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Short Review Article

A Review on Plant Extract Mediated Green Synthesis of Zirconia Nanoparticles and Their Miscellaneous Applications

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Abstract: Development of reliable and environmentally gracious routes for the fabrication of metal oxide nanoparticles is a crucial step in nano-biotechnology. Among the all zirconia nanoparticles (ZrO_2 NPs) draws more attention due to its significant biocompatible, electrical, mechanical, and optical properties. Many natural biomolecules in plant extracts such as alkaloids, amino acids, enzymes, proteins, polysaccharides, polyphenols, steroid, and vitamins could be involved in bioreduction, formation, and stabilization of ZrO_2 NPs. In the last decade, numerous efforts were made to develop ecofriendly methods of synthesis to avoid the hazardous byproducts. In this review, green synthesis of ZrO_2 NPs, their characterization techniques, and miscellaneous applications were discussed.

Key words: Green synthesis, Plant extracts, Nanotechnology, ZrO_2 NPs.

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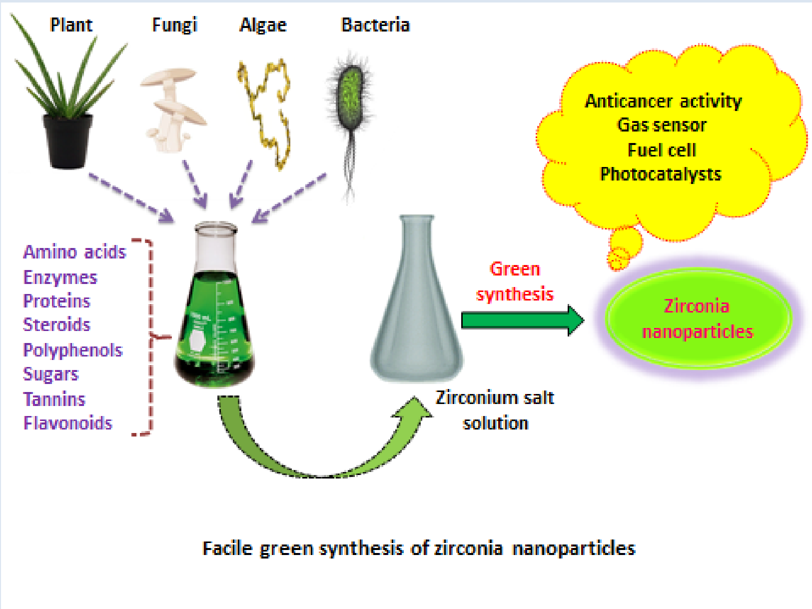
Graphical Abstract:



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Biography

Amol Nikam has completed his M. Sc. Degree from Shivaji University, Kolhapur, India in Organic Chemistry. At present he is pursuing his PhD degree from Mumbai University. His area of research interest is synthesis of nanomaterial and their applications.

Trupti Pagar was born in Surgana (Maharashtra), in **1997**. She completed her BSc (**2019**) degree from Arts, Science and Commerce College, Surgana, Savitribai Phule Pune University, Maharashtra. Her area of research interest is synthesis of nanomaterial and their applications in biological activity.

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Khanderao Pagar has completed his M. Sc. Degree from Satana College, Maharashtra in Organic Chemistry. Currently, he is working as an Assistant Professor at KKHA Arts, SMGL Commerce and SPHJ Science College, Chandwad, Savitribai Phule Pune University, Maharashtra. His area of research interest is synthesis of heterocyclic compounds and their applications.

Shreyas Pansambal obtained his PhD (**2019**) degree from Pune University in Chemistry under the supervisor of Dr. K. K. Deshmukh. Later on, he is working as an Assistant Professor at S.N. Arts, D.J.M. Commerce and B.N.S. Science College, Sangamner, Savitribai Phule Pune University, Maharashtra. He has been actively involved synthesis of heterocyclic compounds using nanocatalyst.

