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Review Article

Focus on Zinc Oxide as a Photocatalytic Material for Water Treatment

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Abstract

Zinc Oxide (ZnO) has been widely utilized for its physical and chemical properties, as well as being a great material for biosensors, solar cells, semiconductors, and photocatalysis. This oxide has adequate band gap energy required for absorbing energy in the UV spectrum. Although, ZnO has the disadvantage of being unable to absorb energy in the visible range of the electromagnetic spectrum, making less desirable for a photocatalytic material. Researchers are now investigating how to modify this band gap to shift its absorption range towards the visible range, in order to maximize its capability as a semiconductor in photocatalytic usage. The main goal of this review is to provide an overview of the most recent developments on ZnO features and applications, including core-shell structures, composites with other metallic oxides, and ZnO doped with other elements. Synthetic approaches will be described for different nanostructures, efficiencies, and future challenges.

Keywords: Advanced Oxidation Processes(AOPS); Metal Oxides; Photocatalysis; Zinc Oxide Nanostructures Nanotoxicity

Introduction

As new compounds are being produced, new ways to prevent toxicity in the environment has to grow as well. Novel pollutants such as dyes, pharmacons, and activated sludge are produced by industries and are being disposed into water bodies. Xenobiotic compounds such as organ chlorinated matter [1]. Hydrocarbons [2], among others do not occur naturally, affecting flora and fauna in aquatic ecosystems. In addition, some of these contaminants are recalcitrant and bioaccumulate in aquatic animals, plants and microorganisms. The harm produced by these novel pollutants to wild-life is not fully known and because these are strange molecules, microorganisms do not metabolize some of them. Moreover, conventional methods for wastewater treatment are not prepared to remove these emergent contaminants [3].

As primary and secondary treatment for wastewater, like separation and coagulation [4], are unable to remove these compounds, alternatives must be taken into consideration. Advanced Oxidation Processes (AOPs) serves as an efficient process to remove compounds with low biodegradability in wastewater or improves its degradability by forming new by-products easy to biodegradation [5,6]. These processes have demonstrated to oxidize a wide selection of organic matter and also can inactivate microorganisms when desired [7].

Advanced Oxidation Processes

AOPs has grown recently, due to its green approach and being one of the most effective methods towards wastewater treatment or inclusive to obtain drinking water [8]. AOPs refer to the oxidation process of pollutants in wastewater in order to get solid minerals or other easy-treatment compounds. The advantages of using AOPs for wastewater treatment include rapid degradation rate, reactions can occur at room temperature, complete mineralization of organic matter, elimination of effects from disinfectants and other residual oxidants, degradation by-products of previous treatments, it does not require external energy, it does not generate sludge, contaminants can be treated at low concentrations, and can be used before biological treatments for pollutants resistant to biodegradation [8,9].

In the oxidation process, the system need reactive oxygen species (ROS), in which AOPs produce one of the most potent in solution, hydroxyl radicals $OH^{\bullet}$. Oxidation potentials of some oxidants are listed on (Table 1) Compared with other oxidant species, hydroxyl radicals have a very high oxidation potential, which is helpful for AOPs. Hydroxyl radicals are not selective, which make them great oxidants of pollutants as they attacking directly and modify their molecular structure into less dangerous by-products [10].

Species	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	2.8
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.7
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

Table 1: Oxidation Potentials of Some Oxidants.

AOPs are classified into degradation of pollutants by UV irradiation, son chemical reactions, ozone based AOP and photo catalysis [11-13]. The main mechanism in any AOP refers to the interaction of hydroxyl radicals with organic matter H-R-H, producing the organic radical HR$^{\bullet}$ by removing an H$^{\bullet}$ to form H_2O. This radical reacts rapidly with dissolved oxygen by forming organic peroxoradical $RHO_2^{\bullet}$, which is highly unstable. The peroxoradical degrades by turning into R$^{\bullet}$, which will react with other free radicals or oxygen and producing a degraded organic compound R [14].

