RECENT ADVANCES IN ECO-FRIENDLY SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES FROM ECOLOGICAL SOURCES FOR BIOMEDICAL AND PHOTOVOLTAIC APPLICATIONS

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Abstract. Studies have demonstrated the remarkable properties of nanoparticles and their many applications due to their size. While conventional synthesis of nanoparticles including physical and chemical methods has proven to be very expensive and sources of environmental pollution and potential health problems, harmless and eco-friendly nanoparticles were obtained by the green approach from biological materials and were used in many sectors of activities. Zinc oxide nanoparticles (ZnONPs) have been recently the subject of intense studies due to their innumerable advantages, among which the most remarkable are their wide band gap, high excitonic binding energy, biocompatibility, and stability. ZnONPs were used for the antimicrobial, antifungal, anti-diabetic, anti-inflammatory, and antioxidant activities, the improvement of agriculture and food industry, and that of photovoltaic devices and storage. This review focuses on the green synthesis of ZnONPs from different biological materials, their characterization, and their potential applications. This review provides a better understanding of the biosynthesis, characterization techniques, and applications of ZnONPs in various sectors of activity.

Key words: ZnO nanoparticles, green synthesis, biological extracts, characterization techniques, biomedical and photovoltaic applications.

INTRODUCTION

Nanoscience and nanotechnology deal with the study and production of nanoscale materials whose size or one of their dimensions is smaller than one hundred nanometers [17, 27, 56, 72, 133]. The nanoscale offers a high surface-tovolume ratio and more reactivity, which endows nanoparticles with functions that are not observed in their bulk materials [65, 70, 86].

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Nanoparticles have various biological, chemical, and physical properties such as catalytic, electrical conductivity, nonlinear optics, mechanical strength, heat capacity, wound healing anti-inflammatory, and antimicrobial properties [74, 120, 127].

Nanotechnology is also used in industry, computing, energy generation and storage, agriculture, optics, drug delivery, and environmental science [49, 86]. The major methods of nanoparticle synthesis are physical, chemical, and biological processes that confer specific shape and size that are essential for their applications in different fields [19, 76, 92, 166]. The green synthesis method is emerging today as the most popular choice to produce nanoparticles to the detriment of traditional approaches (physical and chemical) due to the environmental aspects and potential applications [64, 87]. The green synthesis is a fast, practical, and eco-friendly process that uses biological materials including plants extracts, fungi, bacteria and algae [7, 49, 93, 130, 150, 155].

Zinc oxide (ZnO) is an inorganic material that has a multitude of physical and chemical properties including high chemical stability, high electrochemical coupling coefficient, a wide range of radiation absorption, and high photostability [24, 113]. The various crystal structures of ZnO are hexagonal wurtzite, zinc blende, and rock salt. In addition, ZnO is a semiconductor of the group II–VI that has a band gap of 3.37 eV. It is safe and easily available with good transparency. It possesses a large excitation binding energy of 60 MeV, a high mobility of electrons, negligible cytotoxicity, with strong luminescence at room temperature, and high piezoelectric and pyroelectric properties, which has attracted much interest recently [140, 158]. All these properties enabled various applications of ZnO in multiple fields such as surface acoustics, wave devices, gas detection and optoelectronics, coupled sensors, chemical sensors, electronics of spin, personal care products, coatings and paints [127, 157, 158]. ZnO has been used successfully in some devices including semiconductor lasers, optically transparent electrodes, ultraviolet photodetectors, transparent thin-film transistors and LEDs, solar cells, gas sensors, ceramics, catalysts, and cosmetics [88, 157].

The development of new materials is a necessity, therefore particular attention is paid to the use of nanomaterials because their properties can be modulated by controlling their size and shape [28]. ZnO nanoparticles (ZnONPs) have exhibited enhanced physicochemical properties compared to the bulk form of ZnO [123]. ZnONPs have received much consideration with promising applications in various industrial fields such as solar cells and energy storage, UV light emitting devices, gas sensors, photocatalysts, as well as pharmaceutical, biomedical, cosmetic, and agricultural products [49, 70, 115, 120, 126, 133, 134]. The excellent antimicrobial properties of ZnONPs have facilitated their uses in antiseptic creams, shampoos and calamine lotions for surgical tapes [7], in removing sulfur and arsenic from water [86], and in disinfection of water and wastewater [40].

