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Variation of Green Synthesis Techniques in Fabrication of Zinc Oxide Nanoparticles – A Mini Review

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Abstract. The field of nanotechnology has been one of the major focus of research for scientists across the world. This field deals with the production and usage of nanoscale materials. The popularity of nanotechnology is due to its unique properties that cannot be found in its large counterpart. In these recent years, zinc oxide nanoparticles (ZnO NPs) emerged as an important ceramic material that can be utilized across various fields such as medicine, cosmetics, textiles, wastewater treatment and many others. The fabrication of ZnO NPs can proceed through three major pathways which are physical, chemical and green synthesis. Among these synthesis method, green synthesis is preferable as it is more environmentally friendly. In this review, we summarize the various techniques of green synthesis in fabrication of ZnO NPs.

1. Introduction

In 1959, Richard Feynman introduced nanotechnology into the field of science and since then, it has spread to wide range of applications such as electronic, optical or magnetic device, medicine, energy, agriculture and others [1]. Nanotechnology can be defined as technology that manipulate materials at nanometer range (1 – 100 nm). Due to its size, nanomaterials exhibit unique physicochemical properties which make them favourable to be applied across various fields [2]. In nanomaterials production, there are two main approaches which are top-down and bottom-up approach. In top-down approach, bulk materials are broken down into nanoscale materials via various techniques while bottom-up approach involves the building of nanomaterials through joining of atoms [3]. Bottom-up approach is preferable as the resulted nanomaterials has lesser defects and homogeneous chemical compositions and this approach relies on chemical and green methods of production [3, 4]. Between these two methods, chemical synthesis considered unfavourable due to high cost and usage of toxic chemicals which may lead to environmental pollution. Furthermore, a previous study shows that chemical synthesized nanomaterials interfered in biomedical applications due to its toxicity [5].Therefore, a method that can overcome problems posed by chemical method is needed and green synthesis emerged as the solution.

In these recent years, due to low-cost and eco-friendly of green synthesis, researches regarding the production of nanomaterials has been focused toward this method. Green synthesis which also commonly known as biological synthesis can be defined as a process that uses biomaterials such as plants and their extract, microorganism and biopolymer to produce the target nanomaterials [3, 6]. In green synthesis, the biomaterials can serve both capping or stabilizing agents thus no additional reagents are needed [7]. Besides its low-cost and environmental friendly, green synthesized nanomaterials have similar physicochemical properties to those chemically synthesized [6]. The three main biomaterials used in green synthesis have their own advantages and disadvantages. For plants extract, the synthesis process is simple and economical but polydisperse nanomaterials are generated. This is due to various phytochemical present in the extract. Utilizing microorganisms in nanomaterials production can overcome nanomaterials' polydispersity. However, the growth of microorganisms must be in controlled and sterile conditions which are relatively complex. Production of nanomaterials using biopolymers are relatively easy but some of biopolymers are insoluble in water which make them difficult to handle [7, 8].

There are many different types of nanomaterials classification with the most common being metallic, such as Ag, Au, Pt and Cd, and metal oxide, such as ZnO, TiO_2, ZrO_2 and CeO_2, nanomaterials. Among them, metal oxides, especially ZnO, have been widely investigated due to their unique size and shape dependent properties [9]. It was reported that ZnO has been used in ointments for skin treatment since at least two millennia B.C, in ancient Egypt and Rome. Today, ZnO is currently being used across different industries such as rubber, ceramics, concrete manufacturing, cosmetic, food and others [10]. With the rise of technology, development of micro- and nanosized ZnO are feasible and this can further broaden its applications.

ZnO is a semiconductor materials with a wide band gap width (3.37 ev) and large excitation binding energy (60 meV) [11]. It has strong pyroelectric and piezoelectric characteristic [12]. It has three crystal form which are hexagonal wurtzite, cubic zinc blend and rock salt. Among the crystal structures, wurtzite is the most stable and the other two only occur in special condition [1]. ZnO can also exist in many different nanostructures such as nanospheres, nanoplates, nanorods, nanotubes, nanoneedles, nanoribbons, nanobelts, nanosheets, nanoflowers and many more [10]. These various structures of ZnO can be produced through different synthesis method. US Food and Drug Administration has considered ZnO materials to be GRAS (generally recognized as safe) thus it is frequently used in food packaging as antimicrobial agent [1]. Due to the high interest in green synthesis, the production of ZnO nanoparticles (NPs) in these recent years has been shifted towards this method. Hence this review provides an overview on the green synthesis of ZnO NPs with a focus on type of biomaterials being used in green synthesis and its technique.

2. Green synthesis of ZnO NPs

In general, synthesis of ZnO NPs can proceed through three methods which are physical, chemical and green (biological) method. Physical method belongs to the top-down approach of nanomaterials production. This physical method can be divided into two types which are direct (American) and indirect (French) process. In American process, through heating process with anthracite, zinc ore is reduced followed by oxidation of zinc vapour which then lead to the formation of ZnO NPs. For French process, ZnO NPs is formed through melting of zinc metal and vaporization at 910 °C. [13] Other physical methods for ZnO NPs production include UV irradiation, sonochemistry, laser ablation, radiolysis and other. However, there are several problems posed by physical method which are the agglomeration of the particles, the need for specific instruments, chemical and high power consumption which may lead to high cost [14]. Chemical method is a synthesis method that utilized chemical to produce ZnO NPs. This method can proceed through both top-down and bottom-up approach. Through top-down approach, ZnO NPs production is through mechanochemical method where the mixture of zinc salt and sodium bicarbonate undergo milling process [13]. The bottom-up approach is much more common in ZnO NPs via chemical method. Chemicals of reducing and capping agent are added to the solution which will promote and control the growth of ZnO NPs through nucleation and aggregation of atoms. The main problem with chemical method is the toxicity of the chemicals used in the synthesis process. In some cases, due to the usage of these toxic chemicals, the ZnO NPs produced are unsuitable for certain applications [14]. The need to overcome the problems posed by both physical and chemical methods led to the emergence of green synthesis of ZnO NPs with an increasing attention in the past few years.

