis of metal oxide (MeO) NPs is strongly affected by environmental and experimental variables like the species of plant used, available biomolecules, and synthesis parameters.

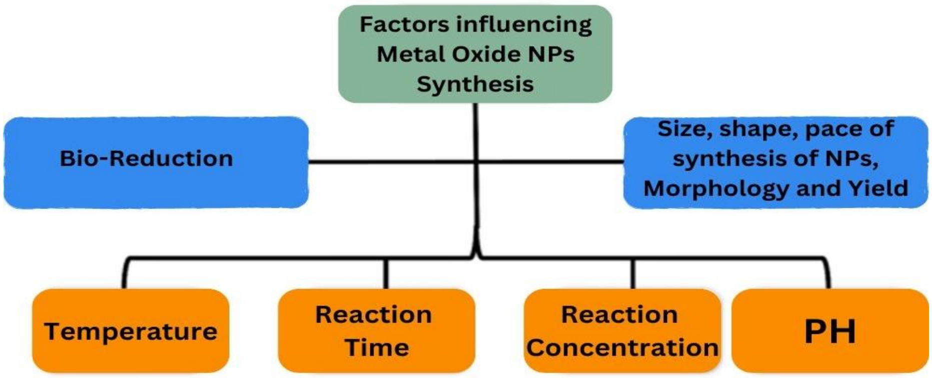

Figure 6. factors affecting the bio-synthesis process of MeO NPs [31].

4.1.1 pH

The pH is one of major factors that affecting the structure of nanoparticles. Together with temperature, pH controls the nucleation center formation. The pH value of the solution during reaction significantly influences the size and shape of resulting NPs. Changing the pH during synthesis can lead to forming particles with different morphology. When using acidic medium, the nanoparticles formed in more various shapes and sizes, in contrast to neutral or lower pH conditions. So, adjusting the pH is a key step for controlling metal oxide nanoparticle (MeO NP) formation. The size and shape of MeO nanoparticles can be altered by adjusting the pH of the process. The sizes and shapes of NPs are regulated by the pH (acidity level) and must remain consistent during the entire process of creating NPs. Phytochemical deprotonation and activation occur in response to an alkaline pH environment. Phytochemicals are hindered by lower pH levels, which cause them to stay in a protonated state. As a result, their ability to reduce or cap metal salts is diminished [31]. In general, nanoparticles produced in a solution with a high pH have a smaller size and exhibit enhanced stability over a period of time. Nanoparticles (NPs) formed under acidic conditions are often more stable due to the inefficient capping process. Large particles are formed by adjusting pH values from lower acidic levels to highly acidic levels. Conversely, a high pH environment promotes the formation of spherical nanoparticles, and it is particularly effective for producing small-sized metal oxide nanoparticles. The surface plasmon resonance (SPR) peak exhibits broadening and red-shifts towards longer wavelengths, leading to the formation of a diverse spectrum of nanoparticles (both cylindrical and triangular in shape) compared to the production of smaller nanoparticles at low pH. The physicochemical properties of NPs produced using green methods are influenced by the reaction process and the drying of the particles, which involves the application of warmth.

4.1.2 Temperature

Temperature is being a crucial factor that must be considered in every synthesis process. It is an important element which can altering the size and morphology of nanoparticles (NPs), as well as influence the stages of their fabrication. The increase in temperature enhances the speed of reaction, which promoting the formation of nucleation center. The synthesis of NPs is often can be described as function depend on temperature, where different shapes and sizes are forming as result. During synthesis by biological sources, increasing the temperature was observed to have catalytic effect-this means that it accelerates the reaction speed and improve the synthesis efficiency. Furthermore, it also changing the structure of obtained nanoparticles. To produce nanoparticles through green approaches, a temperature around 100 °C is generally needed. On other hand, chemical synthesis methods mostly use lower temperatures, while physical techniques required temperatures above 350°C.

4.1.3 Reaction Time

The correlation between reaction time and particle size and the number of produced nuclei is direct. When the allotted time for thorough reduction is exceeded, NPs aggregate, leading to the formation of bigger structures. The size, shape, and yield of synthesized NPs are influenced by the reaction time. It also regulates the structural aspects of NPs.