1. Introduction

The demand and fabrication of nanomaterials have been increased which is used to describe the creation and their fascinating applications in various fields such as space industry, biomedicines, sensors, catalysis, cosmetics, health care, mechanics, electrochemistry, energy, agriculture, electronics, synthetic chemistry, food technology, optics and optical devices, pharmaceutics, and textile industry [1-25]. Among the transition metal oxide nanoparticles, ZrO_2 NPs has attracted major research interest due to its unique electrical, thermal, catalytic, sensing, optical, mechanical, and biocompatible properties [26-31]. However, ZrO_2 NPs is a known p-type semiconductor with piezoelectric characteristics due to its acidic and basic nature. Therefore, ZrO_2 NPs have been widely used in myriad applications (Figure 1), including bone implants [32], dental [33], photocatalysis, refractory, energy [26], fuel cell [34], gas sensor [35], solar cells [36], and seed germination [37]. Therewithal ZrO_2 NPs have antibacterial, antifungal, antioxidant and anticancer properties because of their unusual physiochemical properties [37-39]. Generally, ZrO_2 NPs have three crystal phases, that is, the monoclinic (m- ZrO_2) phase is thermodynamically stable at room temperature, the tetragonal (t-ZrO_2) phase exist in the temperature range between 1100-2370 ˚C and the cubic (c- ZrO_2) phase is fond to stable above 2370 ˚C [40].

Heretofore, ZrO_2 NPs can be easily synthesized using several methods such as hydrothermal [41], laser ablation [42], microwave irradiation [43], sol-gel [44], aqueous precipitation method [45], thermal decomposition [46], low temperature hydrolysis [47], sonochemical method [48], two phase approach [49], solvothermal [50], spray pyrolysis [51], microwave plasma [52] emulsion precipitation [53], pulsed plasma in liquid [54], ball-mill aided precipitation [55], freeze drying [56], ultrasonic assisted [57], thermal plasma route [58], electric arc discharge [59], propellent chemical combustion method [60], polyacrylamide gel method [61], template method [62] and ionic liquid microemulsion [63]. Nevertheless, these synthetic routes require high temperature and pressure, long reaction time, costly and perilous chemical precursors, need of special instruments for experimental work that create a negative impact on the environment. This enhances the urgent need to replace chemical preparation methodology and develop a simple, clean, non-toxic, and environmentally benign process through green synthesis and other biological approaches. Some studies conducted on green synthesis of ZrO_2 NPs using microorganisms including bacteria [64-65] and plants [26,37-39]. However, among the numerous biological routes of ZrO_2 NPs synthesis, microbe mediated synthesis is not a quite simple and suitable for industrial feasibility because of necessities of highly aseptic conditions and their maintenance. So, using plant material extracts for this purpose is probably advantageous over microorganisms due to the ease of improvement, the less biohazard and intricate process of maintaining cell culture [3, 64-65]. It is one of the best platforms for synthesis of nanoparticles as it is free from toxic chemicals, providing natural and herbal capping agents to stabilize ZrO_2 NPs. Currently, plant mediated synthesis of metal oxide nanoparticles is receiving lots of attention due to its simplicity, swift synthesis of nanoparticles of appealing and various morphologies and removal of particular maintenance of cell cultures.

This review draws attention to the current knowledge concerning the capability of plant materials for biosynthesis of ZrO_2 NPs and presents a database that future researchers may be based on the green synthesis of ZrO_2 NPs using plants material sources.

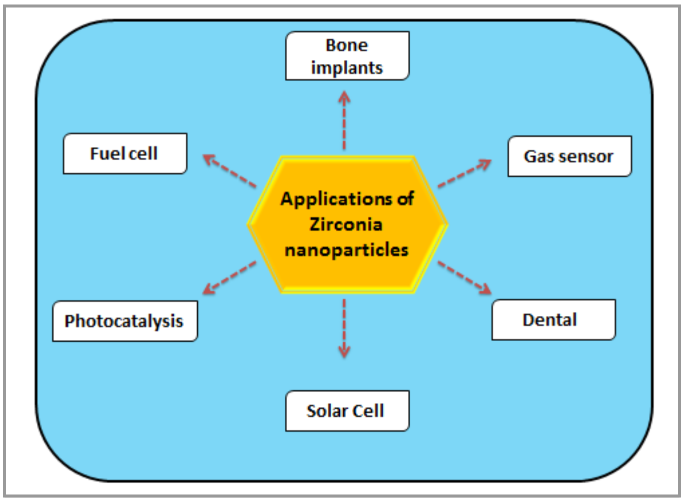

Figure 1. Various applications of ZrO_2 NPs.