Green synthesis or also known as biological synthesis can be defined as a synthesis process that utilizes biological entities or natural products such as plants and their extracts, microorganism and biopolymer in production of ZnO NPs [15]. It has been reported that green synthesized nanoparticles exhibited a better size and morphology compared to physical and chemical methods [14]. The properties of generated nanomaterials are similar to those synthesized chemically [6].Besides that, there are many advantages of green synthesis such as environmentally friendly, easy, simple, economical and mild synthesis condition. With these key advantages, green synthesis is a process that is aligned with green chemistry principle which makes them a favourable method in the production of ZnO NPs over the other methods [15, 16].

2.1. Plants and plant extracts

The most common biomaterial used to green synthesize ZnO NPs is plants and their extracts and this process is also known as phytogenic synthesis [12]. There are two ways to utilize plants in production of ZnO NPs which are through extraction of zinc from hyperaccumulator and mixture of plants' extract and zinc salt. Certain plants have the tendency to absorb metals from the soils by their roots and store these metals in their leaves and shoots. These plants are called as hyperaccumulator and due to their tendency to absorb metals in the soil, they can serve as phytoremediator for contaminated soils [6]. *Sedum alfredii* Hance plant is a zinc accumulator plant and it is found growing on soil contaminated with Zn. The process of obtaining ZnO NPs from hyperaccumulator proceed in three stages. The first stage is extraction of chlorophyllin followed by extraction of zinc (using H_2SO_4) and formation of zinc chlorophyllin and finally synthesis of ZnO NPs through precipitation from zinc chlorophyllin and calcination process [17]. The main advantages of using hyperaccumulator in production of ZnO NPs are it is a renewable and recyclable resource and it can treat the zinc contaminated soil. However, this method has their own disadvantages as well such as low yield, many steps and possible contamination. Besides that, determining hyperaccumulator of zinc also takes some time and cost.

Plant extracts are the most commonly used biomaterials in production of ZnO NPs. The usage of plant extracts in production of nanomaterials began since the early 1900s but the mechanism on nanomaterials production is still not well known and understood [14]. The extract contains various phytochemical compounds such as phenol, alkaloids, tannins, flavonoids, terpenes, saponins and protein. These compounds can act as reducing, capping and stabilizing agent in production of ZnO NPs [5]. In general, the production of ZnO NPs using plant extract has two stages and it began with collection of plant extract. The plants are washed and dried to remove any debris or dust on it. The target part is cut into small pieces or crushed into powder form. They were then boiled in water for specific duration to extract the phytochemical out of the plant. The extract was purified through centrifugation or filtration process and this is the end of the first stage. In the second stage, the purified plant extract was mixed zinc salt solution. The phytochemical in the plant extract which contain many hydroxyl groups will form bonds with the zinc ions and this led to a stable complex. Through heat treatment, ZnO NPs is obtained through decomposition of the complex. High temperature of calcination will improve the crystallinity of produced ZnO NPs [12, 18]. Although ZnO NPs produced using plant extracts is simple and cost effective, this process still have a few disadvantages such as polydisperse nanoparticles due to diverse phytochemicals and reproducibility of ZnO NPs using seasonal plants as variation of season will lead to variation of phytochemical present in the extracts [7].

2.2. Microorganisms

Green synthesis using microorganism, also known as microbial synthesis, is a process that utilizes microorganism such as bacteria, algae, antinomycetes, fungi, algae, virus and yeast as nanofactories for production to ZnO NPs [19]. There are two main ways of microbial synthesis which are intracellular and extracellular. For intracellular microbial synthesis, the production of ZnO NPs occurs within the cell of the microbes. The metal ions are absorbed into the cell well and reduced to a metal atom by the enzymes in the microbes. Then nucleation and growth process occur in the periplasmic space and cytoplasm. The purified nanoparticles are obtained through ultrasonication. In extracellular microbial synthesis, the enzyme from the microbes is secreted in the growth medium. This enzyme is responsible in reduction, nucleation and growth of the nanoparticles. The protein excreted by the microbes serve as capping agent for nanoparticles stabilization. Formation of nanoparticles are indicated by the formation of white precipitate in the medium [5, 20]. However, it should be noted that not all microbes are able to synthesized ZnO NPs as each of them has their own enzyme activities. Therefore, the selection of microbes is crucial and this screening process is a disadvantage as it requires time and cost. Furthermore, the production of ZnO NPs using microbes depend on their ability to tolerate heavy metals and high heavy metal stress may affect their activity [5].

2.3. Biopolymers

Besides plants, plant extracts and microorganism, biopolymers are also being used as green materials to synthesized ZnO NPs. There are many different types of biopolymers such as polysaccharide, protein and others. In this review, polysaccharide such as plant gums are considered as biopolymers although they are obtained from plants. Most of the methods that utilizes biopolymer will follow the same pathway as plant extracts. First the biopolymer was dissolved in water. In cases of insoluble biopolymer being used, similar to plant extraction process will be applied. Then the solubilized biopolymer solution was mixed with zinc salt. ZnO NPs was then obtained through calcination process. Although biopolymers have been used to produce ZnO NPs, their potential are relatively unexplored. This might be due to difficulty in handling the water insoluble biopolymer and high production cost.

3. Synthesis technique

As it has been stated in section 2, green synthesis is a process that utilizes biomaterials to product ZnO NPs. There are various techniques in green synthesis and in this section, the techniques will be explored and discussed. Techniques in this review refer to the methods or procedures that utilize biomaterials to produce ZnO NPs. Table 1 shows the techniques being used in green synthesis of ZnO NPs and the respective biomaterials.