4.1.4 Reactant Concentration

The number of bio-reducing agents employed affects the size and form of nanoparticles. The presence of these substances enhances particle aggregation, whereas the selection of solvent can influence the bio-synthesis process. The size of nanoparticles is closely correlated with the concentration of the precursor. The presence of a large amount of extract accelerates the formation of smaller nanoparticles, which are stabilized using capping agents. However, the absence of sufficient phytochemicals results in the inability to stabilize many nuclei, despite the high precursor concentration [31].

5. Applications of Metal Oxide Nanoparticles

5.1 Para-nitrophenol Reduction

Para-nitrophenol (4-NP), a phenolic compound in insecticides, dyes, and pigments, is a significant environmental pollutant with adverse effects on human health, particularly the liver, central nervous system, and kidneys. Efforts to reduce its impact are ongoing, with eco-friendly techniques being developed [32].

Metal nanoparticles are recognized for their robust catalytic activity in the reduction of a variety of contaminants, including nitrophenol and dyes, and in hydrogenation. The efficiency of Ag nanoparticles (AgNPs) in reducing of 4-nitrophenolate ($NaBH_4$) was investigated in this study by using sodium borohydride, as shown in Figure 7 (A). In the UV-Vis spectrum, a peak at 318 nm was detected; however, after introducing the reductant, another new peak appeared at 401 nm. The catalytic performance of AgNPs was clearly proved through the reducing in the absorption intensity and the color of 4-NP. Moreover, AgNPs increased the adsorption of reactants and helped to lower the kinetic barrier energy (Adebayo & Areo, 2021). As the reaction proceeds, the typical reduction peak of 4-NP at 401 nm was gradually decreased, while the peak at 300 nm, which indicate formation of 4-aminophenol (4-AP), was increased, see Figure 7 (B).

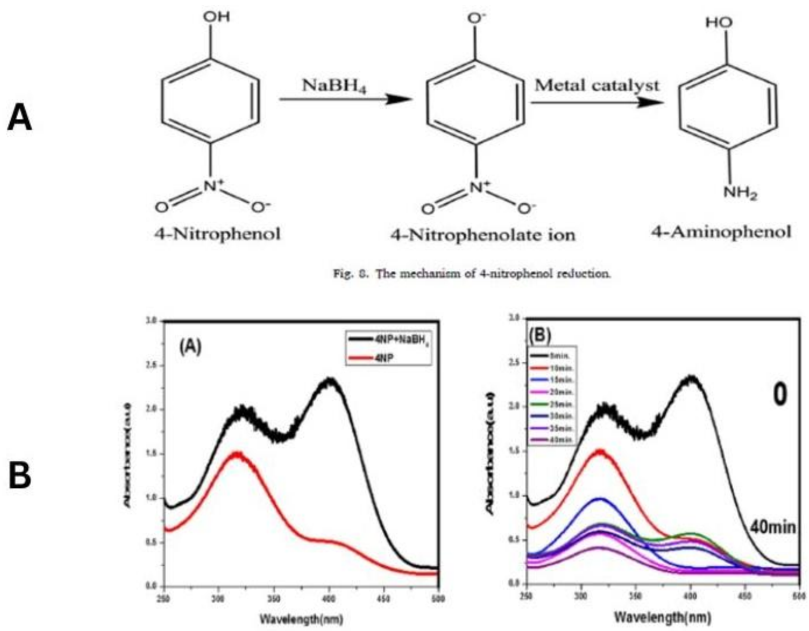

Figure 7. (A) Proposed mechanism of 4-nitrophenol reduction, (B) UV–vis spectra showing reduction process over time in presence of $NaBH_4$ and AgNPs [32].

5.2 Adsorbent for Malachite Green Dye

Malachite green dye, a cationic dye used in textile, paper, and carpet industries, was produced by Kem Light Laboratories PVT, India. The Langmuir isotherm was found to be the most accurate fit for the adsorption of malachite green dye using Ag-NPs. The adsorption process involves a uniform distribution of adsorbate molecules over the surface, with a limited number of sites with the same attraction level. The Langmuir adsorption constant (KL) value of 0.809192 confirms the process's favorable nature. The percentage of MG removal increased with the concentration of adsorbent, as shown in **Figure 8**, attributed to increased surface area and available sites for adsorption [33].