2. Green Synthesis of ZrO_2 NPs

Nowadays, green synthesis of metal oxide nanomaterial has been an emerging research area in the field of nanobiotechnology. The significance of the green synthesis (Figure 2) over chemical and physical methods is: one pot and clean synthesis, environmental friendly, cost effective, swift, facile and easily scaled up for large scale syntheses of nanoparticles, furthermore there is no need to use high amount of temperature, energy, pressure and toxic chemicals [38-39]. The utilization of plant material for the fabrication of ZrO_2 NPs has received lots of attention due to its environmentally gracious, simple, rapid, non-toxic, economical protocol, providing a single step technique for the green synthesis processes [26, 38]. Stabilizing the ZrO_2 NPs by combination of biomolecules such as amino acids, enzymes, proteins, steroids, phenols, tannins, sugar, and flavonoids, which are already established in the plant extracts with medicinal values [3,28]. Some plants are already reported to facilitate ZrO_2 NPs biosynthesis and all of them are mentioned in this review (Table 1). Various parts of plant such as tuber, leaves, fruit, and flower are used to synthesize the ZrO_2 NPs in different morphologies and size by biological approaches. The water soluble heterocyclic components are mainly responsible for formation and stabilization of nanoparticles. Thereafter, the synthesized nanoparticles need to be characterized by using numerous techniques.

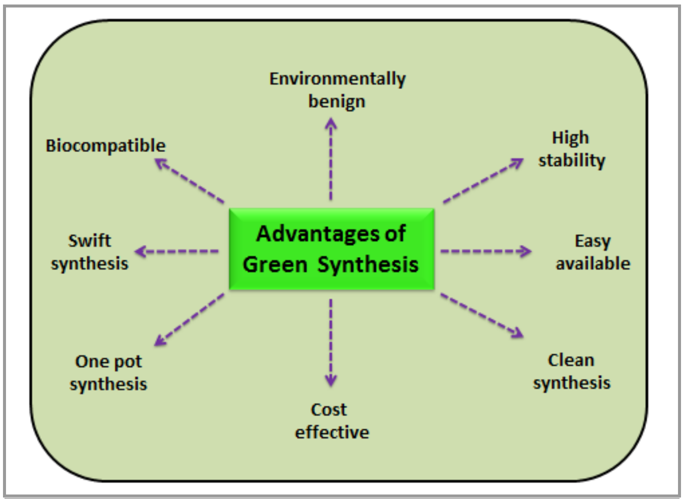

Figure 2. Importance of green synthesis of metal oxide nanoparticles

Table 1. Green synthesis of ZrO2 NPs using different plant source with morphology and size.

Sr. No	Name of Plants	Part	Shape	Size	References
1	Ficus benghalensis	Leaves	Spherical	7 nm	27
2	Capscicum annum	Fruit	Baddeleyite	13.06-22.02 nm	37
	Alium cepa	Fruit	Baddeleyite	13.03-21.97 nm	
	Lycopersicon esculentum	Fruit	Baddeleyite	20.48-21.37 nm	
3	Aloe vera	Leaves	Spherical	50-100 nm	38
4	Eucalyptus globulus	Leaves	Spherical	9-11 nm	39
5	Nyctanthes arbor-tristis	Flower	-	-	66
6	Lemon juice	Fruit	Quasi-spherical	20 nm	67
7	Lagerstroemia speciosa	Leaves	Tetragonal	56.8 nm	68
8	Sargassum wightii	-	Spherical	4.8 nm	69
9	Acalypha indica	Leaves	Cubic	20-100 nm	70
10	Azadirachta indica	Leaves	-	-	71
11	Curcuma longa	Tuber	Chain	41-45 nm	72