Table 1. Techniques in green synthesis

Techniques	Biomaterials	Names (types/parts)	Sizes and shapes	Refs
Sol-gel	Plant extracts	*Beta vulgaris* (leaf) *Commamum tamala* (leaf) *Cinnamomum verum* (leaf) *Brassica pleracea var. Itallica* (leaf)	20 ± 2 nm, spherical 30 ± 3 nm, rod-shape 46 ± 2 nm, spherical 47 ± 2 nm, spherical	[25]
	Plant extract	Quince seed mucilage	25 nm, spherical	[26]
	Plant extract	*Hibiscus sabdariffa* (flower)	5-12 nm, spherical agglomerated	[27]
	Plant extract	*Simarouba glauca* (leaf)	17-37 nm, hexagonal	[28]
	Biopolymer	*Boswellia mukul* gum (Polysaccharide)	20-50 nm, hexagonal	[29]
	Biopolymer	Xanthan gum (polysaccharide) Konjak gum (polysaccharide)	53.5 nm, spherical	[30]
	Biopolymer	Almond gum (polysaccharide)	~25.2 nm, spherical	[31]
Precipitation	Plant extracts	*Spinacia oleracea* (leaf)	22.61 nm, spherical	[32]
	Biopolymer	Sodium alginate (polysaccharide)	20-30 nm, star like cluster	[33]
	Plant extracts	*Punica granatum* (fruit juice)	50 nm, ball-shaped	[34]

	Plant extracts	*Hypericum Triquetrifolium* (aerial parts)	48.69 ± 9.71 nm, nanoflowers	[35]
	Plant extracts	*Calotropis gigantea* (leaf)	149.4-304.8 nm, agglomerated	[36]
	Plant extract	*Ocimum teniuflorum* (leaf)	Nanomushroom Spherical Nanocapsules (Variation of Zn salt conc)	[37]
	Plant extract	*Butea monosperma* (seed)	25 nm, spherical and rod	[38]
	Plant extract	*Sambucus ebulus* (leaf)	40-50 nm, spherical	[39]
	Plant extract	*Durio zibethinus* (rind)	283 nm, spherical	[40]
	Plant extract	Jujube (fruit)	29 ± 8 nm, spherical	[41]
	Plant extract	*Cycas pschannae* (leaf)	177-249 nm, nanorods	[42]
	Plant extract	*Selaginella convolute* (leaf)	40-60 nm, spherical	[43]
	Biopolymer	Starch (polysaccharide)	68.2 nm, rod-like, spherical, hexagonal	[44]
	Plant extract	*Echinochloa frumentacea* (grain)	35-90 nm, hexagonal	[45]
Hydrothermal	Plant extract	*Prosopis juliflora* (leaf)	65 nm, hexagonal	[46]
	Plant extract	*Aerva lanata* (flower) *Aerva javanica* (flower)	10 ± 5 nm, spherical 20 ± 5 nm, spherical	[47]
	Plant extract	*Phyllantus emblica* (fruit)	38 nm, spherical	[48]
	Plant extract	*Thymus vulgaris (*leaf)	46..74 nm, spherical	[49]
	Plant extract	*Psidium guajava* (leaf)	43 nm, aggregated spherical	[50]
Sonosynthesis	Plant extract	*Vaccinium arctostaphylos* (leaf)	21 nm, spherical	[51]
	Plant extract	*Psidium guajava* (leaf)	12 nm, (no shape mention)	[50]
	Plant extract	*Eucalyptus spp.* (Leaf)	20-40 nm, spherical	[52]
	Biopolymer	Gum tragacanth (polysaccharide)	55-80 nm, nanorods	[53]
	Plant extract	*Nasturtium officinale* (leaf)	14 nm, Spindle and spherical	[54]
Microwave	Plant extract	*Azadirachta indica* (leaf)	4.2 nm, spherical	[55]
	Plant extract	*Indian baels* (fruit)	~20 nm, Sheet like, spindle, hexagonal	[56]
Combustion	Plant	Potato (peel)	~10-15 nm, nanocauliflower	[57]
	Plant extract	*Azadirachta indica* (leaf)	10-30 nm, mushroom, bullet, nanobuds, hexagonal flakes in the form of cones, bundles, closed pine like structure	[58]

	Plant extract	*Beta vulgaris* (juice)	52.75-76.45 nm, agglomeration of particles which form sponge-like structure	[59]
Intracellular microbial synthesis	Microorganism	*Lactobacillus plantarum* (Bacteria)	124.2 nm	[60]
Extracellular microbial synthesis	Microorganism	*Bacillus paramycoides* (Bacteria)	35-90 nm, spherical	[61]
	Microorganism	*Escherichia hermannii* (Bacteria)	6-18.5 nm, spherical and cubic	[62]
	Microorganism	*Trichoderma harzianum (Fungi)*	30.34 nm, spherical	[63]
	Microorganism	*Pseudomonas putida (Bacteria)*	25-45 nm, spherical	[64]

3.1. Sol-gel technique

Sol-gel technique was first used as early as 1930s through the production of aerogels. Since then, this technique evolved by including heat treatment to produce nanomaterials in powder form [65]. In the fabrication of ZnO NPs via green synthesis, sol-gel technique is one of the most widely used. The process began by mixing the plant extract with metal salt solution followed by gentle heating and stirring until gel or paste is form. In some research papers, this gel or paste was subjected to drying process before calcination but there have been several literatures that reports immediate calcination after the gel or paste was obtained. Pillai and co-workers reported on the fabrication of ZnO NPs via sol-gel method using four different plant extracts. They found that the properties of ZnO NPs were affected by the types of plant extracts used especially in terms of the particle morphologies [25]. Besides plant extracts, biopolymers were also used in the production of ZnO NPs via sol-gel technique. A mixture of two polysaccharides, xanthan gum and konjak gum, with various weight percentage were dissolved in aqueous solution of zinc salt. The mixture was heated until gel was formed and the gel was dried in the oven before it was subjected to annealing process. This study indicated at 0.8 wt. % of polysaccharides, uniform ZnO NPs was obtained. Higher and lower weight percentage of polysaccharides produced polydisperse ZnO NPs [30]. In another work, the effect of calcination temperature on the production of ZnO NPs using pomegranate peel extract via sol-gel technique was investigated. Based on the result in the study, increased of calcination temperature lead to an increased in the particle size of ZnO NPs [66].