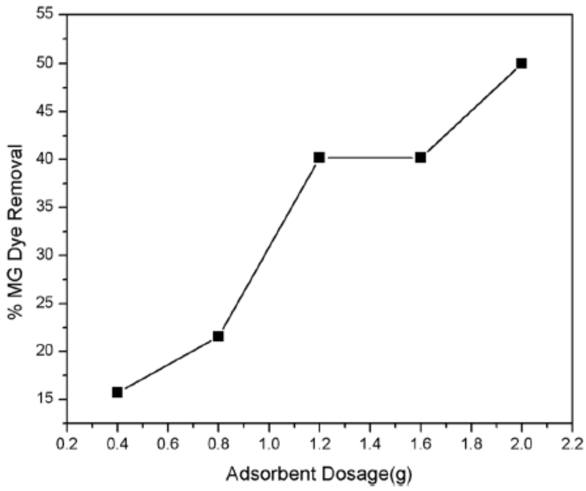

Figure 8. Effect of various AgNPs dose on the removal of MG dye [33]

5.3 Antibacterial and Antimicrobial Activity

The seed exudates of Mung bean and Cowpea exhibited growth inhibitory effects against a variety of bacteria, such as Salmonella Typhi, Pseudomonas Aeruginosa, Staphylococcus aureus, E. coli, and Klebsiella pneumoniae. Copper nanoparticles demonstrated superior antibacterial efficacy against Klebsiella species, while zinc nanoparticles demonstrated superior efficacy against Staphylococcus aureus and Salmonella typhi. Silver nanoparticles demonstrated superior antibacterial efficacy. In comparison to copper sulfate and seed exudates, copper nanoparticles demonstrated superior antibacterial efficacy. The synthesizing process of these nanoparticles is cost-effective, environmentally friendly, and relatively easy to carry out [27].

Ag nanoparticles (Ag NPs) show superior antibacterial activity against both Gram-positive like S. aureus and Gram-negative bacteria, which indicating their potential use in biomedical field. The interstitial and vacancy properties, together with the smaller spherical NPs size, are contributing to the effectiveness, resulting in MIC values of 72.5% and 57.5% against S. aureus and B. pumilus respectively. These values make them suitable candidate for removing of harmful bacteria from human food items and also from agricultural waste[32].

The study was evaluated antimicrobial effectiveness of porous-starch-mediated silver nanoparticles (AgNPs) against both Gram-positive and Gram-negative bacteria through disc diffusion technique. The result was shown that AgNPs effectively inhibit the both type of bacteria. As expected, the starch alone did not exhibit antibacterial activity, since there is no existing report that starch having antimicrobial behavior. The antibacterial property which was observed in both bacterial strains can be assigned to the bactericidal action of released silver cations from AgNPs. Out of three concentrations of AgNPs which were studied, the 10 M concentration shown more stronger effect toward many tested bacterial strains. The lower minimum inhibitory concentration (MIC) value indicates the nanoparticles having more potency, so less amount is required to get the desired antibacterial effect. Earlier studies regarding biosynthesized AgNPs have found similar MIC range, showing good agreement with the current work. Overall, these results confirm that such AgNPs are showing promising potential to be used as antibacterial agent[30].

The zone of inhibition (ZOI) for Staphylococcus aureus was recorded higher in water extract when compare with silver nanoparticles, except for the samples CP1 and CP5 which shown lower values. A unidirectional ANOVA analysis has not shown any statistically significance difference between ZOI of the samples. However, when a one-way ANOVA was conducted on E. coli, it has been showed that the AgNPs had a larger ZOI than the water extracts. Despite such results, there was no statistically significant differences observed between ZOI for S. aureus and E. coli groups[29] , as it is demonstrated in Figure 9.

