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ARTICLE

A Comprehensive Review on the Formation Mechanism of Zinc Oxide Nanoparticles Using Plant Extracts

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Abstract: Nanotechnology is an emerging field of science that concerns the industrial use of nanoparticles (NPs), typically ranging in size from 1 to 100 nm, which are classified into different classes such as inorganic, organic, ceramic, and carbon-based nanoparticles. Zinc oxide (ZnO) NPs are utilized in medicine, pharmaceuticals, cosmetics, sunscreens, water treatment, sensors, textiles, agriculture, and the food industry, making them the focus of this review. Since producing NPs using chemical and physical methods is often expensive and potentially harmful to both the environment and the user, there has been an increasing interest in using biological or green methods to produce metal and metal oxide NPs. Recently, researchers started to utilize green synthesis methods for producing different NPs; however, the mechanisms of NP formation using plant extracts are still under investigation. Consequently, more in-depth studies are needed on how NPs are formed in the plant extract medium. This review highlights the most robust mechanisms of ZnO NPs formation using plant extracts and covers the commonly used plants for ZnO NP synthesis over the last fourteen years. This review will help researchers in understanding the formation mechanisms proposed for nanoparticle synthesis using plant extracts and in identifying knowledge gaps in this field.

Keywords: Nanoparticles, Green synthesis, ZnO nanoparticles, Plant extract, Formation mechanism.

1. Introduction

The field of nanotechnology is one of the important fields of investigation in contemporary materials science. It is developing rapidly and continuously, influencing nearly every sector of human life. This field also generates an increasing interest in life sciences, especially in medical procedures and biotechnology [1]. The word “Nanoparticles” refers to particles having sizes between 1 and 100 nm, while “Nanotechnology” is defined as the field of technology that uses nanomaterials in practical applications, such as in medical devices, coating,

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surface modification, etc. The Greek word "nano" means "dwarf" or "small things", and it relates to one billionth of a meter (10^9 m) [2]. Nowadays, metallic NPs have attracted countless scientific attention due to their special optoelectronic, physical, and chemical properties with applications in fields such as molecular diagnostics [3], drug delivery [4], imaging [5], solar cells [6], catalysis [7], and sensing [8].

In recent years, the focus on zinc oxide nanoparticles (ZnO NPs) and their applications has increased dramatically as a result of their outstanding properties [9]. ZnO NPs are the most broadly used nanoparticles in numerous applications, including smart UV sensors [10], targeted drug delivery [11], antioxidant activity [12], anticancer activity [13], biosensors [14], environmental remediation [15], water purification [16], and even as agents that enhance drought tolerance and serve as nutrient source of crops [17].

NPs synthesis is normally conducted by means of three main approaches: physical, chemical, and green/biological approaches (as shown in Fig. 1) [18]. Each of these methods possesses its own identifiable special properties. Physical and chemical methods have greater efficacy for producing stable nanostructures of a similar size; however, they do not meet the purpose of obtaining long-term sustainability [19]. The most important step in the NPs synthesis method is the selection of eco-friendly solvents as good reducing, capping, and safe stabilizing agents. Yet, physical and chemical methods often rely on using hazardous materials, require advanced equipment, and have a negative impact on the environment. In contrast, the biological or green technique, which uses microorganisms such as bacteria, fungi, yeast, and plant extracts, offers a safer, affordable, dependable, and eco-friendly way to create many kinds of nanomaterials. There is a rising demand for the development of an environmentally friendly NPs synthesis technique that does not use harmful ingredients [20].

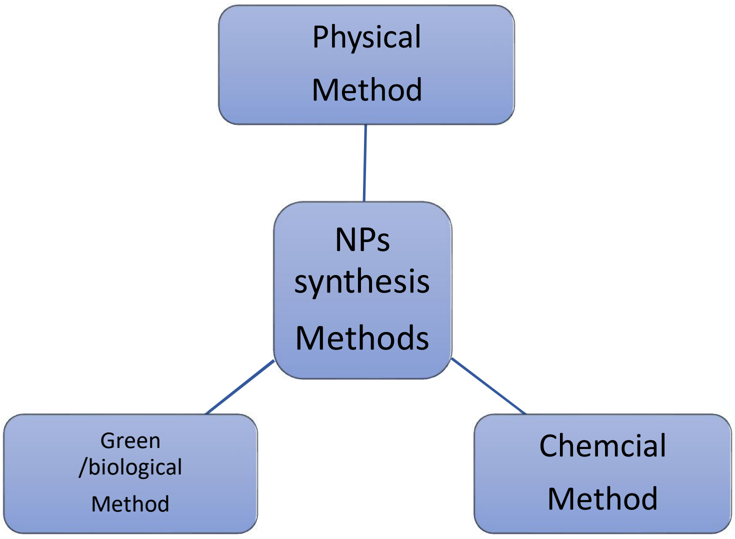

FIG. 1. Methods of synthesizing NPs.

Various studies have been conducted for synthesizing ZnO NPs, using different methods, including green synthesis with plants, algae, bacteria, fungi, and other biological sources. This is owing to the fact that green synthesis is considered the most eco-friendly, affordable, safe, and straightforward method. Plants, in particular, are favored because they enable large-scale production of stable nanoparticles in diverse shapes and sizes, using environmentally friendly, simple, and inexpensive extracts along with other natural components [21]. Owing to the presence of phytochemicals, which act as reducing, capping, and stabilizing agents, various plant parts, including leaves, fruits, roots, stems, and seeds, have been employed to produce NPs. The size and morphology of the resulting NPs can be controlled by the existing phytochemicals, tailoring them for a number of applications [22].

Instead of using toxic chemicals or energy-intensive machines, the green method of nanoparticle synthesis has been proposed. For ZnO NPs, green synthesis is particularly attractive due to its low toxicity and minimal impact on human health and the environment. Compared with microorganism-mediated synthesis, the use of plant extracts is a very straightforward technology to produce ZnO NPs on a large scale, making it one of the most promising green methods.

Although there are numerous contemporary scientific studies on the green synthesis of nanoparticles using different plant extracts, the underlying mechanisms of nanoparticle formation have not yet been extensively addressed [23, 24]. This review aims to fill this gap by focusing specifically on the formation mechanisms of ZnO NPs synthesized using plant extracts. ZnO NPs were selected because of their unique physical and chemical properties and their wide range of advanced applications in medicine, food, healthcare, wastewater treatment, anticancer therapies, and various industrial fields. The novelty of this review lies in its critical evaluation of green synthesis mechanisms, with the goal of advancing understanding of how ZnO NPs are formed, identifying knowledge gaps, and highlighting current and future trends in their production.

2. Role of Phytochemicals in Synthesizing ZnO NPs

Phytochemicals are natural compounds present in plants and are categorized into primary and secondary metabolites based on their function in plant metabolism. Primary metabolites, such as amino acids, proteins, lipids, purines, and pyrimidines of nucleic acids, are required for plant life. Secondary metabolites, by contrast, are not directly involved in basic plant life functions; hence, they do not play a role in the growth and development of plants. The secondary metabolites are categorized into five major classes, according to their compound structure: carbohydrates, terpenoids, phenolics, alkaloids, and polyketides [25].

