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A review on the growth and potential applications of zirconia nanostructures

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Abstract

Nanotechnology is an emerging technology which is applicable in many fields like space crafts, medicine, sensors, catalysis, cosmetics, health care, agriculture, electronics, synthetic industry, food technology, optical devices, pharmaceutics, and textile industry etc, thereby increasing the attention in developing various nanomaterials. Among all, zirconia nanoparticles (ZrO_2NPs) draw more attention due to their significant biocompatible, electrical, mechanical, and optical properties. In this study various physical, chemical, and biological techniques that are being used for the synthesis of ZrO_2NPs and their potential advantages as well as disadvantages are presented in detail. Photocatalytic applications of Zirconia and its composites synthesized by various methods are reviewed. Also, an eye is focussed on various synthesis methods like ball milling, melt extract, hydrothermal, sol gel, vapour deposition, precipitation etc. Bio synthesis methods like Plant synthesis, Bacterial synthesis, Fungi, and algae mediated synthesis are also discussed. The potential application of ZrO_2NPs in photocatalysis is discussed in detail.

Keywords: Applications, Dye degradation, Photocatalysis, Synthesis, ZrO_2NPs

1. Introduction

Now-a-days water pollution is one of the major problems that world is encountering. Many toxic elements like dyes from various factories and industries are polluting many water bodies, as a result of which animal life as well as human life is suffering a lot. The removal of such dyes from these water bodies through homogeneous and heterogeneous photocatalysis has drawn an increasing interest in the recent years. Band gap of the nanomaterials plays an important role in photocatalysis process. The recombination rate of charge carriers makes a significant consideration as the process mainly depends on the energy band gap. Many metal oxide semiconductors were effectively being used as catalysts for the degradation of these pollutants [1-3]. Many studies were performed on various metal oxide based nanostructures such as TiO_2 [4], Fe_2O_3 [5], NiO [6], ZnO [7-9], ZrO_2 [10,11], Bi_2O_3 [12,13] etc and showed excellent degradation capacity and are being used as photocatalystsin commercial applications.Bi_2O_3 is a semiconductor metal oxide with band gap which varies from 2.1 eV to 2.8 eV, making it a visible light photocatalyst but it exhibits fast recombination rate because of its narrow bandwidth [12]. TiO_2 is said to be well known and efficient photocatalyst for the degradation of organic compounds under UV light irradiation [4]. However, TiO_2 has a wide band gap (3.2 eV) and is not suited for solar photocatalysis as most of the solar radiation constitutes visible light. ZnO is another well explored metal oxide semiconductor, which is stable, inexpensive, and nontoxic in nature with a wide band gap (3.37 eV) and a large exciton binding energy (60 meV) [7]. ZnO has the disadvantage of a facile dissolution under UV light irradiation in aqueous solution. Among all these semiconductor metal oxide photo catalysts, Zirconium dioxide (ZrO_2) based materials gained considerable interest due to their wide band gap, long term stability against corrosion, high mechanical strength, and excellent degradation efficiency under UV light [14-15]. ZrO_2 is a promising semiconductor metal oxide material used for photocatalytic applications because of its relatively wide tunable band gap (3.25- 5.1 eV) and the high negative value of the conduction band potential.