$OH^{\bullet} + H\text{-}R\text{-}H \rightarrow RH^{\bullet}$ (Eq. 1)

$RH^{\bullet} + O_2 \rightarrow RHO_2^{\bullet} \rightarrow R^{\bullet} + H_2O$ (Eq. 2)

$R^{\bullet} + H_2O + O_2 + OH^{\bullet} \rightarrow$ oxidation (Eq. 3)

Photocatalysis

The process of catalysis that involves light as source to produce ROS is called photocatalysis. Photo-catalysis involves a photochemical reaction at the surface of the photocatalyst (a metal oxide semiconductor), where electron transfer takes place and spaceman the electron-hole pair is produced by incoming light [15]. This process is capable of modifying inorganic matter, degrading organic matter and inactivate microorganism. UV radiation is the most used energy source due to its adequate energy, viability and being cost effective. Solar energy is the most abundant and clean energy source available today, and it produces the UV radiation that AOPs need. It is known that the amount of solar energy that strikes the earth in an hour is higher than the energy that humanity consumes in a year [16]. This brings the rise in development of materials that can utilize solar irradiation in different areas, such as wastewater treatment and pollution management. However, the solar energy is not used totally, because the common photocatalyst use mainly the UV wave length, which represents only 5%-8% of the solar spectrum at sea level [17], limiting its use.

Photocatalytic mechanisms are distinguished into homogeneous and heterogeneous. This is linked to the type of catalyst used for the process, being the catalyst that are in the same phase where the reaction occurs (homogeneous) and those which are in different phase (heterogeneous). By taking into account their physical nature, the difference between homogeneous and heterogeneous catalysts differ on its uses, stability, and selectivity. (Table 2) shows a comparison of the main advantages and disadvantages of both types of catalysts [18].

Property	Homogeneous	Heterogeneous
Selectivity	Excellent-good	Good-poor
	Single active site	Multiple active sites
Thermal Stability	Poor	Good
Catalyst recovery	Expensive	Cheap
	Difficult to recover	Easy to recover

Table 2: Comparison of main advantages/disadvantages of homogeneous and heterogeneous catalysts.

The electronic structure of semiconductors consists of two energetic levels, the Valence Band (VB) and the Conduction Band (CB), with an energetic difference known as the Band Gap (BG). Electrons (e^-) found in the VB have low energy. If energy is transferred to an electron in VB, they jump to the CB and leave a "Positive-Charged" hole (h^+). Promoted electrons in the CB can later react with another compound and result in an oxidation process. The energy needed for an electron to travel from VB to CB is specific for each semiconductor, and can be obtained from absorbed photons in light. In AOPs, they react with O_2 and H_2O, and produce highly oxidant agents, including hydroxyl radicals [13]. (Figure 1) presents a scheme of the mechanism of the promotion of an electron from the VB to the CB.

Semiconductor + $hv \rightarrow$ Semiconductor ($e^- + h^+$) (Eq. 4)

Semiconductor (e^-) + $O_2 \rightarrow$ Semiconductor + $O_2^{\bullet -}$ (Eq. 5)

Semiconductor (h^+) + $H_2O \rightarrow$ Semiconductor + $HO^{\bullet}$ (Eq. 6)

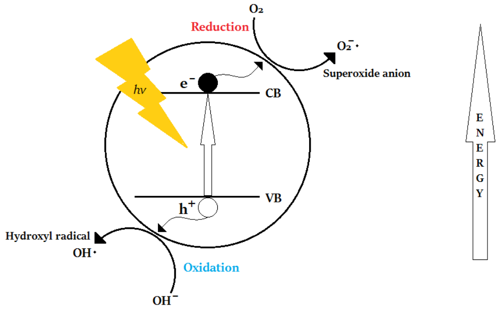

Figure 1: Scheme of the photocatalysis mechanism in the generation of hydroxyl radicals.

Even though this process is very effective, the e^-/h^+pair generation can recombine. Recombination can occur before the electron is transferred to another chemical species, which result in energy dissipation and reduce effectiveness of the process. The recombination is dependent on the properties of the semiconductor. However, the particular properties can be modified to have desirable properties. Specific particle size, doping, and synthesis processes can modify the properties of the semiconductors in order to benefit their performance in AOPs. Modifying the semiconductors can change the BG, and thus the required energy they need to transfer electrons from VB to CB.

Many metal oxides semiconductors have been studied with promising results, such as titanium dioxide (TiO_2), iron (III) oxide (Fe_2O_3), tungsten trioxide (WO_3), zirconia (ZrO_2), zinc oxide (ZnO), among others. All of these oxides are actively used in environmental wastewater treatment [19,20]. The production of hydroxyl radicals from these metal oxides is high enough to degrade pollutants in a short time and with high yield.

Out of all semiconductors, ZnO arises as a candidate as an efficient photocatalyst for its use in green pollutant treatment because of its unique properties. Some appealing characteristics are its wide band gap in the near-UV spectral region, good photocatalytic property, strong oxidation capability, insoluble in water, and low cost production [21,22].