3. Protocol for Biogenic Synthesis of ZrO_2 NPs

Green synthesis of ZrO_2 NPs is a facile, swift, robust, one pot synthesis and environmentally benign without the involvement of any mephitic and perilous chemical. ZrO_2 NPs were synthesized using different parts of plants including, flowers, leaves, fruit, and tuber (Table 1). A very easy and simple protocol is applied for their biosynthesis. The materials of plant parts such as leaves, flowers, fruits, and tuber are collected from different sources and thoroughly washed with ordinary water as well as double distilled water to remove other unwanted entities. The plant parts are either dried or grinded to form the fine powder. The material of plant parts are chopped into very small pieces or grinded and boiled in suitable solvents at suitable temperature to obtain plant extract. The prepared plant extract and various concentrations of zirconium salts as metal precursor can be used for the fabrication of ZrO2 NPs. There is no need to add external chemical such as reducing agent or stabilizers, simply extract is mixed with zirconium salt solution and the phytochemical present in extract acts as a stabilizing agent for the synthesis of ZrO_2 NPs. The detailed protocol of green synthesis of ZrO_2 NPs by Ficus benghalensis leaves extract is described by authors reported in literature [26]. The synthesized ZrO_2 NPs solution is further centrifuged to separate the nanoparticles at high rpm, and wash thoroughly with suitable solvents. The resultant solution is evaporated up to dryness in an oven. The product obtained is grounded using mortar pestle to form a fine powder. Then this powder is calcinated at 500 °C for 3 h in a muffle furnace.

4. Characterization Techniques for ZrO_2 NPs

The biogenic synthesis of ZrO_2 NPs, characterization is a crucial step to study the effect of ZrO_2 NPs on environment and human health, and confirmation of their formation, different routes of their formation and monitoring their impact are required. Some notable characterization techniques are used to characterize synthesis of ZrO_2 NPs.

1) Thermogravimetric analysis (TGA)-TGA is used to determine phase transition, thermal decomposition, and thermal stability of the nanoparticles [7].

2) X-ray diffraction (XRD) is used to examine the overall oxidation state of the particles as a function of time, phase identification, and structure of the nanoparticles [26].

3) Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the common methods for surface and morphological characterization. SEM and TEM are used for the morphological characterization at the nanometer to micrometer-scale. SEM can provide morphological information on the submicron scale and elemental information at the micron-scale; however, TEM has a much higher resolution compared with the SEM. So, to analyze the surface morphology of the prepared nanoparticle sample is used and TEM is useful to evaluate the exact size and shape of the nanoparticles [37].

4) Dynamic light scattering (DLS) is used to characterize the surface charge and the size distribution and quality of nanoparticles. It is also very useful to study the polydispersity index of the prepared nanoparticles.

5) Energy dispersive spectroscopy (EDS) can be used to evaluate the elemental composition of metal nanoparticles, which provides the elemental knowledge of sample [67].

6) Fourier transforms infrared spectroscopy (FTIR) can characterize the surface chemistry as the organic functional groups can be determined to the surface of the nanoparticles [38].

7) X-ray photoelectron spectroscopy (XPS) can be used to analyze the surface chemistry of nanomaterials.

8) Atomic force microscopy (AFM) can characterize nanoparticles at their atomic scale [37].

5. Miscellaneous Applications of Biogenically Synthesized ZrO_2 NPs

ZrO_2 NPs which are fabricateded via biologically green and environmentally gracious route or methods provide many benefits over the synthetically manufactured materials. Therewithal, on one hand, ZrO2 NPs showed their biological activity against microorganisms, good photocatalytic property. On the other hand, they showed potential in fuel cell, gas sensor, and bone implants therapy as well. We have described their significant applications as guidance to new researchers for future prospects (Table 2).

Herein synthesized 15 nm ZrO2 NPs using Ficus benghalensis leaves extract and reported for the photocatalytic activity. They showed that the photodegradation of methylene blue and methyl orange (within 240 min) up to 91% and 69% by using ZrO2 NPs as a catalyst. [26]. Sundrarajan et al. [38] demonstrated the Aloe vera aqueous extract mediated ZrO2 NPs were in the size of 50-100 nm and investigated antimicrobial and antifungal properties which can be utilized in textile finishing [38]. Furthemore, Gowri and co-workers reported biosynthesis of ZrO_2 NPs using flower extract Nyctanthes arbor-tristis and analyzed the antibacterial activity of the prepared nanoparticles. These ZrO_2 NPs exhibited an excellent antibacterial activity against pathogenic bacteria such as E. coli and S. aureus [66].