Over the past decade, plant extracts have been widely used for the creation of numerous metal and metal oxide NPs. Particularly, they have been investigated for the synthesis of zinc oxide nanoparticles. The primary process in the production of zinc oxide NPs using plant extracts is the reduction of zinc ions by phytochemicals and enzymes that are easily found in the extracts [24]. Generally, the green nanoparticle manufacturing process proceeds through three steps: reduction phase, growth phase, and stabilization phase. The first and most essential step is the reduction phase, in which phytochemicals of plant extracts can interact with metal ions. These interactions allow metal ions to be reduced to metal atoms, and then nucleation of the reduced metal atoms occurs [26]. Next, during the growth phase, individual metal atoms unite through the coarsening process to form big particles of a stable size and shape. As the growth phase lengthens, NPs can develop into diverse morphologies such as nanorods, nanotubes, hexahedrons, prisms, and others [27]. The stabilization phase is the last step in the biosynthesis of nanoparticles. When nanoparticles are covered with plant metabolites, they gradually obtain their most favorable and stable form [28]. Typically, the final product is subjected to heat treatment. Differential scanning calorimetry (DSC) reveals a strong exothermic peak around 500 °C, corresponding to the crystallization of ZnO NPs. Figure 2 illustrates the mechanism of ZnO NP formation via plant-based green synthesis.

3. Mechanism of the Formation of ZnO NPs from Plant Extracts

Biosynthesis of nanoparticles offers a promising alternative to chemical and physical methods. Recently, green methods using plant extracts have been developed to synthesize metal oxide NPs. Phytochemicals in plants, such as polysaccharides, polyphenols, flavonoids, vitamins, amino acids, alkaloids, tannins, saponins, and terpenoids, are usually utilized as reducing and capping agents that react with zinc salt solution to form zinc oxide nanoparticles [29]. Plants are often favored in green nanoparticle synthesis because plant substrates are thought to be less expensive, easier to process, and less harmful than other microorganisms. Additionally, there are no health and safety issues imposed on humans due to the use of harmful microorganisms during the process [30].

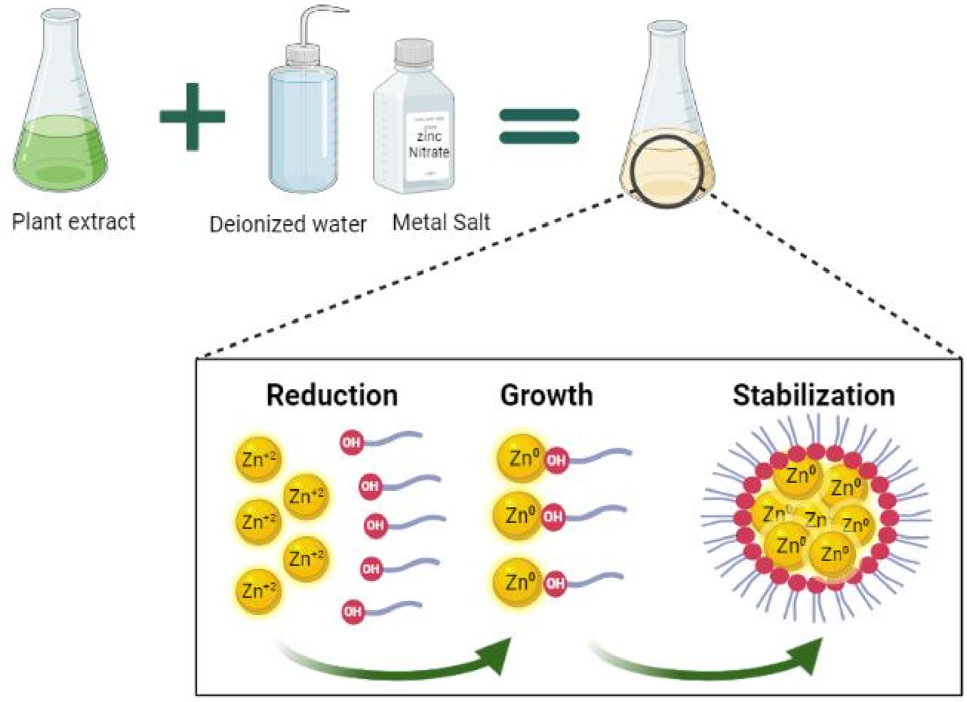

FIG. 2. Proposed mechanism for the green synthesis of ZnO NPs.

Although there are numerous studies showing the benefit of green synthesis in producing metal and metal oxide NPs, the formation mechanism of NPs is not yet clear and requires further investigation. We believe that the real problem lies in the lack of consensus among chemists, physicists, and biologists. An integrated explanation of the nanoparticle formation mechanism requires taking all aspects together rather than viewing this issue from one angle. Consequently, in this study, we summarize the current studies related to the mechanism of formation of zinc oxide nanoparticles utilizing different fragments of plant extracts.

In 2011, Gunalan *et al.* [31] synthesized zinc oxide nanoparticles using *Aloe barbadensis miller* leaf extract. It was found that various terpenoids, phenolic compounds, or proteins adhered to the surface of ZnO NPs and remained there after several washings. Free amino and carboxyl groups that were attached to the zinc surface were believed to be responsible for the stability of the ZnO NPs. However, heterocyclic chemicals that form functional group bonds such as -CO-C-, -CO-O-, and -C=C-, as well as amide domains formed from proteins found in leaf extracts, act as a capping agent around the NPs. Additionally, the presence of the proteins in the medium helps to stabilize the metal nanoparticles by producing a coat around them and preventing agglomeration. Overall, this research provides insights into the formation mechanism of zinc oxide nanoparticles and highlights the role of some phytochemicals in stabilizing the nanoparticles, although there remain some uncertainties associated with unclear scientific explanations.

In 2014, Brajesh *et al.* [32] prepared zinc oxide nanoparticles from *Citrus paradisi* peel extracts and investigated the mechanism of NPs formation. They found that flavonoids, limonoids, and carotenoids with free OH/COOH groups could interact with zinc sulfate to produce ZnO NPs. Based on these findings, they proposed a plausible formation mechanism, illustrated in Fig. 3. To our understanding, this extensive study provides a new technique to explain the formation mechanism of zinc nanoparticles through visual illustration; however, the evidence provided is still insufficient for readers to fully understand all steps of zinc nanoparticle formation.

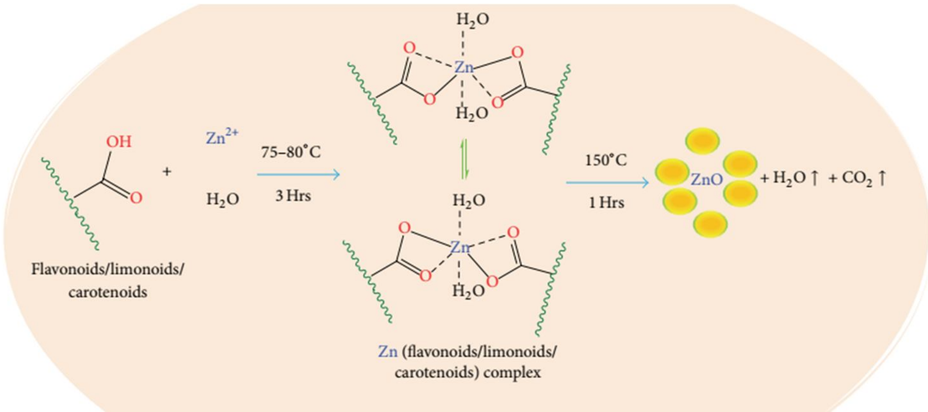

FIG. 3. The possible mechanism of ZnO NPs formation proposed by Ref. [32].