In general, Zirconium dioxide (ZrO_2), a white crystalline powder also known as Zirconia is widely used in many applications. Zirconia is extremely resistant to heat and corrosion. Zirconia is lighter than steel and its hardness is similar to copper. Zirconia mostly occurs in monoclinic crystalline structure which is also called as baddelyte. Zirconia exhibits three thermodynamically stable phases- monoclinic phase, tetragonal phase and cubic phase which are stable up to 1100 °C, 1100-2370 °C, and 2370 °C respectively [16]. At present Zirconium dioxide is used in advanced ceramics and in making dental crowns because of its high mechanical strength and high fracture toughness [17]. Zirconia is a wide band gap semiconductor which becomes more conductive with increasing temperatures. Due to its unique thermal, optical properties, it widely used in applications like optical coatings, corrosion resistant coatings, thermal shields, buffer layers etc. [16,18]. Usage of Zirconium dioxide is also gaining a lot of importance as catalyst because of its excellent photo catalytic properties and is being extensively used for the degradation of various dyes. Zirconium dioxide nanocomposites exhibit wide applications in absorbing various chemical dyes and pollutants present in water and other solvents [10,19]. ZrO_2 can also be used as gas sensor for sensing various dangerous gases in industries and in environment [20]. Many electrochemical studies are also performed on Zirconium dioxide nanoparticles for application in Fuel cells [21]. Also, Zirconia nanoparticles are effectively used in medical field as Bio sensors and for drug delivery. Due to the excellent biocompatibility and mechanical strength, Zirconia particles are well suited for making bone and hip joints used for Orthopaedic applications. Zirconia and Alumina composites are being used for hip arthroplasty since many years [22,23]. Solar cells made by using ZrO_2 Nanoparticles increases film roughness and enhance light scattering effects as they exhibit outstanding power conversion efficiency [24]. Various potential applications of Zirconia nanoparticles are listed in the following Figure 1.

There are research reviews available on the various applications of ZrO_2 based nanocomposites. But in the current review article, concentration is mainly focused on the various methods those can be adopted for the synthesis of ZrO_2 nanostructures. Advantages as well as disadvantages of each synthesis process are explained in detail. Also, emphasis is mainly focused on the applications of ZrO_2 nanoparticles and their composites for photocatalytic applications. Though Photocatalysis is one of the much-explored areas of materials science, still there are few challenges that are to be addressed for effective utilization of these structures. This review article reports the current trends in the synthesis and photocatalytic properties of ZrO_2 nanocomposites and the readers will be benefited with these recent updates.

2. Synthesis methods

Several studies have been carried out in order to assess the possibilities for the synthesis of various nanoparticles with different morphologies. Synthesis of nanoparticles can be performed using several methods. In the present case, ZrO_2 can be synthesised using a wide variety of ways including physical, chemical, and biological routes. The size and structure of the prepared nanoparticles generally depends on the method of synthesis, precursor concentrations, operating conditions, etc. The selection of synthesis method is based on the requirement of particles size and structure, environmental conditions, controllability of structural and morphological parameters, cost of equipment, ease of synthesis, and its applications etc.

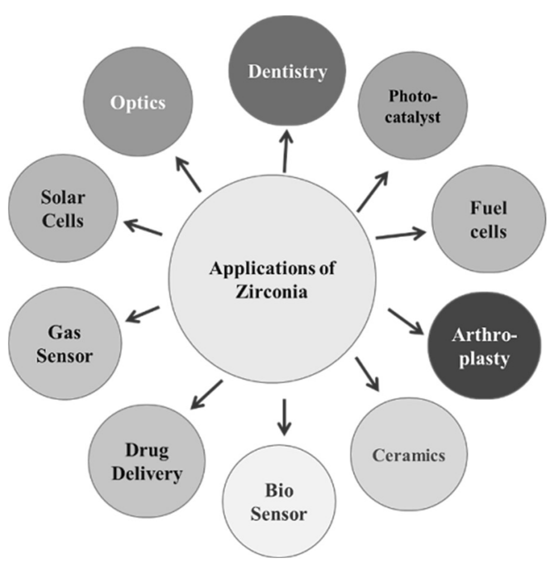

Figure 1 Various Applications of ZrO_2 Nanoparticles.