3.2. Precipitation technique

Precipitation technique is another widely used technique in production of ZnO NPs. Initially, precipitation technique used as a chemical synthesis where precipitating and capping agent were used to generate ZnO NPs with controllable properties. However, in these recent years, precipitation technique has been used in green synthesis. There are two pathways in precipitation technique which are direct and in-direct. In direct precipitation, the biomaterials serve as both precipitating and capping agent. Ali and colleagues reported a direct precipitation fabrication of ZnO NPs using aqueous extract of *Butea monosperma* seed. The extract and aqueous solution of zinc salt were mixed and heated. After a few hours, cream coloured precipitate was obtained. This precipitate was collected and dried. The result indicated that when a higher concentration of plant extract was used, less agglomerated ZnO NPs was obtained [38]. In in-direct precipitation, precipitating agent, typically sodium hydroxide, was added and the biomaterials serve solely as capping or stabilizing agent. Dodero and co-workers reported on production of ZnO NPs using sodium alginate via precipitation method. In this study, the precipitating agent used was sodium hydroxide and sodium alginate served as capping agent. Through addition of sodium hydroxide, zinc hydroxide complexes were formed and formation of this complex was indicated through the presence of white precipitate. Drying of this white precipitate led to ZnO NPs production [33]. In another literature, the precipitate obtained from the synthesis process was subjected to calcination process to improve the crystallinity of ZnO NPs. This work reported that the ZnO NPs produced through precipitation method with the aid of sodium hydroxide and pomegranate juice extract. The formation of ZnO NPs were determined through the appearance of surface plasmon resonance (SPR) through ultraviolet-visible (UV-Vis) spectrophotometer. Once confirmed, the precipitate was collected, washed and subjected to calcination [34].

3.3. Hydrothermal technique
Hydrothermal technique can be defined as a process that employs homogeneous or heterogeneous phase reaction in water at elevated temperature and pressure to crystallize ZnO NPs directly from the solution. The main advantage of this technique is regulable nucleation, growth and ageing rate which can lead to controllable particles morphology. Furthermore, through this technique, highly crystalline ZnO NPs can be obtained directly from the solution without additional sintering process [67]. Similar to precipitation technique, green synthesized ZnO NPs via hydrothermal technique can proceed through two pathways which are direct and in-direct. For direct path, the biomaterials serve as both reducing and capping or stabilizing agent and for in-direct path, the biomaterials only serve as capping or stabilizing agent. Duraimurugan and colleague reported the production of ZnO NPs via direct hydrothermal technique with the presence of *Aerva lanata* and *Aerva javanica* flower extracts. The extract and zinc salt were mixed and autoclaved at 120 °C for 12 hours. The precipitate was directly collected, washed and dried. The TEM images of synthesized ZnO NPs showed that with different flower extracts, the average particle size differ from one extract to the other [47]. Through in-direct hydrothermal technique, sodium hydroxide was added to the mixture of zinc salt and *Thymus vulgaris* leaf extract to facilitate the precipitation of ZnO NPs from the solution during the hydrothermal reaction. The plant extract served as size reducing agent and the effect of its amount on the properties of synthesized ZnO NPs was studied. Overall, with the addition of 1 mL plant extract, the particles obtained were the smallest and free of agglomeration [49].

3.4. Sonosynthesis
Sonosynthesis which also known as ultrasound assisted synthesis is a synthesis process that utilizes bubbles cavitation in water to synthesize materials. The basic principle in sonosynthesis began with irradiation of ultrasound through water which will cause the formation of cavities. The magnitude of cavities can be controlled through manipulating the amplitude and power of the ultrasound. High energy which consist of high pressure (~1000 atm) and high temperature (5000K) will be generated from the collapse of cavities. Using this generated energy, the targeted materials can be synthesized [68-70]. Chauhan and co-workers reported on the production of ZnO NPs with ultrasound assist using *Eucalyptus spp.* leaf extract as the capping agent. In this study, bath sonicator was used as the source of ultrasound and precipitating agent (ammonia) was added to facilitate the formation of ZnO NPs [52]. In another study, tracaganth gum was used as the capping agent in the production of ZnO NPs. Ultrasound probe was used as the energy source and the effect of ultrasound time on the properties of generated ZnO NPs was studied. The morphology of ZnO NPs obtained through this synthesis process was nanorods with average diameter around 55-80 nm and 240 nm in length [53].

3.5. Microwave technique
Microwave is a form of electromagnetic energy with longer wavelength and low energy compared to the other electromagnetic energy. Through microwave irradiation, the materials will absorb the energy and transform them into heat. Thus the heat is generated from the inside of the material while conventional heating involve heat transfer from outside to inside via conduction [71]. This technique has several advantages such as fast process speed, pure products, lower heat lost, low cost of operations and others. However, to utilize this technique, good absorber of microwave energy must be used to ensure that the microwave energy is converted to heat energy which act as the energy source in ZnO

NPs formation [68]. Currently, there are not many reports on the utilization of microwave in the production of ZnO NPs. A work reported on the production of ZnO NPs using domestic microwave oven with *Azadirachta indica* leaf extract as the biomaterial. TEM image indicated that the ZnO NPs obtained through this technique has spherical morphology with average particle size of 4.2 nm [55].