Dawar et al. [67] described lemon juice mediated green synthesis of ZrO_2 NPs at the ambient temperature and its electrical properties. The synthesized ZrO_2 NPs are in the size of 20 nm. They showed ZrO_2 NPs could be possessing significant electrolyte material in the intermediate-temperature solid oxide fuel cell. Santhakumar and co-workers described biosynthesis of ZrO_2 NPs using leaves extract of Lagerstroemia speciosa and they also analyzed the cytotoxicity study and photocatalytic activities of synthesized nanoparticles. The biogenically synthesized ZrO_2 NPs were found to have tetragonal structure. The photocatalytic study suggests the efficiency of these biogenically synthesized nanoparticles in degrading azo dye (degraded up to 94.58%) under sunlight. In addition, the result of in vitro cytotoxicity study against breast cancer cell lines (MCF-7) and evaluated by MTT assay showed that the cell viability was seen at 500 µg/mL when compared against standard [68].

Thereafter, Vijai Anand and co-workers reported that the antibacterial activity against gram positive and gram negative bacterial strain of uniformly monodispersed ZrO_2 NPs (4.8 nm) which are mediated from Sargassum wightii (seaweed) [69]. Moreover, Mandal and co-workers demonstrated the Eucalyptus globulus leaf extract mediated ZrO_2 NPs were in the range of 9-11 nm. They reported their excellent antioxidant activity up to 85.6% scavenging inhibition of free radicals liberated by DPPH molecule and anticancer activity against human lung carcinoma A-549 and human colon carcinoma HCT-116 cell lines [39]. From the antioxidant and anticancer studies, ZrO_2 NPs will be useful in many potential biomedical applications.

Besides, Abdul Jalill and co-workers reported plant mediated synthesis of ZrO_2 NPs using Capscicum annum, Alium cepa and Lycopersicon esculentum and examined the antifungal and antibacterial activity of ZrO_2 NPs against various bacteria. These biosynthesized ZrO_2 NPs showed good antifungal and antibacterial activity against F. moniliforme, F. graminearum, E. coli and S. aruse. Herewith, synthesized ZrO_2 NPs showed the negative effects on seed germination and other growth parameters of Beta vulgaris and Eruca sativa such as reduction in germination percentage, germination value, promoter indicator, mean germination time and mean daily germination but they enhanced germination rate [37].

Table 2. Various applications of ZrO2 NPs fabricated using different plant extracts.

Sr. No	Name of Plants	Applications	References
1	Ficus benghalensis	Photocatalysis	26
2	Capscicum annum Alium cepa Lycopersicon esculentum	antibacterial, antifungal activities and seed germination study	37
3	Aloe vera	antimicrobial and antifungal	38
4	Eucalyptus globulus	antioxidant and anticancer activities	39
5	Nyctanthes arbor-tristis	antibacterial	66
6	Lemon juice	electrical properties	67
7	Lagerstroemia speciosa	cytotoxicity study and photocatalytic activities	68
8	Sargassum wightii	Antibacterial	69

6. Conclusion

This review has summarized the current research work in the area of green synthesis of ZrO_2 NPs by using some plant parts material. This literature surveys shows that major portion of work on biosynthesis of nanoparticles of zinc, gold, and silver nanoparticles in comparison to ZrO_2 NPs. Hence, particularly special attention of scientific community is required to explore this simple, swift, robust, non-toxic, environmentally benign and commercially viable method for fabrication of ZrO_2 NPs through this green chemistry bottom to top approach. Among some biological routes of ZrO_2 NPs synthesis, microbes mediated biosynthesis is not of industrial feasibility due to the requirements of special aseptic conditions and their careful maintenance. Therefore, the utilization of plant material extracts for this purpose is potentially effective over microorganisms. Furthermore, much more plant species are in way to be exploited and reported in future era towards simple and rapid green synthesis of metal oxide nanoparticles. Because, utilization of plant material extracts also minimizes the cost of micro-organisms isolation and their culture media which enhance the cost competitive feasibility over nanoparticles preparation by microbes. Further research is required to develop applications, use of plant parts for synthesis of the exact mechanism behind the synthesis of ZrO_2 NPs.

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