The current market demand concerns the manufacture of novel nanomaterials for refining petrochemicals, healthcare, microelectronics, cosmetics, and energy

production. Therefore, nanoparticle synthesis methods from ecological, non-toxic, and advantageous sources are of paramount importance to prevent environmental and health problems [8]. This review covers the synthesis methods of ZnONPs using different ecological sources, as well as their characterization techniques. Various sectors of applications are also discussed.

THE SYNTHESIS OF NANOMATERIALS

Since the discovery of nanomaterials, several methods have been investigated to optimize their synthesis process. The synthesis methods of nanoparticles are based on two main approaches: the bottom-up approach and the top-down approach [48, 81, 149]. Synthetic techniques are summarized in Fig. 1.

Fig. 1. Different synthesis methods of nanoparticles.

TOP-DOWN APPROACH

The top-down approach consists of disintegrating the bulk material into the required nanostructure. This approach generally relies on physical methods including laser ablation, evaporation-condensation, ball milling, pulsed wire discharge, vapor and gas phases and lithography. Most of them are used in the synthesis of ZnONPs [7, 86, 104]. Previous studies have revealed that the laser ablation method offers unique advantages as it allows the production of a narrow size and shape distribution, and high purity [94]. The efficiency and morphological features depend on the ablation time and the wavelength of the laser [85]. Unfortunately, physical synthesis methods are expensive and time-consuming, have high energy consumption, and require a large space for equipments [49, 157, 163].

BOTTOM-UP APPROACH

In the bottom-up approach, nanoparticle synthesis is based on the selfassembly of atoms into a particle at the nanometric scale. The bottom-up approach uses chemical and biological methods [98]. The synthesis of nanoparticles can utilize chemical methods comprising chemical reduction, sonochemistry, photochemistry, electrochemistry, pyrolysis, sol-gel transformations, microwave oven processing, solvothermal processes, and coprecipitation [86, 104].

The sol-gel method is the most widely used among these methods because of its simplicity, robustness, repeatability, and relatively mild conditions [113]. ZnONPs synthesis process uses a chemical reagent and a zinc precursor salt to regulate the pH of the solution and prevent the precipitation of $Zn(OH)₂$. Subsequently, the solution is heat-treated at high temperatures to obtain ZnONPs [30]. Chemical stabilizers, such as citrates or polyvinylpyrrolidone, are generally added during the synthesis process to control morphological properties and prevent agglomeration of ZnONPs [158]. It has been reported that the concentration of zinc precursor and other reagents used during the synthesis process significantly affect the shape and the size of ZnONPs, which could range from nanometers to micrometers [98].

Chemical methods have the disadvantage of involving toxic products, high temperatures and pressures, and expensive equipment and reagents [100]; therefore, they can lead to environmental contamination. Chemical methods have proven to produce nanoparticles containing debris of toxic compounds on their surface, which would limit their medical applications [130]. Therefore, biological or green synthesis methods of nanoparticles are considered better choices than physical or chemical methods [10, 25, 159].

THE GREEN SYNTHESIS OF ZINC OXIDE NANOPARTICLES

Green synthesis is a reliable, reproducible, low-cost and environmentally friendly method [21]. Green synthesis uses plants, bacteria, fungi, microbial cellbased systems, yeasts, enzymes, biomolecules, and microorganisms. The process is usually carried out at mild pH, low pressure, room temperature, avoiding hazardous materials and conditions; moreover, it is also cost effective [86]. Green synthesis from plants is becoming one of the most preferred and explored methods [97], because it is clean, cost-effective, fast, often uses one-step protocols, allows for controlled synthesis with well-defined size and shape. The nanoparticles prepared by green synthesis are non-toxic, and can be used in many different sectors, including medicine [99, 158].