3.6. Combustion technique
Combustion technique involve self-sustaining chemical reaction accompanied by rapid heat release that typically occur in the form of high temperature. This technique has short reaction time and produces product with unique electrochemical, physical, biological and mechanical properties. In general, there are three types of combustion technique which are solid phase combustion, gas phase flame synthesis and solution combustion. In solid phase combustion, thermal is supplied as ignition to the combustion process which will then convert the precursor to the desired product. Gas flame synthesis occur between gaseous components and this method is used for large-scale manufacturing for carbon black. Solution combustion involves the usage of fuels and oxidizer in the water which make a reactive mixture. Through ignition, combustion of the solution will occur. This solution combustion technique is most commonly used in the production of ZnO NPs. Solid combustion was used to produce ZnO nanocauliflower with powder of potato peel and zinc nitrate as the precursor [57]. Various ZnO morphology was produced through solution combustion process with neem extract as the fuel. Through this study, it was discovered that varying the amount of neem extract will change the morphology of the ZnO NPs produced [58].

3.7. Microbial synthesis
Synthesis using microorganism is also known as microbial synthesis. As it has been explained in section 2.2, there are two ways for microbial synthesis which are intracellular and extracellular. For intracellular microbial synthesis, the production of ZnO NPs occurred within the cell of the microorganism while for extracellular microbial synthesis, the extract from the microorganism was collected and used to produce the ZnO NPs [72]. From the literatures search, it was discovered that extracellular microbial synthesis is more common compared to intracellular microbial synthesis. Saravanakumar and colleague reported on the production of ZnO NPs using fungi via extracellular microbial synthesis. TEM result indicated that the ZnO NPs produced exhibited spherical morphology with average particle size of 30.34 nm [63]. In another work, a bacteria, *Pseudomonas putida* extract was used to produce ZnO NPs [64]. Intracellular microbial synthesis of ZnO NPs was successful using *Lactobacillus plantarum* strain TA4. The ZnO NPs was extracted out of the cell of the bacteria through sonication process [60].

4. Conclusion
In conclusion, there are numerous studies have been reported on production of ZnO NPs through green synthesis. Overall, the biomaterials used in green synthesis can be generally categorized into three which are plants and their extracts, biopolymers and microorganism. Further investigation through literatures of green synthesized ZnO NPs, there are various techniques being used for its fabrication. Some of the main techniques being used are sol-gel, precipitation, hydrothermal, sonosynthesis, microwave and combustion. These techniques specifically used plants and their extracts and biopolymer as the biomaterials to synthesize ZnO NPs. For microorganism, there are only two techniques which are intracellular and extracellular microbial synthesis. Between these two microbial techniques, the most commonly use is extracellular microbial synthesis where the extract of the microorganisms is collected and used to synthesize ZnO NPs. It is noted that there are variation of techniques and in some cases, combination of techniques were also used. However, in this review, only singular and main techniques are being discussed. All the ZnO NPs produced through all these techniques have various application across fields of energy, environmental, biomedical and others.

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References
[1] Kim I, Viswanathan K, Kasi G, Thanakkasaranee S, Sadeghi K and Seo J 2020 ZnO Nanostructures in Active Antibacterial Food Packaging: Preparation Methods, Antimicrobial Mechanisms, Safety Issues, Future Prospects, and Challenges *Food Reviews International* 1-29
[2] Akbar S, Tauseef I, Subhan F, Sultana N, Khan I, Ahmed U and Haleem K S 2020 An overview of the plant-mediated synthesis of zinc oxide nanoparticles and their antimicrobial potential *Inorganic and Nano-Metal Chemistry* **50** 257-71
[3] Vijayaraghavan K and Ashokkumar T 2017 Plant-mediated biosynthesis of metallic nanoparticles: A review of literature, factors affecting synthesis, characterization techniques and applications *Journal of Environmental Chemical Engineering* **5** 4866-83
[4] Jin S E and Jin H E 2019 Synthesis, Characterization, and Three-Dimensional Structure Generation of Zinc Oxide-Based Nanomedicine for Biomedical Applications *Pharmaceutics* **11**
[5] Mohd Yusof H, Mohamad R, Zaidan U H and Abdul Rahman N A 2019 Microbial synthesis of zinc oxide nanoparticles and their potential application as an antimicrobial agent and a feed supplement in animal industry: a review *J Anim Sci Biotechnol* **10** 57
[6] Vishnukumar P, Vivekanandhan S, Misra M and Mohanty A K 2018 Recent advances and emerging opportunities in phytochemical synthesis of ZnO nanostructures *Materials Science in Semiconductor Processing* **80** 143-61
[7] Ovais M, Khalil A T, Ayaz M, Ahmad I, Nethi S K and Mukherjee S 2018 Biosynthesis of Metal Nanoparticles via Microbial Enzymes: A Mechanistic Approach *Int J Mol Sci* **19**
[8] Saratale R G, Karuppusamy I, Saratale G D, Pugazhendhi A, Kumar G, Park Y, Ghodake G S, Bharagava R N, Banu J R and Shin H S 2018 A comprehensive review on green nanomaterials using biological systems: Recent perception and their future applications *Colloids Surf B Biointerfaces* **170** 20-35
[9] Theerthagiri J, Salla S, Senthil R A, Nithyadharseni P, Madankumar A, Arunachalam P, Maiyalagan T and Kim H S 2019 A review on ZnO nanostructured materials: energy, environmental and biological applications *Nanotechnology* **30** 392001
[10] Borysiewicz M A 2019 ZnO as a Functional Material, a Review *Crystals* **9**
[11] Ong C B, Ng L Y and Mohammad A W 2018 A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications *Renewable and Sustainable Energy Reviews* **81** 536-51
[12] Hameed S, Iqbal J, Ali M, Khalil A T, Ahsan Abbasi B, Numan M and Shinwari Z K 2019 Green synthesis of zinc nanoparticles through plant extracts: establishing a novel era in cancer theranostics *Materials Research Express* **6**
[13] Basnet P, Inakhunbi Chanu T, Samanta D and Chatterjee S 2018 A review on bio-synthesized zinc oxide nanoparticles using plant extracts as reductants and stabilizing agents *J Photochem Photobiol B* **183** 201-21
[14] Khandel P, Yadaw R K, Soni D K, Kanwar L and Shahi S K 2018 Biogenesis of metal nanoparticles and their pharmacological applications: present status and application prospects *Journal of Nanostructure in Chemistry* **8** 217-54
[15] Bandeira M, Giovanela M, Roesch-Ely M, Devine D M and da Silva Crespo J 2020 Green synthesis of zinc oxide nanoparticles: A review of the synthesis methodology and mechanism of formation *Sustainable Chemistry and Pharmacy* **15**