In 2015, Buazar *et al.* synthesized zinc oxide nanoparticles by utilizing potato extracts and explored the formation mechanism [33]. It was shown that potato is a high-carbohydrate crop that is mostly made up of starch, a natural polymer. The presence of a large number of hydroxyl groups in starch can help the complexation of zinc ions with the molecular matrix, whereas the aldehyde terminals assist in the reduction of Zn(II) ions to Zn(0). Beyond these mechanistic roles, starch offers several advantages as a renewable protective agent. First of all, starch may be dispersed in H_2O; as a result, organic solvents can be avoided totally. Second, the starch-metal nanoparticle binding relationship is a bit weak compared with the interactions between NPs and typical thiol-based protective groups; this indicates that the protection should be simply changeable at comparatively above-average temperatures, allowing for particle separation. Using the multifunctional (reducing and capping) characteristics of starch-rich potato extract, Buazar *et al.* proposed a streamlined technique of organic phase synthesis of zinc oxide nanoparticles through a green approach (Fig. 4). This study provided a comprehensive explanation of the formation mechanism of ZnO NPs and highlighted the role of starch in both complexation and reduction. However, while weak starch–nanoparticle binding is advantageous for particle recovery, it may pose challenges in applications requiring stronger stabilization, where insufficient binding could compromise nanoparticle stability.

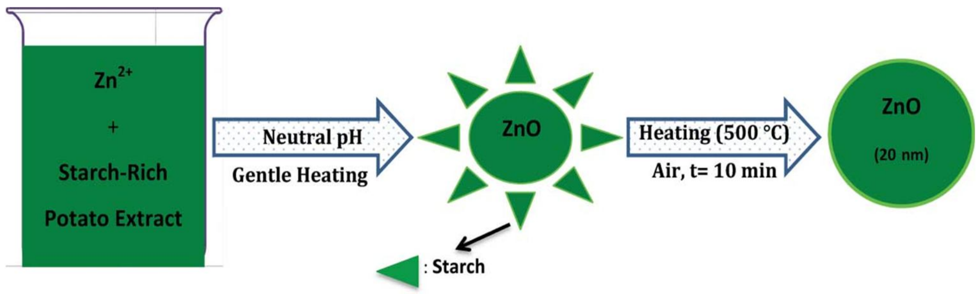

FIG. 4. Plant extract as both reducing and stabilizing agent of ZnO NPs [33].

In 2016, Prasanta *et al.* synthesized zinc oxide nanoparticles by utilizing tomato (*Lycopersicon esculentum*) extracts and investigated the mechanism of NPs formation [34]. Their study demonstrated that tomato extract through ascorbic acid is reducing Zn^{+2} ions and forms ZnO NPs. Ascorbic acid initially changes into a free radical ion known as "semihydro-ascorbic acid" and then oxidizes to become dehydro-ascorbic acid. Also, ascorbic acid behaves as a stable (electron + proton) donor during interactions. Therefore, ascorbic acid was capped with zinc ions, and Zn^{2+} was reduced within the nanoscale template to generate Zn(0) atoms.

In 2017, Senthilkumar *et al.* synthesized zinc oxide nanoparticles from *Tectona Grandis* leaf extracts [35]. It was shown that the primarily available chemical elements in the *Tectona Grandis* leaf extracts are phenols and flavonoids. It was clarified that through the available phenols and flavonoids in the aqueous leaf extract, the manageable size of ZnO NPs can be produced. The OH groups in phenols and flavonoids act as reducing and capping agents. Secondary metabolites were found in almost all medicinal plants, including phenols and flavonoids, which have been studied for their role as bio-reducing agents of metallic ions in aqueous medium. These phytochemicals also have a wide range of biological roles, ranging from antioxidants to anti-carcinogenic properties. Also, it was explained that the detected vibrational bands in the Fourier-transform infrared spectrum show the functional groups responsible for the reducing, capping, and stabilizing agents. To the best of our knowledge, the aptitude of these secondary metabolites to bind to zinc surfaces and induce nanoparticle formation is an essential step towards understanding the basic mechanisms of NPs formation. Likewise, the remark of these compounds as potential capping agents and their ability to control the size of the nanoparticles offers a new view of these compounds and the size of ZnO NPs. However, more technical information about the actual chemical events might help us understand the phenomena better.

In 2018, Joghee *et al.* synthesized ZnO NPs from *Costus pictus D. Don* leaf extract and investigated their formation mechanism presented in Fig. 5 [36]. They believed that zinc oxide nanoparticles are formed by diosgenin ($C_{27}H_{42}O_3$), a phyto-steroid sapogenin. It was explained that when diosgenin reacts with a metal nitrate, weak hydrogen bonds produce a complex (for example, a metal-diosgenin complex). This complex solution is then put in a high-temperature oven for eight hours to be transformed into hydroxide forms. The bio-synthesized hydroxide complex material is calcined to generate metal oxide NPs. Although *Costus pictus* leaf extracts contain numerous phytochemicals, the study focused specifically on a diosgenin compound because it easily attracts metals due to its phenolic content. According to our understanding, a more detailed description of this mechanism might improve comprehension of the process. While the formation of the metal–diosgenin complex was described, the precise chemical interactions and pathways were not fully elaborated. Additionally, although the authors emphasized the role of phenolic content in metal attraction, they did not clarify why phenolic groups are critical in this process.

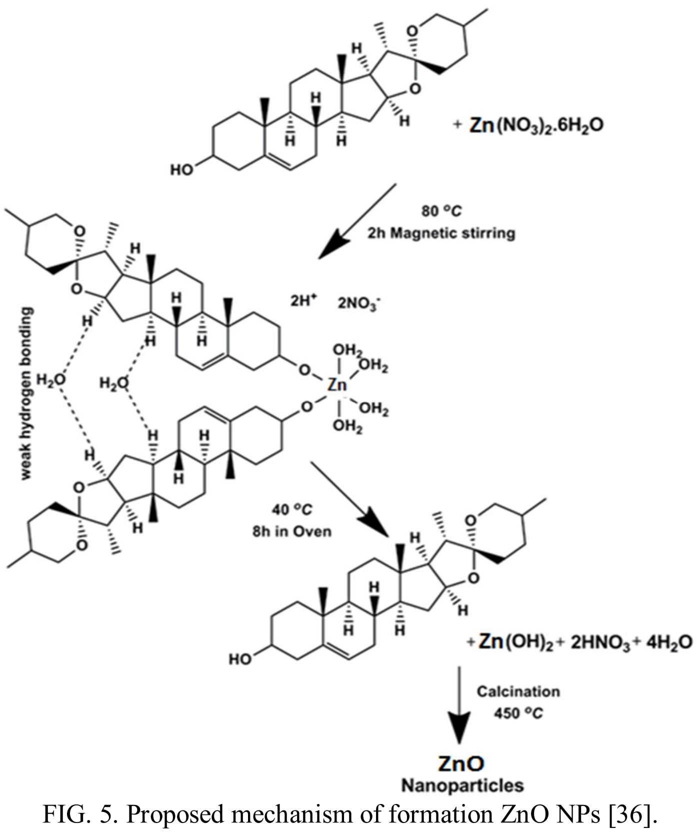

FIG. 5. Proposed mechanism of formation ZnO NPs [36].

In 2018, Luque *et al.* [37] produced zinc oxide nanoparticles using orange (*Citrus sinensis*) peel extract and explored the mechanism of the NPs formation. It was proposed that the synthesis process of ZnO NPs using *C. sinensis* peel extract can potentially occur through a reaction mechanism. This mechanism involves the interaction between the functional molecules present in the orange peels and the zinc precursor. Within these components, certain aromatic hydroxyl groups possess the ability to bind with zinc ions, thereby forming zinc-ellagate structures. Upon heat treatment at 400 °C, these structures undergo direct decomposition, leading to the liberation of the freshly synthesized ZnO nanoparticles. Figure 6 displays the mechanism of zinc oxide nanoparticle formation utilizing *C. sinensis* peel extract. However, the information provided appears insufficient to fully elucidate the mechanism of NPs synthesis. In particular, specific details regarding the key phytochemicals responsible for reduction, capping, and stabilization were not addressed.