FROM MICROBES

Bacteria are also used for the green synthesis of nanoparticles, but this approach has drawbacks such as the high cost related to the media for the production of bacteria, and the long time for screening microbes to prevent possible contamination [4]. Nevertheless, several microbial strains have been studied and are involved in the synthesis of ZnONPs. For example, the probiotic bacterium *Lactobacillus plantarum* VITES07 was used as an ecological reducing and styling agent to synthesize stable ZnONPs in hexagonal phase, with a roughly spherical shape and an average particle size between 7 and 19 nm [137]. A metabolically versatile actinobacteria *Rhodococcus pyridinivorans* NT2 was used also to synthesize a stable, hexagonal phase, roughly spherical ZnONPs, with an average particle size between 100 and 120 nm to improve anti-UV, self-cleaning and antibacterial properties [77]. The ureolytic bacterial species *Serratia ureilytica* (HM475278) were used to synthesize ZnONPs on cotton fabric and the particle size ranged from 7 to 19 nm and the shape was a spherical nanoflower [38]. The biosynthesized ZnONPs from reproducible bacteria, *Aeromonas hydrophila* as an environmentally friendly reducing and styling agent were investigated and an absorbance peak of 374 nm was obtained. The resulting nanoparticles had a spherical and oval shape with an average size of 57.72 nm. The antimicrobial activities of the ZnONPs against *Pseudomonas aeruginosa* and *Aspergillus flavus* showed a zone of maximum inhibition [66]. The synthesis of ZnONPs mediated by *Lactobacillus sporogens*, a probiotic microbe, was improved successfully and the resulting particles had a hexagonal structure with a size-range from 5 to 15 nm [107]. Table 1 lists important results from the use of microbes in the synthesis of ZnONPs.

FROM FUNGI

Fungi excrete important extracellular reducing enzymes, making them good candidates for nanoparticle synthesis [69]. Their proven tolerance to metal ions and their bioaccumulation capacities are linked to their capacity to produce nanoparticles [86]. ZnONPs have been synthesized using several fungal strains [129]. Thus, *Candida albicans* was successfully used to synthesize ZnONPs and revealed a size varying from 15 to 25 nm [140]. The *Aspergillus fumigatus* was employed in the synthesis of ZnONPs and confirmatory tests showed a nanoparticle with an average size of 3.8 nm [119]. Table 2 shows some fungi used for the synthesis of ZnONPs.

Table 2

synthesis of steroidal pyrazolines

Examples of ZnONPs using fungi

FROM SEAWEED

enzyme secretion and gum content of

truss bean

Algae are photosynthetic aquatic chlorophyllous plants with no basic plant structure such as roots, leaves, flowers, and seeds [4]. Seaweed extracts are a rich source of many bioactive compounds characterized by a higher amount of

out

polysaccharides, compared to plant extracts [63]. Their functional compounds are metal ion-reducing and capping agents that could create a sustainable coating on nanoparticles in a single production step [17, 79]. The green synthesis of ZnONPs using seaweed extracts has gathered substantial interest due to their rapid growth, environmentally benign nature, and cost-effective protocols [55, 84]. Studies have shown that seaweed can be used in the synthesis of nanoparticles of silver, gold [138], metal oxides, and semiconductors [80]. Extracts of brown marine macroalgae *Sargassum muticum* were successfully used to synthesize ZnONPs which average size ranges from 30 to 57 nm in hexagonal wurtzite structure [25]. The synthesis of ZnONPs using *Ulva lactuca* was reported with particles of average crystallite size range from 10 to 50 nm, and maximum absorption at 325 nm [60]. Table 3 shows representative articles in which algae were used for the synthesis of ZnONPs.