[16] Kumar H, Bhardwaj K, Kuca K, Kalia A, Nepovimova E, Verma R and Kumar D 2020 Flower-Based Green Synthesis of Metallic Nanoparticles: Applications beyond Fragrance *Nanomaterials (Basel)* **10**
[17] Wang D, Liu H, Ma Y, Qu J, Guan J, Lu N, Lu Y and Yuan X 2016 Recycling of hyper-accumulator: Synthesis of ZnO nanoparticles and photocatalytic degradation for dichlorophenol *Journal of Alloys and Compounds* **680** 500-5
[18] Ahmad F, Ashraf N, Ashraf T, Zhou R B and Yin D C 2019 Biological synthesis of metallic nanoparticles (MNPs) by plants and microbes: their cellular uptake, biocompatibility, and biomedical applications *Appl Microbiol Biotechnol* **103** 2913-35
[19] Gahlawat G and Choudhury A R 2019 A review on the biosynthesis of metal and metal salt nanoparticles by microbes *RSC Advances* **9** 12944-67
[20] Khanna P, Kaur A and Goyal D 2019 Algae-based metallic nanoparticles: Synthesis, characterization and applications *J Microbiol Methods* **163** 105656
[21] Fouda A, Hassan S E, Salem S S and Shaheen T I 2018 In-Vitro cytotoxicity, antibacterial, and UV protection properties of the biosynthesized Zinc oxide nanoparticles for medical textile applications *Microbial Pathogenesis* **125** 252-61
[22] Moghaddam A B, Moniri M, Azizi S, Rahim R A, Bin Ariff A, Saad W Z, Namvar F, Navaderi M and Mohamad R 2017 Biosynthesis of ZnO Nanoparticles by a New Pichia kudriavzevii Yeast Strain and Evaluation of Their Antimicrobial and Antioxidant Activities *Molecules* **22**
[23] Taghavi Fardood S, Ramazani A, Moradi S and Azimzadeh Asiabi P 2017 Green synthesis of zinc oxide nanoparticles using arabic gum and photocatalytic degradation of direct blue 129 dye under visible light *Journal of Materials Science: Materials in Electronics* **28** 13596-601
[24] Zhang G, Shen X and Yang Y 2011 Facile Synthesis of Monodisperse Porous ZnO Spheres by a Soluble Starch-Assisted Method and Their Photocatalytic Activity *The Journal of Physical Chemistry C* **115** 7145-52
[25] Pillai A M, Sivasankarapillai V S, Rahdar A, Joseph J, Sadeghfar F, Anuf A R, Rajesh K and Kyzas G Z 2020 Green synthesis and characterization of zinc oxide nanoparticles with antibacterial and antifungal activity *Journal of Molecular Structure* **1211** 128107
[26] Tabrizi Hafez Moghaddas S M, Elahi B and Javanbakht V 2020 Biosynthesis of pure zinc oxide nanoparticles using Quince seed mucilage for photocatalytic dye degradation *Journal of Alloys and Compounds* **821** 153519
[27] Soto-Robles C A, Luque P A, Gómez-Gutiérrez C M, Nava O, Vilchis-Nestor A R, Lugo-Medina E, Ranjithkumar R and Castro-Beltrán A 2019 Study on the effect of the concentration of Hibiscus sabdariffa extract on the green synthesis of ZnO nanoparticles *Results in Physics* **15** 102807
[28] Hemanth Kumar N K, Murali M, Satish A, Brijesh Singh S, Gowtham H G, Mahesh H M, Lakshmeesha T R, Amruthesh K N and Jagannath S 2020 Bioactive and Biocompatible Nature of Green Synthesized Zinc Oxide Nanoparticles from Simarouba glauca DC.: An Endemic Plant to Western Ghats, India *Journal of Cluster Science* **31** 523-34
[29] Nourbakhsh M, Darroudi M and Gholizadeh M 2020 Role of bio-derived zinc oxide nanoparticles in antifungal and photocatalytic activities *Research on Chemical Intermediates* **46** 243-52
[30] Liu J, Wu X and Wang M 2019 Biosynthesis of Zinc Oxide Nanoparticles Using Biological Polysaccharides for Application in Ceramics *Journal of Electronic Materials* **48** 8024-30
[31] Theophil Anand G, Renuka D, Ramesh R, Anandaraj L, John Sundaram S, Ramalingam G, Magdalane C M, Bashir A K H, Maaza M and Kaviyarasu K 2019 Green synthesis of ZnO nanoparticle using Prunus dulcis (Almond Gum) for antimicrobial and supercapacitor applications *Surfaces and Interfaces* **17** 100376