ZnO as a Photocatalyst

ZnO is one of the most used semiconductors worldwide. In aqueous solutions, it produces H_2O_2 if exposed to O_2 and UV radiation, which turn into hydroxyl radicals. ZnO has a BG energy of 3.37 eV, large excitation binding energy (60 meV) and UV absorption at room temperature, which make this oxide an adequate photocatalysts [23]and used as antibacterial, antifungal [24], and antifouling agent [25].

ZnO has advantages over TiO_2, another well-known semiconductor used in photocatalysis. While both semiconductors possess a very similar BG energy, ZnO exhibits a higher absorption efficiency across a wide fraction of the solar spectrum [26,27]. In presence of organic matter, electron transfer degrades the organic molecule up to CO_2 as a final product. To explain this, a transferred electron from the ZnO momentarily produces Zn^{+1}, which reduces the O_2 near the photocatalyst in order to form H_2O_2. This transfer produces a positively charged ZnO. If organic matter is present, an electron is donated to the semiconductor, which results on the oxidation of the organic matter [28].

$ZnO \rightarrow Zn^{+1}O^{-2}$ (Eq. 7)

$Zn^{+1} + O_2 \rightarrow Zn^{+2} + O_2^{-}$ (Eq. 8)

$(ZnO)^{+} + RH \rightarrow ZnO + RH^{+}$ (Eq. 9)

$RH^{+} \rightarrow RO_2$ (Eq. 10)

Even if ZnO has great properties for oxidation processes, ZnO faces challenges on its own nature. First, it can only absorb UV radiation with wavelengths near 387 nm, which can be associated with the BG energy of the ZnO. Secondly, and as mentioned before recombination of the e^-/h^+ pair that hinders the performance of the ZnO. This is why research on ZnO modifications is needed in order to expand its absorption range and maximize its performance as a photocatalyst. Several novel studies are aimed to improve the optical properties of ZnO, focusing on minimizing BG energy and inhibiting recombination of the photo-generated e^-/h^+ pair, and new synthetic methodologies and the effect of various modification methods.

Synthesis of ZnO Nanostructures

Research on ZnO structures has emerged as a potential candidate for many pronounced applications. Other than wastewater treatment, ZnO is subject for energy harvesting, biomedicine, and electronic devices. The versatility of ZnO permits various synthesis methods, with the ability to adopt many morphologies and sizes. Physical and chemical parameters, such as solvent type, pH, temperature, and Zn precursor, can be modified to adapt the properties of the ZnO structures for a desired application. Each nanostructure has specific structural, optical, electrical, and physicochemical properties [24].

Standard methodologies that enable better control of both size and morphologies include sol-gel technique, hydrothermal synthesis, self-combustion, thermal evaporation, double-jet precipitation, solution synthesis and polymerized complex method [29].

Some synthesis routes utilize a huge amount of energy or solvents. Approaches for a green route synthesis of ZnO Nanoparticles (NPs) have been studied by using a biological method. A study used *Aloe babadensis* miller leaf extract to synthesize highly stable and spherical ZnO NPs. These NPs show poly dispersity and particle ranges from 25-45 nm [30]. Another synthesis consisted on the use of the fruit trifoliate orange (*Poncirus trifoliata*) extract as a way to avoid using toxic reagents. The biosynthesized ZnO NPs showed catalytic properties as it was tested on a reaction procedure of Claisen-Schmidt condensation of 3, 4-dimethyl benzaldehyde with acetophenone, with a yield of 80% [22].

ZnO can also adopt different morphologies. ZnO nanorods (NRs) are efficient to degrade methyl orange shown by Dan wittayakul et al. Methyl orange was degraded up to 95% with UV radiation for 3 h [31]. In a similar matter, Vega-Vaudrit & Corzo Lucioni in 2012 published the kinetic study of rhodamine B (RhB). The author found out that a high initial concentration of both target dye and photocatalyst increase the degradation rate, with optimum concentrations of 20 mg/L of RhB and 200 mg of ZnO for each 100 mL of solution [32].

A methodology to produce ZnO nanostructures with higher surface area for photocatalysis was published by Khoa et al. ZnO nanoparticle-assembled hollow spheres (nPAHS) can be achieved using a self-assembly route [33]. The growth mechanism of the ZnO hollow structures is assisted by trisodium citrate, where the hydroxyl and carboxyl groups in citrate ions cap Zn^{2+} precursors and direct the growth of the ZnO structure. After annealing at 500°C, the citrate ions are removed and improve the crystalline structure of the remaining ZnO in order to form the nPAHS.