Table 3

Examples of ZnONPs based on some algae

FROM PLANT EXTRACTS

Plant parts constitute the most used ecological source of nanoparticles; especially the roots, leaves, stems, seeds, fruits, and rhizomes are used for the synthesis of ZnONPs, thanks to their abilities to produce functional phytochemicals [4, 48, 56]. These phytochemicals are oxidants including flavonoids, polyphenols, amino acids, lipids, proteins and reducing sugars, carboxylic acids, amides, ketones, aldehydes, and alkaloids, which vary from plant to plant. They are used in the synthesis process as the reducing agents of ions into nanoparticles and stabilizers through capping processes [7, 77, 133]. For the plant extract: briefly, the plant part is thoroughly washed with distilled or deionized water, and could then be dried, ground into powder using a grinder, and dissolved in deionized water or alcohol. It is usually heated up to 60 °C for a few hours, or simply soaked, because prolonged exposure to high temperatures can lead to the decomposition of phytochemicals in the plant extract. The solution is then filtered using Whatman filter paper N° 1 to obtain the plant extract [32, 106, 161, 167]. Concerning ZnONPs synthesis, the extract could be used directly or could be dried to ensure the concentration of solid extracts. If the extract is in the form of an aqueous solution, it is then mixed with a solution of zinc salt; otherwise, the zinc salt and the solid extract of the plant are mixed in distilled water or alcohol. A sodium hydroxide solution is generally added to the mixture to bring the pH of the reaction medium back to 11, ideal for the synthesis of ZnONPs. The zinc salt acts as a precursor of ZnONPs, from which a precipitate is produced. The precipitate is then calcined to produce ZnONPs [62, 159, 172]. Figure 2 illustrates diverse procedures of ZnONPs synthesis from ecological sources. Phytochemicals were involved to contribute to the reduction and formation of nanoparticles, and to the stabilization as a capping agent by adhering to the surface of the nanoparticles as a protective layer and in controlling the size of particle [143, 163].

Fig. 2. Mechanism of the synthesis of ZnO nanoparticles from biological source.

Recent studies revealed that the concentration of plant extracts, the concentration of the precursors, the reaction time, the pH level, and the calcination temperature constitute the factors that determine the morphology and size of ZnONPs [27, 48, 172]. Table 4 shows the most remarkable achievements in ZnONPs synthesis from extracts of different plant parts.

Plants used for extraction	Part used	Size (nm)	Shape/ structure	Functional groups	Activity performed
Artemisia pallens [54]	plant	50–100	hexagonal wurtzite	hydroxyl groups, aromatic ring, ketonic derivatives, atmospheric carbon dioxide impurity	antimicrobial activity
Cinnamomum verum [10]	leaf	$18 - 25$	spongy and flower		anti-cancer activity
Plumbago auriculata ^[87]	flower	35.34	hexagonal	gallic acid, chlorogenic acid and catechin	antiviral evaluation
Camellia sinensis $[28]$	leaf		hexagonal wurtzite	phenolic compounds, aromatic cycle, polyphenols	photocatalytic and biological applications
Carica papaya [51]	leaf	21	hexagonal wurtzite	alcohols, phenols, carboxylates, aromatic aldehydes	photocatalytic degradation
Annona muricata [136]	leaf	37	hexagonal of wurtzite	O-H, C-N, flavonoids, polyphenols and alkaloids	antibacterial activity
Brassica oleracea var. botrytis [83]	leaf	52	hexagonal wurtzite	hydroxyl, carbonyl, carboxylic and phenol groups	photocatalytic, antimicrobial and larvicidal activity
Grape seeds [58]	fruit	15.86			antibacterial and antioxidant activities
Tabernaemontana divaricate [114]	leaf	36.82	pure hexagonal wurtzite	steroids, terpenoids, flavonoids, phenylpropanoid, phenolic acids	photocatalytic and antimicrobial activity
Cucumis melo $[22]$	fruit	12.8	pure hexagonal	aliphatic amine, carboxylic acid, ether, alkynes	antibacterial activity
Vigna mung [62]	seed	26.47	spherical	OH groups, alkene group and amide II, ZnO	antibacterial, anticancer activity
Aspalathus linearis ^[39]	plant		quasi- spherical	phenolic compounds	
Pelargonium odoratissimum ^[1]	leaf	34.12	pure hexagonal Wurtzite	-ОН, –СН, О=С=О, C=C, CN, CO, -CH, $Zn-O$	antioxidant, antibacterial and anti-inflammatory activities

Different plants used for the synthesis of ZnONPs

THE CHARACTERIZATION TECHNIQUES OF ZnO NANOPARTICLES

The physical and chemical characteristics of nanoparticles are of interest both from the fundamental and applicative points of view. The optical, mechanical, magnetic, and electrical properties are essential characteristics of ZnONPs for their potential applications including electronics and energetics. Biomedical and environmental applications, on the other hand, mainly rely on their chemical properties, including reactivity, stability, sensitivity, and toxicity [74].