[32] Thangapandiyan S and Monika S 2020 Green Synthesized Zinc Oxide Nanoparticles as Feed Additives to Improve Growth, Biochemical, and Hematological Parameters in Freshwater Fish Labeo rohita *Biological Trace Element Research* **195** 636-47
[33] Dodero A, Alloisio M, Vicini S and Castellano M 2020 Preparation of composite alginate-based electrospun membranes loaded with ZnO nanoparticles *Carbohydr Polym* **227** 115371
[34] Barzinjy A A, Hamad S M, Esmaeel M M, Aydın S K and Hussain F H S 2020 Biosynthesis and characterisation of zinc oxide nanoparticles from Punica granatum (pomegranate) juice extract and its application in thin films preparation by spin-coating method *Micro & Nano Letters* **15** 415-20
[35] Al Sharie A H, El-Elimat T, Darweesh R S, Swedan S, Shubair Z, Al-Qiam R and Albarqi H 2020 Green synthesis of zinc oxide nanoflowers using Hypericum triquetrifolium extract: characterization, antibacterial activity and cytotoxicity against lung cancer A549 cells *Applied Organometallic Chemistry* **34** e5667
[36] Rajashekara S, Shrivastava A, Sumhitha S and Kumari S 2020 Biomedical Applications of Biogenic Zinc Oxide Nanoparticles Manufactured from Leaf Extracts of Calotropis gigantea (L.) Dryand *BioNanoScience*
[37] Sharma S, Kumar K, Thakur N and Chauhan M S 2020 Ocimum tenuiflorum leaf extract as a green mediator for the synthesis of ZnO nanocapsules inactivating bacterial pathogens *Chemical Papers*
[38] Ali S G, Ansari M A, Alzohairy M A, Alomary M N, Jalal M, AlYahya S, Asiri S M M and Khan H M 2020 Effect of Biosynthesized ZnO Nanoparticles on Multi-Drug Resistant Pseudomonas Aeruginosa *Antibiotics-Basel* **9** 14
[39] Alamdari S, Ghamsari M S, Lee C, Han W, Park H H, Tafreshi M J, Afarideh H and Ara M H M 2020 Preparation and Characterization of Zinc Oxide Nanoparticles Using Leaf Extract of Sambucus ebulus *Applied Sciences-Basel* **10** 19
[40] Ravichandran V, Sumitha S, Ning C Y, Xian O Y, Yu U K, Paliwal N, Shah S A A and Tripathy M 2020 Durian waste mediated green synthesis of zinc oxide nanoparticles and evaluation of their antibacterial, antioxidant, cytotoxicity and photocatalytic activity *Green Chem. Lett. Rev.* **13** 102-16
[41] Golmohammadi M, Honarmand M and Ghanbari S 2020 A green approach to synthesis of ZnO nanoparticles using jujube fruit extract and their application in photocatalytic degradation of organic dyes *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **229** 117961
[42] Sudha K G, Ali S, Karunakaran G, Kowsalya M, Kolesnikov E and Rajeshkumar M P 2020 Eco-friendly synthesis of ZnO nanorods using Cycas pschannae plant extract with excellent photocatalytic, antioxidant, and anticancer nanomedicine for lung cancer treatment *Applied Organometallic Chemistry* **34** e5511
[43] Xu K, Yan H, Cao M and Shao X 2020 Selaginella convolute extract mediated synthesis of ZnO NPs for pain management in emerging nursing care *Journal of Photochemistry and Photobiology B: Biology* **202** 111700
[44] Abd Elkodous M, El-Sayyad G S, Abdel Maksoud M I A, Abdelrahman I Y, Mosallam F M, Gobara M and El-Batal A I 2020 Fabrication of Ultra-Pure Anisotropic Zinc Oxide Nanoparticles via Simple and Cost-Effective Route: Implications for UTI and EAC Medications *Biol Trace Elem Res* **196** 297-317
[45] Velsankar K, Sudhahar S, Parvathy G and Kaliammal R 2020 Effect of cytotoxicity and aAntibacterial activity of biosynthesis of ZnO hexagonal shaped nanoparticles by Echinochloa frumentacea grains extract as a reducing agent *Materials Chemistry and Physics* **239** 121976
[46] Sheik Mydeen S, Raj Kumar R, Kottaisamy M and Vasantha V S 2020 Biosynthesis of ZnO nanoparticles through extract from Prosopis juliflora plant leaf: Antibacterial activities and a new approach by rust-induced photocatalysis *Journal of Saudi Chemical Society* **24** 393-406