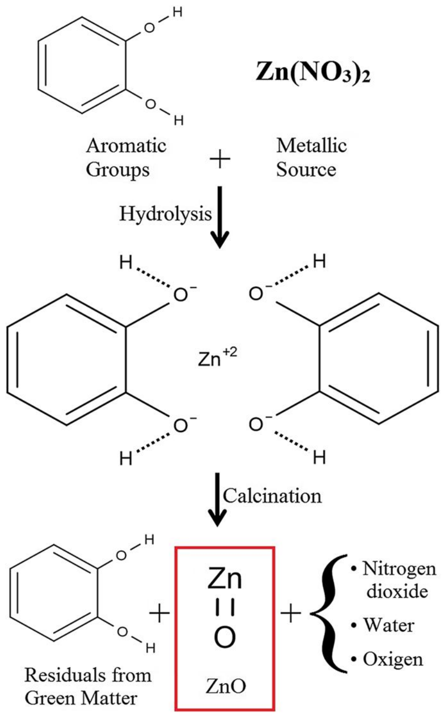

FIG. 6. Proposed mechanism of formation of ZnO NPs from Ref. [37].

In the same year, Mina *et al.* [38] prepared zinc oxide nanoparticles using *Thymus vulgaris* leaf extracts and investigated their synthesizing mechanism. It was reported that the presence of phenol byproducts (thymol and flavonoid) in the leaf extract works as a size reducer throughout the zinc oxide NPs producing process, preventing further development of ZnO crystals. The OH/COOH groups found in phenol are bonded to the surface of zinc oxide particles and behave as surfactants, stabilizers, and size-reducing agents. As a result, they prevent overreaction, the formation of additional compounds, and the growth of ZnO. Figure 7 depicts the possible mechanism of this process.

$$Zn\,(NO_3)_2.6H_2O + 2NaOH \xrightarrow{\Delta} Zn\,(OH)_2 + 2NaNO_3$$

$$Zn\,(OH)_2 + NaNO_3 \xrightarrow{Thymus\ leaf\ extract} ZnO\ \text{nanoparticles}$$

Basically, this study highlighted the essential role of OH/COOH groups in phenol as reducing and stabilizing agents. These findings may guide further research toward plants rich in such functional groups for more effective green synthesis of ZnO nanoparticles.

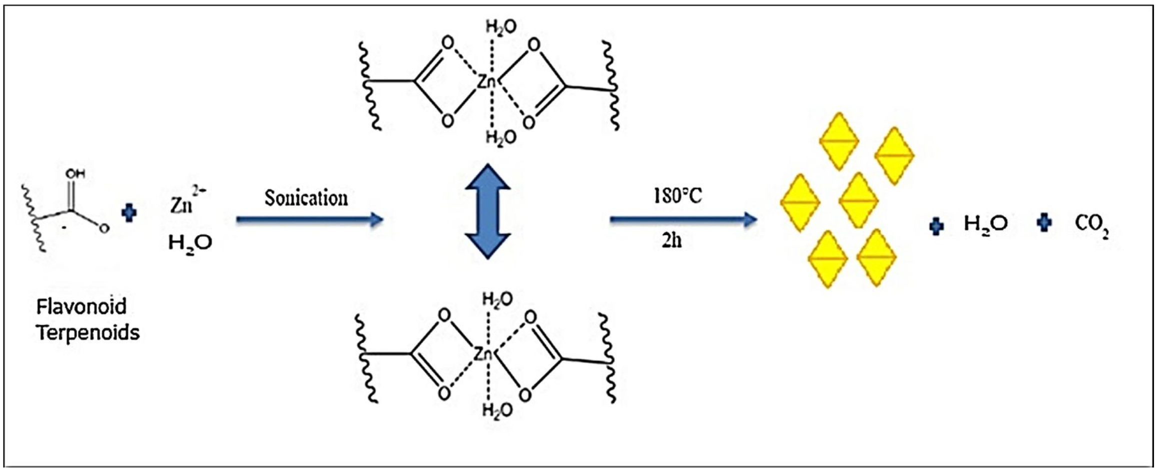

FIG. 7. Possible mechanism of ZnO NPs synthesis and formation using Ref. [38].

In 2020, Vijayakumar *et al.* prepared zinc oxide NPs by utilizing *Acalypha fruticosa L.* leaf extracts and explained the mechanism of ZnO NPs construction [39]. It was shown that *A. fruticosa* leaf extract contained nine chemicals, six of which were flavonoids, one terpenoid, and two glycosides. It was explained that only flavonoids are taken into account because they contribute to the structure of the dominant chemicals found in the extracts, namely 2-Methyl-5,7-dihydroxyl chromone, 9,12-Octadecadienoic acid, Kaempferol-3-Orutinoside, Quercetin, Acalyphin, and Apigenin. The proposed mechanism involves the reaction of 2-Methyl-5,7-dihydroxylchromone with zinc acetate dihydrate [Zn $(CH_3COO)_2{:}2H_2O$], where oxidation by free radicals in the extract leads to the formation of dehydro-2-Methyl-5,7-dihydroxylchromone. Electrostatic attraction between these free radicals and zinc cations facilitates reduction and nucleation. Figure 8 depicts the formation mechanism of ZnO NPs. While flavonoids were emphasized due to their key functional groups acting as reducing agents, it is also important to consider the roles of glycosides and terpenoids, which likely contribute to capping, preventing aggregation, and ensuring long-term nanoparticle stability.

In 2019, Barzinjy *et al.* synthesized ZnO NPs using pomegranate (*Punica granatum*) juice extract and explored their formation mechanism [40]. The extract was shown to be rich in polyphenols, which possess phenolic rings with multiple hydroxyl groups (Fig. 9). These groups act as reducing and capping agents, enabling interaction with Zn^{+2} ions to form zinc hydroxide complexes. Upon annealing, these complexes are converted into ZnO nanoparticles. This study presented a clear and straightforward mechanism that is accessible even to readers without extensive knowledge of phytochemicals.

Subsequently, in 2020, Barzinjy *et al.* reported another study, this time utilizing *Eucalyptus globulus Labill.* leaf extracts for the synthesis of ZnO NPs [41]. They proposed the following possible mechanism of formation:

$$nZn^{2+} + 2Ar - (OH)_n \rightarrow nZn^0 + 2nAr = O + 2nH^+$$

$$2(x + 1)\,Zn^0 + 2Ar = O + yO_2 \rightarrow 2(ZnO - Zn_xO_y - Ar = O)$$

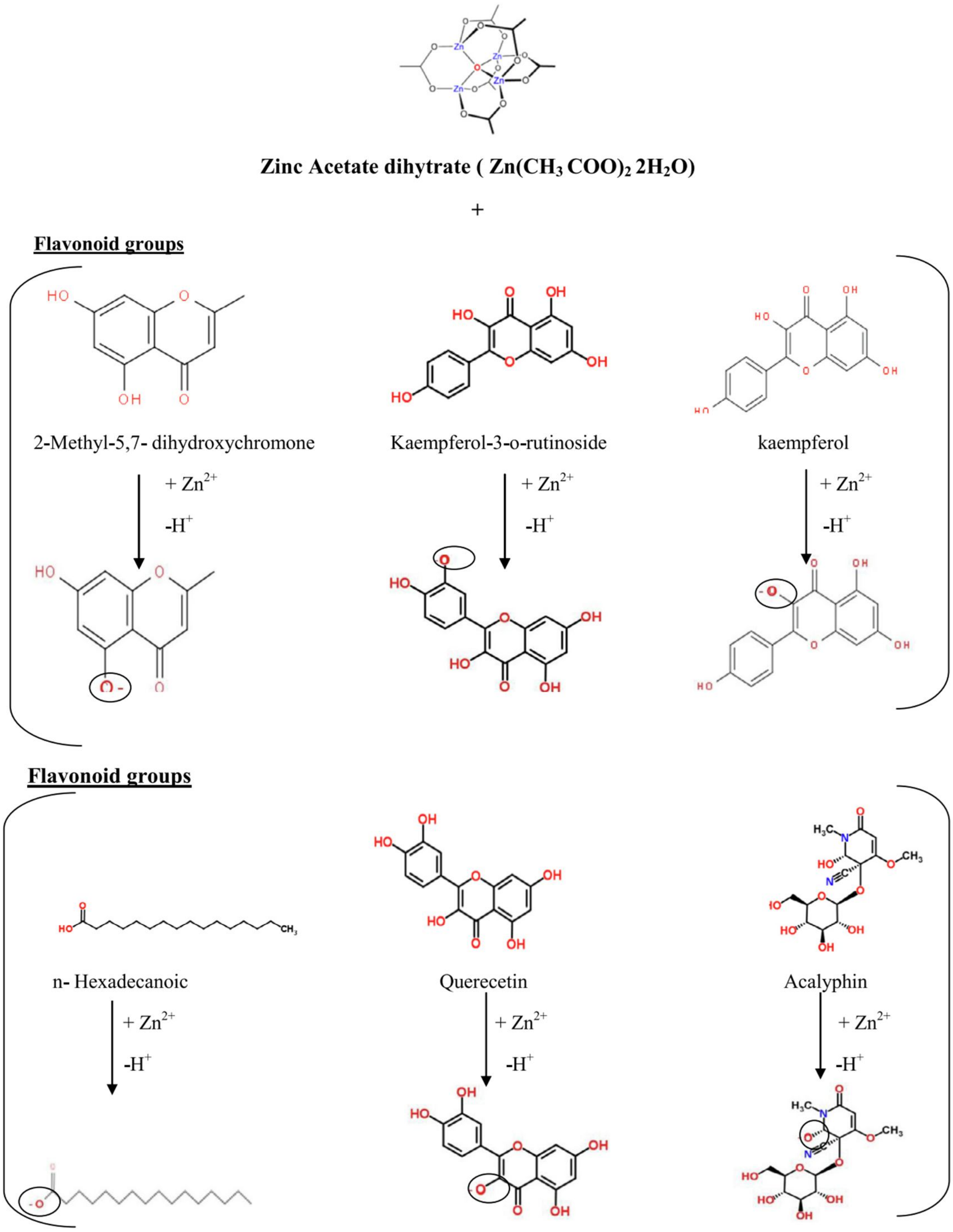

FIG. 8. Proposed mechanism of ZnO NPs formation, adapted from Ref [39].

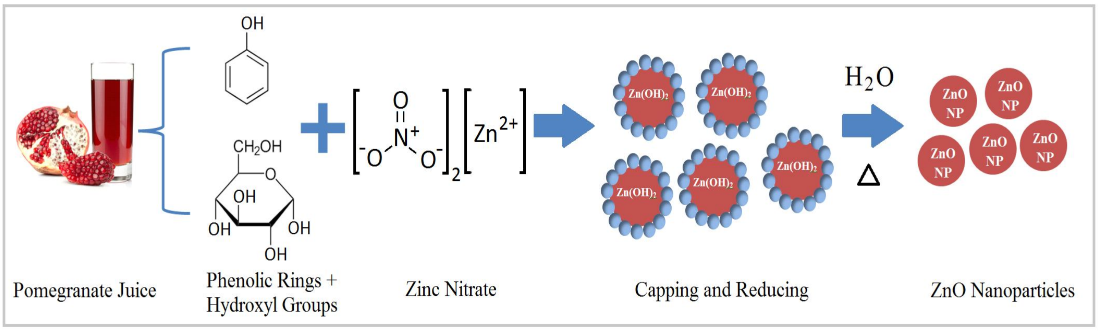

FIG. 9. Proposed mechanism of ZnO NPs formation, adapted from Ref [40].

The natural compounds found in *Eucalyptus globulus* leaf extracts, such as tannins and flavonoids (Ar-$(OH)_n$), play a crucial role in ZnO nanoparticle formation. These biomolecules have the ability to release electrons, thereby aiding in the efficient reduction of Zn^{2+} ions to Zn^0. This process creates a Zn^0-phenolate complex due to a chelating effect, which promotes the nucleation and growth of nanoparticles at a temperature of 60 °C. As the temperature increases to 100 °C in the presence of air, this complex directly decomposes, leading to the formation of Zn nanoparticles. Consequently, the natural phenolic compounds demonstrate a positive influence on the ZnO NPs preparation. From our perspective, this highlights the positive role of natural phenolic compounds in the ZnO nanoparticle synthesis process. Also, this might offer a clear understanding of the potential benefits of utilizing plant extracts in nanomaterial production. However, the formation of a Zn^0-phenolate complex and its subsequent decomposition, possibly, does not provide a complete scenario of the underlying chemical mechanisms for readers who are not knowledgeable in this field.

In 2021, Vishnu *et al.* published an article in which they prepared ZnO NPs by using *Scoparia Dulcis* leaf extracts and explained the mechanism of formation [42]. They reported that several phytochemicals in the extract act as both stabilizers and reducing agents. Specifically, the hydroxy and oxo substituents of plant metabolites interact with Zn^{2+} ions, enabling the reduction process. Figure 10 presents the plausible mechanism for ZnO NP formation mediated by *S. dulcis* phytochemicals. To propose the mechanism, the authors selected 2-hydroxy-2H-1,4-benzoxazol-3-one, an active compound found in all parts of the plant. The mechanism involves deprotonation of the hydroxyl group, generating a negatively charged oxygen center. Zinc ions are then chelated at this site, leading to complex formation and ultimately the generation of ZnO nanoparticles. In our assessment, this study demonstrates that hydroxy and oxo substituents play a central role in Zn^{2+} interaction. However, the specificity of these interactions remains unclear. Furthermore, clearer descriptions of the roles of individual phytochemicals would greatly enhance readers' understanding of the proposed mechanism.

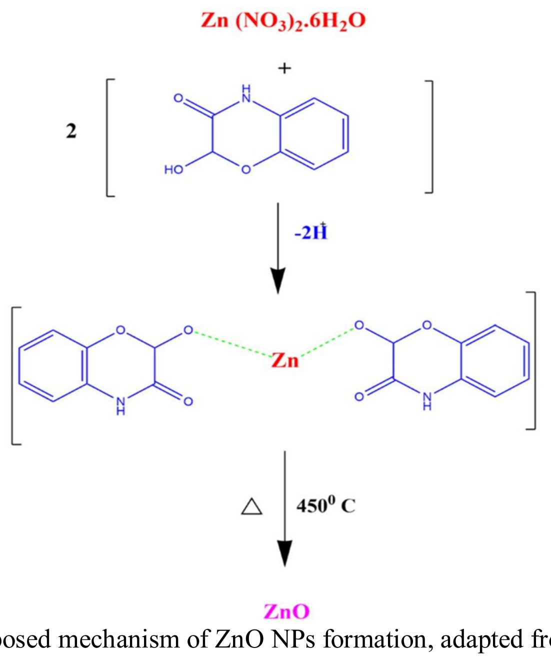

FIG. 10. Proposed mechanism of ZnO NPs formation, adapted from Ref. [42].