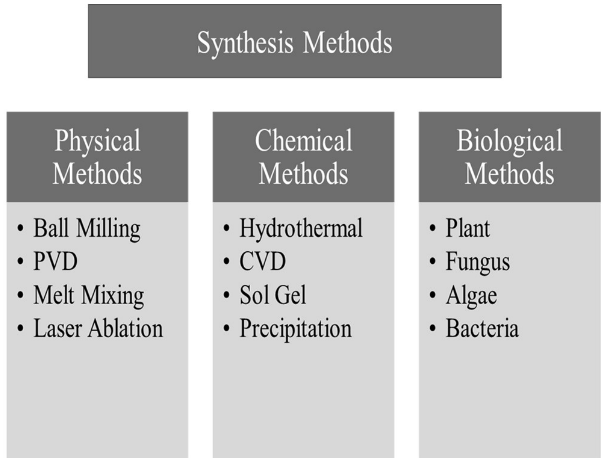

Figure 2 Nanoparticles Synthesis Methods.

2.1 Physical methods

Physical synthesis methods include mechanical as well as vapour deposition methods. Usually mechanical methods come under Top-down approach in which miniaturisation takes place to atomic levels.

2.1.1 Mechanical ball milling

In Mechanical ball milling method the source material is grinded into extremely fine powders. The collision between the tiny rigid balls in a concealed container will generate localized high pressure required for grinding. Producing ultrafine particles is difficult by using milling process. Due to its low cost of production and simple operation, this method is extensively being used in the production of nanoparticles. Milling speed, time of milling, operating temperature, atmospheric conditions, size of balls etc are some of the factors affecting the final product of this method [25]. This method effectively works at room temperature for producing nanoparticles for various optoelectronic, sensing, energy conversion and storage applications.

2.1.2 Melt mixing

Melt mixing or Melt blending is a method which is preferably used for preparing the clay–polymer nanocomposites of thermoplastic and elastomeric polymeric matrix. The polymer is melted and combined with the desired amount of the intercalated clay using Banbury or an extruder [26].

2.1.3 Physical vapour deposition

Physical vapour deposition (PVD) method is a Vacuum deposition method which can be used to produce thin films and coatings. Sputtering is a widely used physical vapour deposition technique which involves ejecting material from a source to a substrate by the bombardment of high energetic particles. Electric arc deposition is another PVD technique which uses an electric arc to vaporise material from a cathode target. Coatings using physical vapour deposition technique are harder and more corrosion resistant than electroplated coating [27].

2.1.4 Laser ablation

Laser ablation or photo ablation is the process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam. Mostly ND YAG lasers are used for producing laser beams. The amount of ejection depends on the intensity, pulse length, wavelength of the laser, and the material. This process can be used to deposit thin film on a surface [25].

2.2 Chemical methods

Chemical synthesis techniques are simple, inexpensive, and widely used techniques through which large quantities of material can be obtained with different structure and morphology. Moreover, doping of ions is also possible which enhances the properties of nanoparticles. Most of the chemical synthesis methods come under bottom–up approach in which self-assembly of particles takes place. Hydrothermal synthesis, precipitation, sol-gel, electrodeposition etc, are some of the well-known chemical synthesis approaches.

2.2.1 Hydrothermal method

Hydrothermal method of synthesis is a simple method of producing nanoparticles. In this method the size and structure of the produced nanoparticles can be controlled by controlling the process parameters like pressure and temperature. In Hydrothermal method aqueous solution is used as a solvent to dissolve the precursors. Many metal oxide nanoparticles were developed using this method. In the preparation of ZrO_2, Sagadevan S et al, used $ZrOCl_2$.$8H_2O$ and KOH as starting materials [14,18]. These materials in required proportions are mixed and kept in an autoclave at particular pressure and temperature to obtain the ZrO_2 nanoparticles. This is one of the most promising methods of preparing nanoparticles with utmost purity, desired size and morphology. Solvo thermal synthesis is the one which uses non aqueous solution as solvent.