[47] J D, G S K, S S, R R, R A, P.M A and P M 2020 Hydrothermal assisted phytofabrication of zinc oxide nanoparticles with different nanoscale characteristics for the photocatlytic degradation of Rhodamine B *Optik* **202** 163607
[48] Shubha P, Gowda M L, Namratha K, Manjunatha H B and Byrappa K 2019 In vitro and In vivo evaluation of green-hydrothermal synthesized ZnO nanoparticles *Journal of Drug Delivery Science and Technology* **49** 692-9
[49] Zare M, Namratha K, Thakur M S and Byrappa K 2019 Biocompatibility assessment and photocatalytic activity of bio-hydrothermal synthesis of ZnO nanoparticles by Thymus vulgaris leaf extract *Materials Research Bulletin* **109** 49-59
[50] Saha R, Subramani K, Petchi Muthu Raju S A K, Rangaraj S and Venkatachalam R 2018 Psidium guajava leaf extract-mediated synthesis of ZnO nanoparticles under different processing parameters for hydrophobic and antibacterial finishing over cotton fabrics *Progress in Organic Coatings* **124** 80-91
[51] Bayrami A, Alioghli S, Rahim Pouran S, Habibi-Yangjeh A, Khataee A and Ramesh S 2019 A facile ultrasonic-aided biosynthesis of ZnO nanoparticles using Vaccinium arctostaphylos L. leaf extract and its antidiabetic, antibacterial, and oxidative activity evaluation *Ultrasonics Sonochemistry* **55** 57-66
[52] Chauhan A K, Kataria N and Garg V K 2020 Green fabrication of ZnO nanoparticles using Eucalyptus spp. leaves extract and their application in wastewater remediation *Chemosphere* **247** 125803
[53] Ghayempour S, Montazer M and Mahmoudi Rad M 2016 Tragacanth gum biopolymer as reducing and stabilizing agent in biosonosynthesis of urchin-like ZnO nanorod arrays: A low cytotoxic photocatalyst with antibacterial and antifungal properties *Carbohydr Polym* **136** 232-41
[54] Bayrami A, Ghorbani E, Rahim Pouran S, Habibi-Yangjeh A, Khataee A and Bayrami M 2019 Enriched zinc oxide nanoparticles by Nasturtium officinale leaf extract: Joint ultrasound-microwave-facilitated synthesis, characterization, and implementation for diabetes control and bacterial inhibition *Ultrasonics Sonochemistry* **58** 104613
[55] Saravanan P, SenthilKannan K, Divya R, Vimalan M, Tamilselvan S and Sankar D 2020 A perspective approach towards appreciable size and cost-effective solar cell fabrication by synthesizing ZnO nanoparticles from Azadirachta indica leaves extract using domestic microwave oven *Journal of Materials Science: Materials in Electronics* **31** 4301-9
[56] Mallikarjunaswamy C, Lakshmi Ranganatha V, Ramu R, Udayabhanu and Nagaraju G 2020 Facile microwave-assisted green synthesis of ZnO nanoparticles: application to photodegradation, antibacterial and antioxidant *Journal of Materials Science: Materials in Electronics* **31** 1004-21
[57] Alharthi F A, Al-Zaqri N, El marghany A, Alghamdi A A, Alorabi A Q, Baghdadi N, Al-Shehri H S, Wahab R and Ahmad N 2020 Synthesis of nanocauliflower ZnO photocatalyst by potato waste and its photocatalytic efficiency against dye *Journal of Materials Science: Materials in Electronics* **31** 11538-47
[58] Madan H R, Sharma S C, Udayabhanu, Suresh D, Vidya Y S, Nagabhushana H, Rajanaik H, Anantharaju K S, Prashantha S C and Sadananda Maiya P 2016 Facile green fabrication of nanostructure ZnO plates, bullets, flower, prismatic tip, closed pine cone: Their antibacterial, antioxidant, photoluminescent and photocatalytic properties *Spectrochim Acta A Mol Biomol Spectrosc* **152** 404-16
[59] Pavan Kumar M A, Suresh D, Nagabhushana H and Sharma S C 2015 Beta vulgaris aided green synthesis of ZnO nanoparticles and their luminescence, photocatalytic and antioxidant properties *The European Physical Journal Plus* **130** 109
[60] Yusof H M, Mohamad R, Zaidan U H and Rahman N A 2020 Sustainable microbial cell nanofactory for zinc oxide nanoparticles production by zinc-tolerant probiotic Lactobacillus plantarum strain TA4 *Microb. Cell. Fact.* **19** 17

[61] Dharmaraj D, Krishnamoorthy M, Rajendran K, Karuppiah K, Jeyaraman R and Ethiraj K 2020 Protein Leakage Induced Marine Antibiofouling Activity of Biosynthesized Zinc Oxide Nanoparticles *Journal of Cluster Science*

[62] Gad El-Rab S M F, Abo-Amer A E and Asiri A M 2020 Biogenic Synthesis of ZnO Nanoparticles and Its Potential Use as Antimicrobial Agent Against Multidrug-Resistant Pathogens *Current Microbiology* **77** 1767-79

[63] Saravanakumar K, Jeevithan E, Hu X, Chelliah R, Oh D-H and Wang M-H 2020 Enhanced anti-lung carcinoma and anti-biofilm activity of fungal molecules mediated biogenic zinc oxide nanoparticles conjugated with β-D-glucan from barley *Journal of Photochemistry and Photobiology B: Biology* **203** 111728

[64] Jayabalan J, Mani G, Krishnan N, Pernabas J, Devadoss J M and Jang H T 2019 Green biogenic synthesis of zinc oxide nanoparticles using Pseudomonas putida culture and its In vitro antibacterial and anti-biofilm activity *Biocatalysis and Agricultural Biotechnology* **21** 101327

[65] Sakka S 2013 *Handbook of Advanced Ceramics,* pp 883-910

[66] Sukri S, Shameli K, Wong M M T, Teow S Y, Chew J and Ismail N A 2019 Cytotoxicity and antibacterial activities of plant-mediated synthesized zinc oxide (ZnO) nanoparticles using Punica granatum (pomegranate) fruit peels extract *Journal of Molecular Structure* **1189** 57-65

[67] Basnet P and Chatterjee S 2020 Structure-directing property and growth mechanism induced by capping agents in nanostructured ZnO during hydrothermal synthesis—A systematic review *Nano-Structures & Nano-Objects* **22**

[68] Kharissova O V, Kharisov B I, Oliva Gonzalez C M, Mendez Y P and Lopez I 2019 Greener synthesis of chemical compounds and materials *R Soc Open Sci* **6** 191378

[69] Gogate P R 2020 Improvements in Catalyst Synthesis and Photocatalytic Oxidation Processing Based on the Use of Ultrasound *Top Curr Chem (Cham)* **378** 29

[70] Dheyab M A, Aziz A A, Jameel M S, Khaniabadi P M and Mehrdel B 2020 Mechanisms of effective gold shell on Fe3O4 core nanoparticles formation using sonochemistry method *Ultrason Sonochem* **64** 104865

[71] Zhu X H and Hang Q M 2013 Microscopical and physical characterization of microwave and microwave-hydrothermal synthesis products *Micron* **44** 21-44

[72] Narayanan K B and Sakthivel N 2010 Biological synthesis of metal nanoparticles by microbes *Adv Colloid Interface Sci* **156** 1-13