ZnONPs are investigated using numerous complementary analytical techniques reported in the literature [16]. The optical energy band gap of crystalline and amorphous materials was obtained using ultraviolet-visible (UV-Vis) spectroscopy [35, 36]. X-ray diffraction (XRD) analysis was used to determine the crystal structure, the phase and the average size of ZnONPs from the diffraction peaks [34, 74]. Energy dispersive X-ray analysis (EDX) was used to determine the purity and the elemental composition of ZnONPs [23]. The details about the surface morphology and topography were investigated using atomic force microscopy (AFM) imaging [141]. Isolated and aggregated particles could be identified using transmission electron microscopy (TEM) imaging [71]. Fourier transform infrared spectroscopy (FTIR) revealed the functional behavior of ZnONPs. Scanning electron microscopy (SEM) imaging confirmed the shape, structure, and size of the nanoparticles. FTIR used in attenuated total reflectance (ATR) mode can be used as nondestructive technique for identifying metabolites, and other chemicals. Figure 3 presents a summary of ZnONPs characterization techniques.

Raman spectroscopy helps to characterize the quality of the crystal structure, oxygen vacancies, and zinc excess, or surface impurities. X-ray photoelectron spectroscopy (XPS) analysis can be used for morphology, bioactive surface, and surface chemistry characterization [82]. Dynamic light scattering (DLS) analysis is considered as a non-destructive approach to characterize compounds in suspensions and solutions. Photoluminescence analysis (PL) was used to determine the band gap, crystalline purity, and to spot impurities. Thermal gravimetric-differential thermal analysis (TG-DTA) was used to characterize the thermal stability, phase transition, and effect of the oxidative and reductive environment of the nanoparticles [4, 68, 156].

Fig. 3. Main characterization techniques of ZnONPs.

APPLICATIONS OF ZnONPs

ZnONPs have many fields of application; this section discusses part of them, with main focus on biology and energy production.

APPLICATIONS IN AGRICULTURE

The use of pesticides in agriculture and the use of antibiotics for the treatment of farm animals has led to the increase of multi-resistant bacterial and fungal strains [3, 90]. Therefore, metal nanoparticles have received considerable attention in agriculture recently [50, 91, 119, 126]. In particular, ZnONPs were used in the treatment of fungal and other microbial infections in farm animals and plants, being considered an effective alternative to conventional antibiotics. ZnONPs have been reported to demonstrate excellent pesticidal efficacy against *Artemia salina* larvae [172]. The pesticidal effects were investigated on soils infested with the *Fusarium* and the *Verticillium wilt* fungi, respectively by spraying ZnONPs on tomato and eggplant to increase their yields [43]. The small size and appropriate chemical composition of ZnONPs enhance their interaction with the bacterial wall and favor their penetration in bacteria to damage and kill them.

Furthermore, the use of ZnONPs as nanofertilizer could increase the yield and growth of food crops. ZnONPs were used to promote seed germination, seedling vigor, and plant growth [132]. The increase of stem and root growth of peanuts by the use of ZnONPs was demonstrated effectively in literature [108]. ZnONPs colloidal solution can substitute organic fertilizers to enhance the development of plants. The use of these nanoparticles as biological fertilizers could reduce chemical residues in vegetables, could revive soils, and could increase the growth and yield of crops [89, 171]. Nanofertilizers offer the advantage of being used in very small quantities [11]. Nanopowders of metallic nanoparticles can also be successfully used as fertilizers and pesticides to obtain an increase in yield of plants such as wheat plants [29].