2.2.2 Chemical vapour deposition

Chemical Vapour Deposition (CVD) is a widely used technique in preparation of thin films and 2D nanomaterials on the desired solid substrates. In this technique, the precursors, gas or vapour, will react or decompose on the preselected substrate at high temperature and vacuum/inner atmosphere in the CVD chamber. Based on the mode of activation, CVD can be classified into atmospheric-pressure CVD, low-pressure CVD, ultrahigh vacuum CVD, plasma enhanced CVD, microwave plasma assisted hot filament CVD, metal–organic CVD, and photo-initiated CVD [28].

2.2.3 Precipitation

Precipitation method is cost effective and capable of scaling up for mass production. Precipitation is used to remove metal ions from aqueous solution. Nanoparticles of higher surface areas are commonly prepared by using this method. Co-precipitation reactions involve the simultaneous occurrence of nucleation growth, coarsening, and agglomeration processes [28]. Hemalatha E, et al, used precipitation method for the synthesis of Zirconium oxide nanoparticles in which $ZrOCl_2$.$8H_2O$ was mixed with distilled water and NaOH is added while stirring uniformly. After some time, precipitates are collected at the bottom. The hence formed Zirconium oxide thin films can be used for sensing ammonia gas [20].

2.2.4 Sol-gel process

The sol-gel process is a wet chemical technique in which the sol (solution) evolves gradually to forma gel. The sol-gel process which is also known as chemical solution deposition, involves several steps in the preparation of Zirconium oxide nanoparticles. In an article, Shukla S, et al, used Sol-gel method of synthesis where zirconium (IV) *n*-propoxide, anhydrous ethanol was used as precursors which undergone several stages like hydrolysis, condensation, precipitation, drying to form ZrO_2 nanostructures [29]. Nanostructures with different size and morphology can be obtained by this method. Sol gel method is an easy and inexpensive technique for preparing nanoparticles with high purity.

2.3 Biological methods

The synthetic chemical and physical routes need high pressure and temperature, long reaction time, costly chemical precursors and specific experimental setup to grow nanostructures of interest. The solvents and reagents used in these processes are toxic and will generate harm to the environment by releasing harmful residues. So there is a need to develop a simple, clean, non-toxic, and eco-friendly approach for synthesising nanoparticles. Biological synthesis is considered as an interesting and environmentally friendly approach for the synthesis of various nanoparticles in which natural bio molecules extracted from plants, fungi, algae, bacteria etc can be used as the precursors/source material for the synthesis of nanoparticles. The bio synthesis of metal oxide nanoparticles has gained a lot of attention now a days due to its simple and environmentally friendly approach.

2.3.1 Plant synthesis

Plant synthesis is a simple, single step, nontoxic, eco-friendly technique which uses plant material for the fabrication of nanoparticles. In this clean synthesis method several parts of the plant like leaves, flowers, roots, fruits etc are used for the synthesis of nanoparticles. In a report by Nimare P, et al, azadirachta indica (neem) leaf powder was used as a reagentin the preparation of ZrO_2 nanoparticles. It was observed that plant synthesis method has advantages over other methods because of its cost-effectiveness, simple procedure, and relative reproducibility [30]. Various other parts of different plants are also being used in the synthesis process which are listed in the below table 2.

2.3.2 Algae-mediated biological synthesis

The algae-assisted synthesis of nanoparticles is economical and environmentally friendly technique, because the synthesis takes place in water under normal conditions. Toxic chemicals are not involved in the synthesis instead the seaweeds and marine algae are used. Different species like Rhizocloniumfontinale, Ulva intestinalis, Chara zeylanica and Pithophoraoedogoniana are collected for screening the possibility of usage. Investigations are being carried out by many researchers to optimise the process parameters to obtain desirable size and shape control of the products [31,32].

2.3.3 Fungi mediated synthesis

Fungi are said to be excellent biological agents for the synthesis of metal and metal oxide nanoparticles. Fungi are able to synthesize larger amounts of nanoparticles when compared to bacteria. Initially fungi are allowed to grow on agar and then it is transferred to a liquid medium. The produced biomass is transferred to water for release of compounds that are used in the synthesis. Aspergillus oryzae, Trichothecium Sp, Aspergillus fumigates, etc are examples of some fungi used by researchers in nano material synthesis [33,34].