In 2022, Supin *et al.* prepared ZnO NPs using *Lepidagathis ananthapuramensis (LA)* leaf extract and explained the mechanism of formation [43]. It was shown that the *LA* leaves extracts contain flavonoids, alkaloids, phenols, and quinones, which participate in producing ZnO NPs via chemical reduction and oxidation processes. These phytochemicals function not only as reducing and oxidizing agents but also as effective capping agents during the formation process. Also, it was mentioned that the actual mechanism for synthesizing ZnO nanoparticles from leaf extracts is not totally understood. Nevertheless, they proposed that two main steps are sufficient to explain the likely formation process, as follows:

1. $Zn(OH)_2$ is formed from the corresponding $Zn(NO_3)_2.6H_2O$ salt.
2. Calcination of the resulting intermediate produces ZnO NPs.

During the process, Zn^{2+} ions available in the zinc electrolytic solution [$Zn(NO_3)_2.6H_2O$ solution] are reduced to the stabilized compound by chelating to phytochemicals, including polyphenols and flavonoids contained in the leaf extract. Through extracting a proton from the phytochemicals, the anionic component of thezinc salt is removed as the corresponding acid. Water molecules attempt to transfer their protons to the corresponding phytochemicals. As a result, the hydroxyl group in the reaction mixture (biomolecule or solution) forms a bond with the stabilized metal species, resulting in the formation of zinc hydroxide ($Zn(OH)_2$). All of these procedures take place at the same time, as illustrated in Fig. 11. According to our assessment, this study aimed to explain the formation mechanism in detail. However, the authors acknowledged that the process is not yet fully understood. Further improvements could include specifying the exact phytochemicals involved, elaborating their roles, and providing a step-by-step description of the formation mechanism to help other researchers address these gaps.

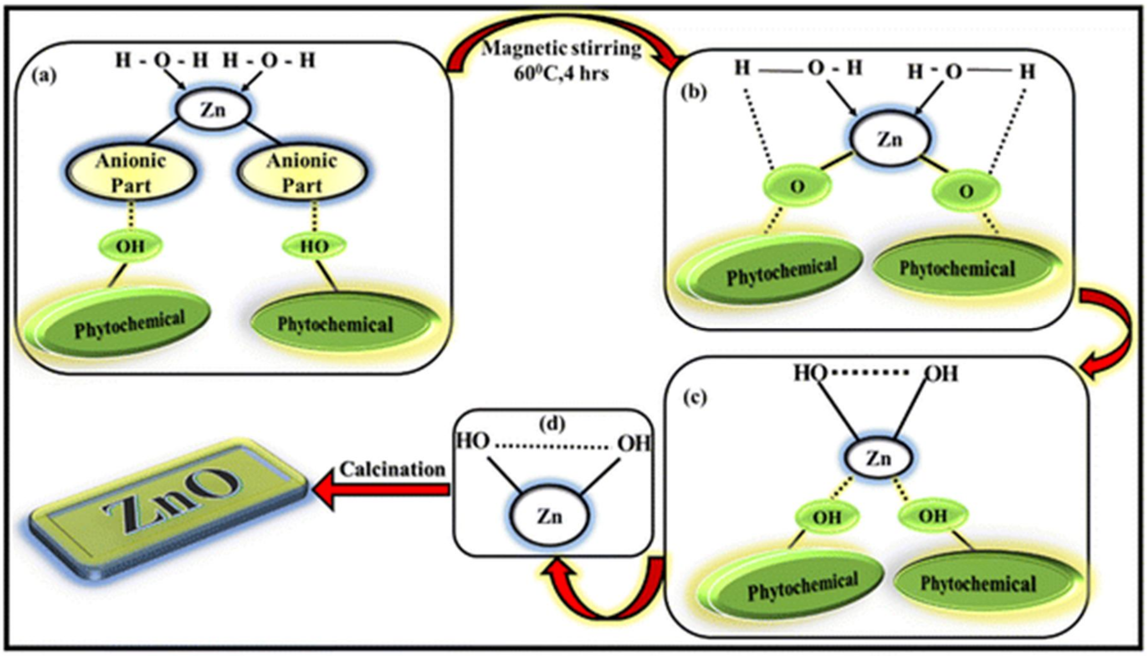

FIG. 11. Proposed mechanism of ZnO NPs formation, adapted from Ref. [43].

In 2023, Maymounah *et al.* synthesized ZnO nanoparticles using *Ziziphus jujuba* leaf extracts and clarified the formation mechanism [44]. The study revealed that *Ziziphus jujuba* plants contain a rich variety of phytochemicals, including terpenoids, tannins, phenolic compounds, saponins, alpha-tocopherol, beta-carotene, flavonoids, alkaloids, sterols, and fatty acids, which work as both reducing and capping agents to avoid ZnO NPs agglomeration, likely due to the presence of long-chain natural products in the extract. These compounds may convert Zn^{2+} to Zn^0, which may then be oxidized to ZnO NPs during the heating process. Moreover, complexation may occur between Zn^{2+} ions and phytochemicals such as polyphenols, leading to the formation of zinc hydroxide ($Zn(OH)_2$) hydrolysis. Upon heating, the complex decomposes to yield stable ZnO nanoparticles. However, the study did not specify which phytochemicals play the most dominant role in the formation process, leaving some uncertainty about the key contributors.

4. Zinc Oxide Nanoparticles Synthesis from Plant Extracts

Plant extracts have recently been used as green media for nanoparticle synthesis because they act as natural chemical factories that are cost-efficient and require minimal maintenance. Various parts of plants, including flowers, leaves, fruits, stems, and roots, have been widely utilized in green synthesis due to the presence of bioactive phytochemicals. These compounds, such as terpenoids, alkaloids, phenols, tannins, and vitamins, simultaneously act as stabilizing and reducing agents during nanoparticle formation [45].

Numerous plants have been reported so far for synthesizing zinc oxide nanoparticles. Ravindra *et al.* were the first to use the milky latex of the plant *Calotropis procera* to successfully biosynthesize ZnO NPs [46]. Their research showed that the ZnO nanoparticles have a spherical shape, and the nanoparticle sizes were in the range of 5-40 nm. The synthesized ZnO NPs were characterized by UV–Vis spectroscopy, scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and photoluminescence (PL). Their research also highlighted the potential applications of these nanoparticles in biosensing devices and nanoelectronics due to their environmentally friendly characteristics.

In another study, Gunalan *et al.* prepared ZnO nanoparticles by utilizing *Aloe barbadensis Miller* leaf extracts and obtained stable spherical ZnO NPs [31]. Moreover, the biosynthesis of ZnO NPs produced polydisperse NPs, with the average particle sizes of 25 to 45 nm. Niranjan *et al.* prepared zinc oxide nanoparticles by utilizing *Hibiscus subdariffa* leaf extracts by dissolving 1 g of zinc acetate in 50 mL of distilled water, gradually adding the solution to 20 mL of plant extract preheated at 50 °C for 10 minutes [47]. After 30 minutes of stirring, the mixture reduced to zinc hydroxide, which was then vacuum-dried at 30 °C. Additional samples were dried at 60 °C and 100 °C. SEM analysis revealed that the drying temperature influenced the morphology: irregular surfaces were observed at 30 °C, spherical structures at 60 °C, and dumbbell-shaped, more crystalline structures at 100 °C.

Javed *et al.* biosynthesized ZnO NPs by utilizing *Elaeagnus angustifolia L.* leaf extracts and explored their multiple in vitro biological applications [48]. UV–Vis spectroscopy confirmed the synthesis, showing a surface plasmon resonance (SPR) peak at 399 nm. The resulting nanoparticles were spherical with an average size of around 26 nm. The study demonstrated that ZnO NPs exhibited strong antibacterial, antifungal, antioxidant, biocompatibility, anticancer, and enzyme inhibition activities. Sangeetha and Thambvani compared two approaches for ZnO NP synthesis: a chemical method using sodium hydroxide and zinc acetate precursors, and a biological method using *Coriandrum sativum* leaf extract with zinc acetate [49]. SEM and XRD analyses showed that the biosynthesized ZnO NPs had an average size of 66 nm, whereas the chemically synthesized ones were slightly larger at 81 nm. The authors concluded that the green method was superior due to its eco-friendly and cost-effective nature.