ANTIMICROBIAL AND ANTIBACTERIAL USES

Infectious diseases caused by parasites, protozoa, bacteria, viruses and fungi constitute a major concern for researchers around the world [125]. The development of antibiotics, antimicrobials, antifungals, and antivirals aims to fight infectious diseases [6, 121]. However, the administration of high doses of antibiotics generates high toxicity and increases resistance to drugs [122, 136]. Therefore, several nanomaterials are used as antimicrobial and antiviral agents for various applications such as drug delivery, biosensing, and tumor cell elimination, demonstrating high efficiency compared to conventional techniques [5, 101, 148]. Stan et *al.* investigated anti-bacterial activity of biosynthesized ZnONPs using extracts of *Allium sativum*, *Rosmarinus officinalis* and *Ocimum basilicum* against *Staphylococcus aureus*, *Bacillus subtilis*, *Listeria monocytogenes*, *Escherichia coli*, *Salmonella typhimurium,* and *Pseudomonas aeruginosa* bacterial strains and their results demonstrated that the antibacterial and antioxidant activities of the green synthesized nanoparticles were enhanced compared to their chemically synthesized counterparts [151]. The combination of antibiotics and ZnONPs using *Aloe vera* extract demonstrated an effective clinical elimination of isolates of methicillin resistant *Staphylococcus aureus* [15]. The biosynthesized ZnONPs using the extract of *Dysphania ambrosioides* demonstrated similar inhibitory effect on *S. aureus* and *S. epidermidis* compared to the use of chlorhexidine [18]. The inhibitory effect on the growth of *B. subtilis* and *P. aeruginosa* was carried out using ZnONPs synthesized from *Lawsonia inermis* leaf extract [172]. The use of *Trifolium pratense* flower extract based ZnONPs on strains of *S. aureus* and *P. aeruginosa* and standard strain of *E. coli* has shown an effective inhibitory effect [42]. The antibacterial activity of ZnONPs synthesized using the *Artemisia* plant pallens was carried out against grampositive *B. subtilis*, *S. aureus* and gram-negative *E. coli* and it demonstrated an inhibitory effect [62]. Excellent antioxidant and bactericidal activities were obtained using biosynthesized ZnONPs from *Cassia fistula* plant extract on *Klebsiella aerogenes, E. coli, Plasmodium desmolyticum* and *S. aureus* [155]. ZnONPs biosynthesized using *Sambucus ebulus* antibacterial activity was carried out against *B. cereus*, *S. aureus* and *E. coli* bacteria [12]. Excellent bactericidal activity was demonstrated using *Ulva lactuca* based ZnONPs against gram-positive (*Bacillus licheniformis* and *Bacillus pumilis*) and gram-negative (*E. coli* and *Proteus vulgaris*) bacteria [60]. The effective inhibitory effect of ZnONPs obtained using grape seed extract was demonstrated on the growth of *S. aureus* [58].

PHOTOCATALYTIC ACTIVITY

Water quality is a global challenge nowadays and the increase of environmental pollution is caused by water contamination [78]. The treatment of water and wastewater by the approach of photocatalytic degradation of the organic pollutants is a promising approach to the detriment of current methods of inactivation, such as adsorption on activated carbon, filtration, chemical treatment, sedimentation, and biological treatment as they fail to achieve extensive removal of pollutants to fully purify the water [62, 73, 83, 112].

ZnONPs have been frequently used for the degradation of many organic pollutants due to their larger surface area, smaller particle size, and UV radiation absorption [83, 155, 172]. The photocatalytic activities of ZnONPs biosynthesized using biological source extracts such as the *Prunus fruit*, the *Cassia fistula* plant, *Sambucus ebulus*, and *Camellia sinensis* leaf, were carried out successfully under UV and solar lighting for the degradation of a methylene blue solution [2, 12, 134, 148, 155]. ZnONPs are considered one of the best photocatalysts to disinfect wastewater, break down pesticides and herbicides, and corrupt methylene blue dye [60, 124, 145].

ANTIOXIDANT ACTIVITY

The high antioxidant properties of ZnONPs can be explained by the presence of phenolic species in plant extracts, which is an important characteristic for bioapplications. ZnONPs synthesized using biological extracts showed interesting antioxidant activities [58, 122, 160]. The comparison between the antioxidant activities of ZnONPs obtained from extracts of *Allium sativum*, *Rosmarinus officinalis* and *Ocimum basilicum* was carried out and a strong effect was observed [12].