2.3.4 Bacteria mediated synthesis

Although some synthetic methods are widely used in the production of nanoparticles, wide number of bacterial species are also being used in green nanotechnology because of its naturalprocess. Biomass and cell extractsof bacteria are used in the synthesis of nanoparticles. Lactobacillus Sp, Bacillus subtilis, corynebacteriumsp are some of the bacterial species previously used [35].

As microbe mediated synthesis is not quite simple and feasible, plant mediated synthesis gained a lot of importance. Plant synthesis/Green synthesis methods which use plant extracts as the major source of synthesis are very much preferred over physical and chemical methods because of easy availability, high stability, cost effective, biocompatible and clean synthesis [36].

Thus obtained nanoparticles can be used for many applications like dental care, catalysis, solar cells, fuel cells, bone implants, gas sensors, thermal coatings, antibacterial, and antifungal and anti-cancer agents etc.

3. Microscopic images

The Scanning Electron microscopy (SEM) and Transmission electron microscopy (TEM) reveals the morphology and microstructure of the synthesised nanoparticles. From SEM images we can obtain information about the surface morphology, shape and structure. TEM result discloses the particle size, size distribution, and microstructural information. The below image (Figure 3) is taken from the article by Tao XY, et al, which shows the report on Hydrothermal synthesis of star like ZrO_2nanoparticles [14]. The star like structures of ZrO_2 are clearly observed in the microscopic images. Wecan produce nanoparticles with different shapes and sizes by altering the process conditions.The magnified images with high resolution can be observed. Selective Area Electron Diffraction (SAED) patterns are used to find the d-spacing of the crystal planes.

High-resolution transmission electron microscopy (HRTEM) is an imaging mode of specialized transmission electron microscopes (TEMs) that allows for direct imaging of the atomic structure of the sample.)

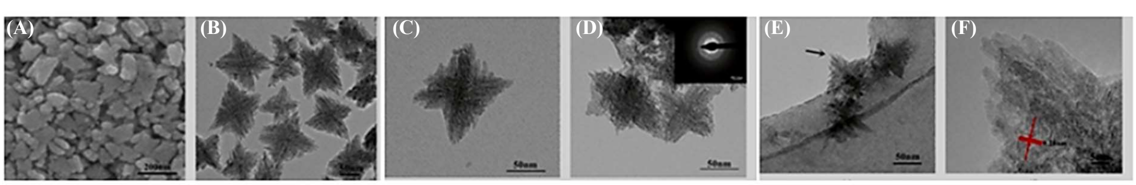

Figure 3 SEM image (A), TEM image (B, C), SAED patterns (D), TEM image (E) of the synthesized ZrO2, and (F) HR-TEM image of the area denoted by the black arrow in (E) Ref [14].

4. Observation on photocatalytic properties of ZrO_2 nanoparticles

Photocatalysis is a technique in which dye degradation in the water is achieved using a suitable catalyst in the presence of light. For wastewater treatment semiconductor nanoparticles are considered as suitable catalysts due to their wide band gap. In this article, a study was performed on various Zirconia metal oxide composites formed by different synthesis routes which can be used for various photo catalytic applications. The photocatalytic property which is altered is also indicated. Many structural and optical properties like band gap, surface area, recombination rate, adsorption, and reduction of ions etc, got altered when different materials are doped with zirconium. Many organic and inorganic dyes like Rhodamine B, Methylene Blue, Methyl orange, Congo red, Methyl violet etc. are tested and the degradation ratios at various time intervals are noted.

Table 1 Various Zirconium metal oxide composites formed using different chemical routes used for photo catalytic applications.