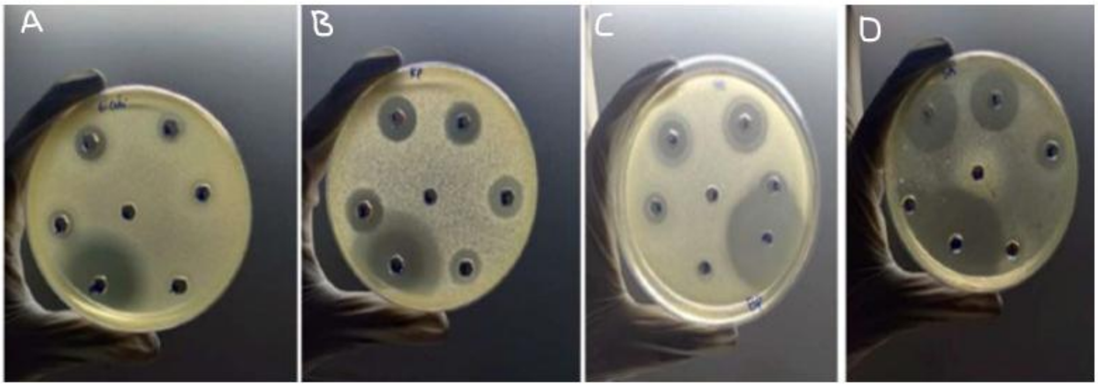

Figure 9. Antimicrobial activities of Ag NPs toward Escherichia coli (E. coli) (B), Klebsiella pneumonia (KP) (C), Bacillus pumilus (BP) (D), and Staphylococcus aureus [32] .

5.4 Photocatalytic Degradation of Organic Pollutants

Green-synthesized metal oxide nanoparticles exhibit excellent photocatalytic activity under UV and visible light irradiation. These nanomaterials can generate reactive oxygen species (ROS), such as hydroxyl radicals (•OH) and superoxide anions ($O_2•^-$), which are responsible for the degradation of toxic organic pollutants. Studies have reported efficient degradation of common dyes such as methylene blue, rhodamine B, and Congo red using biosynthesized ZnO, TiO_2, and CuO nanoparticles[34]. The presence of plant-derived phytochemicals on the nanoparticle surface enhances charge separation and improves photocatalytic performance, making these materials promising candidates for wastewater treatment applications[35].

5.5 Antioxidant Activity and Biomedical Potential

Metal oxide nanoparticles synthesized using plant extracts often exhibit significant antioxidant activity due to the presence of bioactive compounds such as flavonoids, phenolics, and alkaloids acting as capping agents. These nanoparticles can effectively scavenge free radicals and reduce oxidative stress. Consequently, green-synthesized nanoparticles have attracted increasing attention in biomedical applications, including wound healing, drug delivery, and anticancer research[34]. The biocompatibility and reduced toxicity of plant-mediated nanoparticles make them more suitable for biomedical use compared to chemically synthesized counterparts[36].

6. Conclusion

In this review, we summarized various metal oxide nanoparticles synthesis methods, factors affecting their synthesis, mechanisms of formation, and their various applications. The strategies in this review utilized natural reducing and stabilizing agents found in cowpea, minimizing the environmental impact compared to traditional chemical, physical and biological methods. Moreover, various characterization technique for metal oxide nanoparticles is notify. X-ray diffraction (XRD) to investigate crystallinity and phase composition; the morphology and composition analysis of nanoparticles are studied using a scanning electron microscope fitted with an energy-dispersive X-ray analyzer (EDX); transmission electron microscopy (TEM), UV–vis spectrum, FTIR, and TGA analysis are also among the characterization tools used. The resulting nanoparticles exhibit versatile applications across various fields, including catalysis, biomedical applications, and environmental remediation. The integration of cowpea in nanoparticle synthesis not only promotes sustainability but also enhances the functional properties of the nanoparticles, paving the way for innovative solutions to contemporary challenges. Finally Green synthesis is an efficient alternative to physical and chemical methods because it is nontoxic, cost effective, provides rapid synthesis, is eco-friendly, monodispersed, produces little waste, and can be produced on a large scale.

Authorship contribution statement

L.L.M.: Conceptualization, Data Curation, Methodology, Writing-Original Draft. S.SH.MA: Investigation, Validation, Software, Writing-Original Draft. A.K.Q.: Supervision, Writing - Review & Editing. K.M.O.: Supervision, Writing - Review & Editing

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