ANTILARVICIDAL APPLICATION

Various studies reported the antifungal and antilarvicidal activities of ZnONPs biosynthesized for the treatment of yeasts, fungi, and harmful insects which are major ailments in agriculture and mosquito larvae that cause malaria [33, 154]. *Scadoxus multiflorus* leaves extract-based ZnONPs exhibited effective ovicidal and larvicidal properties against the fungal agents (*Aspergillus flavus* and *Aspergillus niger*) and insects [14]. The effects of biosynthesized ZnONPs treatment on the morphology and histology of mosquito larvae have been monitored and that revealed significant larvicidal activity [60, 83].

ANTICANCER ACTIVITY

In 2020, approximately 10 million deaths were registered in the world due to cancer [153]. Standard cancer treatment options including surgery, chemotherapy, and radiation therapy have harmful side effects [41].

Alternative cancer treatments are requested to overcome these limitations, and the potential candidates are biosynthesized nanomaterials with a targeted drug therapy approaches that reduce side effects [146]. ZnONPs have excellent anticancer properties, and their effects increased while their concentration increased [9, 62, 128].

PHOTOVOLTAIC APPLICATION

Nanomaterials are widely used in solar energy production and are expected to reduce the cost and improve the performance of solar devices [59]. ZnO is an inorganic semiconductor of low cost and easy synthesis. Moreover, ZnO has good optoelectronic properties (high conductivity, high electron affinity, and excellent electron mobility), non-toxicity, and high stability. ZnONPs have been used in solar cells, supercapacitors, flexible piezoelectric nanogenerators, ultraviolet photodetectors, and photodiodes. Many organic and hybrid solar cells have been investigated since these remarkable properties were discovered for ZnONPs [105, 168]. A dye-sensitized solar cell (DSSC) is a photovoltaic device based on electrochemical principles that converts visible light into electricity, through sensitive dye absorption [99]. ZnO is an important photoanode semiconductor for DSSC [45, 169].

One-dimensional ZnO nanostructures are used in DSSC due to their high electron transport with a low yield. Furthermore, their incorporation into porous films increased their efficiency [57]. Shashanka *et al.* fabricated a ZnONP-based dye solar cell from *Tilia tomentosa* leaf extract, and their characteristics have been performed and high efficiency was observed [144]. Synthesized DSSCs using dyes extracted from *Ixora* flower, *Pongame* leaf, *Neem* leaf, and *almond* fruit were investigated, and the efficiency of the *almond* extract solar cells was higher than that of the other four solar cells [135]. Optoelectronic studies were performed on ZnO nanoflowers synthesized from watermelon rind agricultural waste that demonstrated a potential use as a photosensitive device like solar cells, LEDs, and photodetectors [147]. ZnONPs synthesized using the *Terminalia* leaf extract were used as a photoanode in the DSSC fabrication with higher efficiency at $pH = 9$ [46]. The ZnONPs-based DSSCs using different plant extracts (onion, cabbage, carrot, and tomato) were investigated by measuring the voltage-current density behavior in the presence of artificial sunshine [37]. ZnONPs-based DSSC from methyl orange dye reached an efficiency of 2.3 % [13]. Figure 4 presents an overview of diverse fields of application of ZnONPs.

Fig. 4. Main characterization techniques of ZnONPs.

CONCLUSION AND FUTURE PERSPECTIVES

This review provides a state-of-the-art overview of synthesis methods, characterization techniques, and potential applications of biosynthesized ZnONPs from different biological sources. It demonstrates that ZnONPs display a range of favorable properties for diverse applications. Green synthesis approaches using a variety of plants, fungi, bacteria, and algae are widely explored and adopted nowadays because of their low cost and environmentally friendly protocols. The active molecules such as phenols, flavonoids, saponins, glycosides, steroids, amino acids, tannins, and alkaloids found in these different species are used as stabilizing and reducing agents.

ZnONPs stand out as one of the most versatile materials, due to their remarkable properties and functionalities, which lead to applications in fundamental research and diverse technological fields. Further research on the green synthesis of nanoparticles, and in particular on ZnONPs, may focus on the development of industrial-scale applications.

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