Metal oxide formed	Starting materials used	Synthesis method	Photo catalytic property altered	Observation	% of Degradation	Reference
Pt doped ZrO_2-SiO_2	$Si(OC_2H_5)_4$, $Zr(OCH_2CH_2CH_3)$, H_2PtCl_6	Sol-gel	Reduced Band gap	Degradation of cyanide	100% in 20 min	[37]
ZrO_2-ZnO	$ZnSO_4·5H_2O$, $ZrOCl_2·8H_2O$	Precipitation	Narrow Band gap	Removal of Methylene Blue	97%	[38]
Star like ZrO_2	CH_3COONa, $Zr(NO_3)_4·5H_2O$	Hydrothermal	Reduced band gap	Degradation of RhB	Nearly100% in 30 min	[14]
ZrO_2	(Zr (OEt)4), (Zr (OH)4)	Hydrothermal	Band gap	--		[39]
C doped ZrO2	--	Sol-gel	Band gap	Enhanced antibacterial activities		[40]
Tetragonal ZrO_2	$ZrOCl_2·8H_2O$, NH_4OH	Hydrothermal	Adsorption	Degradation MO	99%	[41]
ZrO_2 - TiO_2	$ZrOCl_2·8H_2O$, $TiCl_4$, NH_4OH	Hydrothermal	Surface Area	Application in acid–base catalysis		[10]
Tetragonal star-like ZrO_2	$ZrOCl_2·8H_2O$ CH_3COONa	Hydrothermal	Adsorption	Photo-degradation of anionic and cationic dyes	MO,CR,RhB 95%in 40 min, 100% in 60 min MV 65.7%, CV 64%, RhB 86% in 40 min	[42]
Zr doped ZnO	$Zr(NO_3)_3$, $Zn(NO_3)_2$	Sol-gel	Band gap	Degradation of methylene blue	Zr-ZnO 58% in 180 min ZnO 41% in 180 min	[7]
ZrO_2-SnO_2	$ZrCl_4$, $SnCl_2.2H_2O$, NaOH	Hydrothermal	Band gap	Photo-degradation of Congo red	96% in 30min	[43]
ZrO_2-MoS_2	$(ZrO(NO_3)_2)$, $(NH_4)_6Mo_7O_{24}·4H_2O$, (C_8H_6S)	Hydrothermal	Low recombination rate of the electron and hole pairs	Degradation of MO	95% in 12 min	[44]
NiO-CeO2-ZrO2	Ni(NO3)2·8H2O, Ce(NO3)3 ZrO(NO3)2·xH2O	Hydrothermal	Surface Area	Steam reforming of ethanol		[45]

Table 1 gives us information on the degradation performance of Zirconia catalysts and various photo catalytic properties which are affected by doping various metals or metal oxides to Zirconium. This data is collected based on various works carried out by many researchers. Thus, from the inferences we can say that we can have better catalytic performance when Zirconium is mixed with some other metal oxide to form a Hetero junction structure. Also, the method of synthesis and various precursor materials used also plays a major role. From the above analysis we can further use Zirconium with various composite combinations, and this can be well used for catalysis purpose by tuning the parameters like band gap, surface area and recombination rate etc. Also, we can observe the change in the structure of the zirconium nanoparticles when the precursors are changed. The nanoparticles with a different morphology are most suitable for catalytic applications [14,41]. Thus, we can say that the precursors used in the production of materials also play a significant role.

This review also draws attention to the knowledge concerning the usage of plant extracts for synthesis of Zirconium oxide nanoparticles and presents some information that future researchers may use relating to the green synthesis of ZrO_2 NPs using various plant extracts, whose outcomes may be effectively used to perform catalytic activity. Park TJ, et al made a study on advances in microbial biosynthesis of metal nanoparticles and listed out various microorganisms employed for the synthesis of metal nanoparticles. In a paper by [47], synthesized zirconium oxide nano particles with high purity using acalypha indica leaf extract. Similarly, many eco-friendly methods are also evolved in the production of metal and metal oxide nanoparticles using naturally available bio molecules.