Suresh *et al.* reported the synthesis of ZnO NPs using *Cassia fistula* extracts through a green synthesis method aimed at harnessing antioxidant and antibacterial properties [50]. TEM and XRD analyses revealed nanoparticles with sizes ranging from 5 to 15 nm and a hexagonal wurtzite structure. The ZnO NPs showed high efficiency in degrading methylene blue dye under both UV and sunlight exposure. They also exhibited excellent antioxidant activity, effectively scavenging DPPH free radicals, and demonstrated antibacterial activity against *Plasmodium desmolyticum*, *Klebsiella aerogenes*, *Staphylococcus aureus*, and *Escherichia coli*.

Barzinjy *et al*. synthesized ZnO NPs using *Euphorbia petiolata* leaf extracts mixed with an aqueous zinc nitrate solution [51]. The reaction resulted in the reduction of zinc ions and the formation of ZnO nanoparticles, confirmed by UV–Vis spectroscopy (SPR peak at 360 nm). XRD analysis revealed a hexagonal wurtzite structure with average particle sizes of 55–60 nm. In another study, Barzinjy and Himdad synthesized ZnO NPs from *Eucalyptus globulus Labill.* leaf extracts combined with zinc nitrate hexahydrate [41]. The mixture, stirred continuously at 60 °C, changed color from light green to yellowish paste, indicating nanoparticle formation. The ZnO NPs were spherical with average sizes between 27 and 35 nm. Characterization showed a band gap of 2.67 eV, high stability (zeta potential and BET surface area of 23.481 m^2/g), and thermal behavior confirmed by DSC, which revealed two endothermic peaks (water evaporation and zinc hydroxide conversion) and an exothermic peak (ZnO crystallization and organic material degradation).

Farjana *et al.* produced zinc oxide nanoparticles with an average size of 16.6 nm from the leaf extracts of *Cocos nucifera* through an easy, inexpensive, and green process [52]. Various techniques, including UV-Vis spectroscopy, XRD, FTIR, EDX, and SEM investigations, were utilized to identify and characterize the produced NPs. According to UV-Vis spectroscopy measurements, the aqueous solution of the produced zinc oxide nanoparticles displayed absorption maxima, λ_{max}, at 370 nm. XRD analysis showed that the produced ZnO NPs have a hexagonal wurtzite shape. The produced nanoparticles showed strong photocatalytic activity and modest antioxidant activity. Based on these findings, the authors concluded that the produced zinc oxide nanoparticles could be utilized in biological, therapeutic, and pharmacological applications, as well as used as photocatalysts in the dye degradation process. Recently, Muthu Kathija *et al.* used *Pisonia alba* leaf extract to prepare zinc oxide nanoparticles [53]. In this investigation, XRD, UV–Vis, FTIR, XPS, and FESEM with EDS were utilized to study the morphological and structural characteristics of the produced ZnO NPs. The highest absorbance was observed at 375 nm, corresponding to an energy gap of 2.96 eV. The average particle size, according to XRD analysis, was 48 nm. In addition, green ZnO NPs showed antimicrobial efficacy against both Gram-positive (*S. aureus*) and Gram-negative (*K. pneumoniae*) bacteria. Table 1 lists 80 different plants reported in the literature for the green synthesis of ZnO nanoparticles.

TABLE 1. Plant extracts used for synthesizing ZnO NPs.

Plant name	Plant part	NPs Size (nm)	Morphology	Surface Plasmon Resonance (SPR)	Year	Reference
Cicer arietinum	Seeds	20–30	spherical	401, 482 and 524	2010	[54]
Aloe barbadensis Miller	Leaves	25-40	Spherical	375	2011	[31]
Physalis alkekengi L	roots, leaves, stems, and fruits	72.5	triangular and elongated	-	2011	[55]
Sedum alfredii Hance	-	53.7	pseudo-spherical	-	2011	[56]
Calotropis procera	Milky latex	5-40	Spherical, granular	368	2011	[46]
Teucrium polium L	Flower	-	elongated	250 to 380	2013	[57]
Parthenium hysterophorus L.	Leaves	27 ± 5 and 84 ± 2	spherical and hexagonal	374 and 370	2013	[58]
P. trifoliate	Fruit	21.12	spherical	327	2013	[59]
Calotropis gigantea	Leaves	30–35	Spherical	-	2013	[60]
Corriandrum sativum	Leaves	66	Cubic	-	2013	[49]
Sargassum myriocystum	Leaves	36	Spherical	-	2013	[61]
Camellia sinensis	Leaves	16	hexagonal	325	2014	[62]
Hibiscus rosa-sinensis	Leaves	30-35	Spongy	-	2014	[63]
Tabernaemontana Divaricate	Leaves	36 ± 5	Spherical	-	2014	[64]
Murraya koeininggi	Leaves	30-35	Hexagonal	-	2014	[65]
Plectranthus amboinicus	Leaves	88	a rod	390	2015	[66]
Pongamia pinnata	Leaves	100	spherical	358	2015	[67]
Solanum nigrum	Leaves	20–30	wurtzite hexagonal	358	2015	[68]
Vitex trifolia L	Leaves	28	spherical	372.56	2015	[69]
Murraya koenigii	Leaves	12	spherical	373	2015	[70]
Azadirachta indica	Leaves	9.6-25.5	spherical	377	2015	[71]
Corymbia citriodora	Leaves	64	polyhedron	386	2015	[72]
Trifolium pratense	Flower	100–190	-	283	2015	[73]
Laurus nobilis	Leaves	47.27	hexagonal	338	2016	[74]
Potato	Roots	20∓1.2	Hexagonal	-	2016	[33]
Ocimum tenuiflorum	Leaves	15 -132 ± 10	rod	380	2016	[75]
Carissa edulis	Fruits	50–55	flower	358	2016	[76]
Limonia acidissima L	Leaves	12-53	spherical	374	2016	[77]
Boswellia ovalifoliolata	Stems	20	spherical	240	2016	[78]
Lycopersicon esculentum	Fruits	50 and 90	spherical	360	2016	[34]

Plant name	Plant part	NPs Size (nm)	Morphology	Surface Plasmon Resonance (SPR)	Year	Reference
Ruta graveolens (L.)	Stems	~28	spherical	355	2016	[12]
Passiflora caerulea	Leaves	70	spherical	380	2017	[79]
Tectona grandis (L.)	Leaves	54	spherical	360	2017	[35]
Sechium edule	Leaves	36.2	a spherical	362	2017	[80]
Musa paradisiaca	Leaves	23.3	spherical	338	2017	[81]
Ziziphus nummularia	Leaves	17.33	spherical/irregular	370	2017	[82]
Imperata cylindrica L	Leaves	11.9	wurtzite hexagonal	359	2017	[83]
Calotropis procera	Leaves	15–25	hexagonal wurtzite	397	2017	[84]
Ipomoea pes-caprae	Leaves	2–20	hexagonal wurtzite	322	2017	[85]
Melia dubia	Leaves	13.39	hexagonal wurtzite	-	2017	[86]
Citrus aurantifolia	Peel	50	Hexagonal	-	2017	[87]
Bauhinia tomentosa	Leaves	22–94	hexagonal	370	2018	[88]
Aristolochia indica	Leaves	22.5	quasi-spherical	367	2018	[89]
Andrographis paniculata	Leaves	96–115 and 57 ± 0.3	spherical and hexagonal	375	2018	[90]
Vaccinium arctostaphylos L	Fruits	-	spherical	420	2018	[91]
Crinumlatifolium	Leaves	10–30	hexagonal and spherical	320	2018	[92]
Coccinia abyssinica	Tuber	10.4	hexagonal	365	2018	[93]
Lawsonia inermis	Leaves	75-100	hexagonal	-	2018	[94]
Citrus sinensis	Peel	-	hexagonal wurtzite	-	2018	[37]
Costus pictus D. Don	Leaves	40	Hexagonal and spherical	-	2018	[36]
Justicia wynaadensis	Leaves	~39	hexagonal wurtzite	329	2019	[95]
Papaver somniferum L	Pod	48	irregular and spherical	360	2019	[96]
Costus igneus	Leaves	26.55	hexagonal wurtzite	365	2019	[97]
Ocimum americanum	-	21	spherical	316	2019	[98]
Pandanus odorifer	Leaves	~90	spherical	~399	2019	[99]
Plectranthus amboinicus	Leaves	88	Spherical	-	2019	[100]
Thymus vulgaris	Leaves	50−60	Irregular	~ 370	2019	[38]
Euphorbia petiolata	Leaves	55-60	hexagonal-wurtzite	360	2019	[51]
Laurus nobilis L	Leaves	21.49-25.26	spherical	350	2019	[101]
Mentha spicata	Leaves	11 to 88	spherical	-	2020	[102]
Sesbania grandiflora	Leaves	70–150	spherical and flakes	375–378	2020	[103]
Punica granatum	Fruits	~60	hexagonal wurtzite	364	2020	[104]
Eucalyptus globulus Labill	Leaves	27 and 35	hexagonal	375	2020	[41]
orange	Fruit Peel	10–20	Spherical	-	2020	[105]
Azadirachta indica	Leaves	20–30	Spherical	-	2020	[106]
Acalypha fruticosa L	Leaves	55	dispersion and spherical	310	2020	[39]
Capparis zeylanica	Leaves	32 to 40	Spherical	356	2020	[21]
Aquilegia pubiflora	Leaves	34.23	Spherical	-	2021	[107]

Plant name	Plant part	NPs Size (nm)	Morphology	Surface Plasmon Resonance (SPR)	Year	Reference
Knoxia sumatrensis	Leaves	50–80	rod	354	2021	[108]
Syzygium Cumini	Leaves	11.35	hexagonal packing	375	2021	[109]
R. tuberosa	Leaves	40–50	rod	320	2021	[110]
Syzygium cumini	Leaves	30	spherical	320	2021	[111]
Carica papaya	Leaves	15-50	semi-spherical, non-spherical, and flower	360	2021	[112]
Lantana Camara	Leaves	35	Spherical	-	2022	[113]
Pelargonium odoratissimum (L.)	Leaves	21.6	spherical and hexagonal	370	2022	[114]
Cocos nucifera	Leaves	16.6	hexagonal wurtzite	370	2022	[52]
Ailanthus altissima	Leaves	13.27	Spherical	327	2023	[115]
Camellia sinensis	Leaves	19.380 ± 2.14	hexagonal	509	2023	[116]
Lepidagathis ananthapuramensis	Leaves	10–15	hexagonal	372	2023	[43]
Pisonia Alba	Leaves	48	hexagonal	378	2023	[53]

Plants have numerous biological properties, and their parts, such as roots, leaves, seeds, stems, and fruits, are excellent resources for nanoparticle production. Extracts derived from these parts act as reducing, capping, and stabilizing agents, with their effectiveness influenced by parameters such as pH, temperature, reaction time, salt concentration, and the available phytochemicals, which control the quality, stability, and quantity of the synthesized nanoparticles. In addition, it was documented that different parts of the same plant can produce different nanoparticle shapes and sizes depending on the type of phytochemicals present [117]. Different groups of phytochemicals were noted by Pawan *et al.* in different parts of *Calendula officinalis L.* as shown in Fig. 12 [118]. Based on our analysis of Table 1, approximately 78% of studies have relied on leaf extracts for ZnO nanoparticle synthesis (Fig. 13). Leaves are relatively easy to obtain and typically contain a wide range of phytochemicals—such as chlorophyll, flavonoids, tannins, alkaloids, carotenoids, phenolic acids, and terpenoids—which play crucial roles as reducing, capping, and stabilizing agents in nanoparticle synthesis [119]. Moreover, because the concentrations of these bioactive compounds vary among different types of leaves, the specific chemical composition of leaf extracts significantly impacts the biosynthesis of nanoparticles [120].

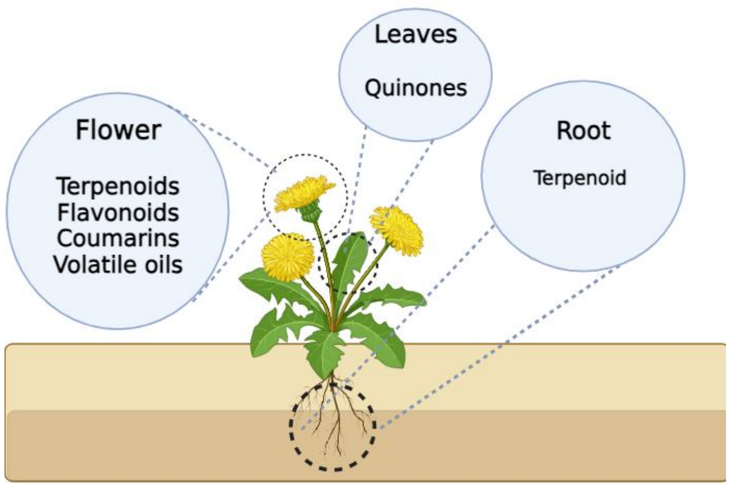

FIG. 12. Different phytochemicals present in the *Calendula officinalis* extract.

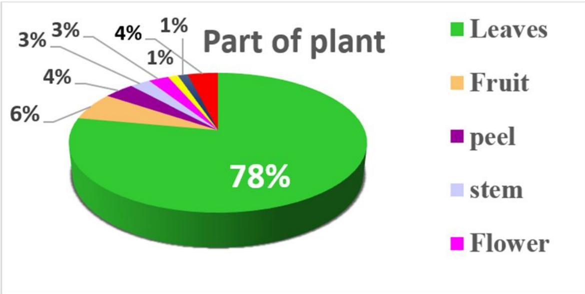

FIG. 13. Contribution of different plant parts in ZnO NPs formation.

5. Conclusions

This investigation aimed to summarize recent research on the biosynthesis of zinc oxide nanoparticles utilizing plant extracts as reducing, capping, and stabilizing agents. Although the complexity of phytochemical structures remains a challenge in evaluating the biosynthesis of nanoparticles, more research on the mechanism of formation of the biosynthesized zinc oxide nanoparticles is required to obtain a better understanding of the chemical processes and reactions that occur during the synthesis. This review includes a comprehensive analysis of 14 distinct articles that offer detailed insights into the green synthesis of ZnO nanoparticles. This review also critically discusses the information available in recent investigations regarding the formation mechanism of biosynthetic ZnO nanoparticles. Moreover, this study covers most of the important plants used in the synthesis of ZnO NPs of various sizes and shapes. Therefore, we believe this review will assist researchers in choosing a suitable plant to modify the NPs' properties for diverse applications. Last but not least, the results of this research showed that about 78% of innovative researchers used the plant leaf extract instead of other parts to synthesize zinc oxide NPs.

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Conflict of interest:

The authors report no conflicts of interest.

Reference:

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