Various works have been carried out based on plant (green) synthesis of nanoparticles [48]. Table 2 can be considered as a database of various plant extracts which can be used for the synthesis of ZrO_2 nanoparticles. Thus, prepared zirconia particles can be used as catalysts in many applications as many observations are made on the photocatalytic properties like adsorption, reduction, change in bandgap, surface area etc. Also, the application of such synthesized nanoparticles in catalysis is noted in the below table 2.

Table 2 Zirconium oxide nanostructures formed by green synthesis used for various catalytic applications.

Material prepared	Scientific name of Plant	Common name	Size of nanoparticle	Property altered	Application	Reference
ZrO_2	Azadirachta Indica	Neem		Band gap		[30]
ZrO_2	Ficus benghalensis	Banyan	15nm	Band gap, surface area	Photo-catalysis	[49]
ZrO_2	Eucleanatalensis	Natal gwarri	5.25 to 41.71 nm	Adsorption	Catalyst	[50]
ZrO_2	Acalypha Indica	Indian nettle	20-100nm	Absorbance	--	[47]
ZrO_2	Citrus aurantifolia	Lemon fruit	21nm	Particle size	Solid oxide fuel cells	[51]
ZrO_2	Capsicum annum	Bell peppers	22.029 nm 13.069 nm	Structural and optical	Antifungal and antibacterial activity	[52]
ZrO_2	Allium cepa	Garden onion	11.039 nm 21.97 nm	Structural and optical	Antifungal and antibacterial activity	[52]
ZrO_2	Lycopersicon esculentum	Tomato	21.370nm 20.489nm	Structural and optical	Antifungal and antibacterial activity	[52]
nZrO2, nZrO2-Alalig	Sapindus plant	Soap berry	10.91nm	adsorption	Phosphate removal	[53]
$Ag/Fe_3O_4ZrO_2$	Centaurea cyanus	Corn flower	--	Reduction	Catalyst	[54]
ZrO_2	Nephelium lappaceum	Rambutan	--	Reduction	Catalyst	[55]

Hence from all the above observations we can easily synthesize an efficient catalyst from Zirconia and its composites which can be used in the degradation of several organic and inorganic dyes. Based on all such observations we can say that (1) semiconductors with large band gap and (2) materials which utilize maximum solar spectrum are the best suited photocatalysts. For that a combination of several metal oxides can also be explored. Semiconductors when combined with ZrO_2 can provide a better photocatalytic activity and some of such heterojunction catalysts are also reviewed in this article. Moreover, keeping in mind the present environmental pollution situation, there is a need for developing eco-friendly techniques for Nanoparticle synthesis avoiding the use of toxic chemicals thereby reducing the environmental deterioration. Many such natural synthesis methods were introduced among which synthesis of nanoparticles using plant extracts plays a prominent role.

5. Conclusion

This review shows the various physical, chemical, and biological methods of synthesis used in the preparation of ZrO_2 nanoparticles. Also, the various applications of ZrO_2 in various fields are studied. ZrO_2 combined with several other metal oxides seems to be effectively used as a catalyst in various applications. The capacity of adsorption or reduction of various pollutants like methylene blue, methyl orange, Congo red, RhB etc makes ZrO_2 a potential catalytic agent. The variation of catalytic properties can be observed when we add the ZrO_2 composite mixtures to the wastewater. So that we can help in reducing the harmful compounds entering into the huge water bodies and thus polluting them. This literature survey also focussed on the plant synthesis method of preparing ZrO_2 nanoparticles which is an easy and environmental friendly approach avoiding the hazardous chemical by-products. This plant synthesis method gains a great advantage of reducing the usage of chemicals in the synthesis and has got a lot of future. The advancements in the green synthesis method over last decade show that there is a great future for this method.

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