Bijanzad et al. used Zn(anic)$_2$, a coordination compound obtained from 2-aminonicotinic acid (Hanic) and $Zn(NO_3)_2$, as a precursor to obtain hollow microbricks of ZnO after the calcination (550°C, 4 h). These novel nanostructures possess large surface area of 8.13 m^2/g and a pore size of 22.6 nm, ideal for photocatalysis. The micro bricks were applied in the photodegradation of Congo red (CR) dye from aqueous solution. Even with a natural 3% of degradation of CR under the light source, CR removal efficiency after 3 h using the microbricks was 96% [34].

Mesoporous ZnO nanofibers were synthesized by electro spinning method. Synthesis consisted on adding polyacrylonitrile and Zn precursor into DMF solvent. After calcinations, the polymer decomposes and produces porous ZnO nanofibers. The fibers were used for the degradation of anthracene and naphthalene dyes. These nanofiber mats may find varied applications, as they resulted to be reusable and effective in photocatalysis [2]. Bercoff et al. demonstrated that ZnO decomposes the dye orange II in a first-order kinetic and a half-life $t_{1/2}$ = 58 min. ZnO was used as a doping agent for ferromagnetic particles, acquiring the additional property of being reusable photocatalyst [35].

ZnO Composites and Doping with other Elements

Just as TiO_2, ZnO needs improvement due to rapid charge recombination from the generated e^-/h^+ pair. A novel structure of TiO_2-ZnO composite sphere was achieved, with ZnO decoration by using solvothermal method [36]. The isolated ZnO synergizes with the TiO_2-ZnO composite, as the composite (type II heterojunction) delay the charge recombination. In contrast with TiO_2-ZnO, TiO_2, or ZnO alone, the novel composite showed better photo-activity in degrading RhB and faster photo-assisted isomeration of norbornadiene, which supported the proposed electron transfer mechanism.

Priyanka and Srivastava modified the ZnO structure by doping it with Fe. By using solution combustion synthesis method, iron-doped ZnO can be synthesized. By using this synthetic route, a mixture of microporous and mesoporous ZnO-Fe can be achieved, with high crystallinity. The study also tested these catalysts for the photocatalytic oxidation of acid red 1 dye, with variable parameters in order to achieve optimization. Optimum conditions for both synthesis (Fe 2.5 wt%, calcination temperature = 400°C, calcination time = 4h) and photocatalysis tests (pH = 2, catalyst dose = 1.25 g L^{-1}, oxidant dose = 6 mmol L^{-1}, temperature = 50°C) were studied, having the best results of 94% of dye degradation and 41% of total organic carbon removal [37].

Cho et al. synthesized sulfur-doped star-shaped hexagonal ZnO nanowires (NWs). These structures were obtained after doping ZnO NWs with thiourea $SC(NH_2)_2$. This transformation only occurred with thiourea, but not with urea. The cross-sections of the NWs transformed from hexagon to a hexagram. In order to understand the role of sulfur doping in this transformation, *ab initio* simulations were conducted. Results on the simulation suggest that sulfur causes a local change in charge distribution that is stronger on the vertices of the NWs than in the edges, leading to the change in the morphology [38].

On another study, Emin et al. doped ZnO films with CdX (X = S, Se) in order to modify the usable electromagnetic spectrum range. On a first step, plate films of simonkelloeite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) grew electrochemically, followed by annealing at 450°C. Once the porous ZnO electrodes were ready, they were used for photoelectrochemical studies. The authors sensitized the ZnO electrodes with CdX quantum dots, and as expected photocurrent density increased with the doping. The results demonstrate that these new materials could be potentially useful in light-harvesting applications [39].

NPs decorated with various metals, such as Ag, Au, and Pd, modify the charge carrier dynamics. Lin et al. presented these novel materials and their correlation between the metallic charge carrier dynamics and their photocatalytic properties. The metal content varied from 0.6 to 2.3 at%, showing that an Au content of 1.3 at% can effectuate the largest electron transfer rate constant for ZnO-Au nanocrystals. The three kinds of decorated nanocrystals were employed on the degradation of methylene blue (MB), showing that ZnO-Pd had the best photocatalytic performance [40].

Saoud et al., reported highly crystalline Ag spheres on ZnO NRs which presented photocatalytic activity and antibacterial properties under visible light. Photocatalytic tests were performed on the degradation of MB with visible and UV light sources. Results could demonstrate that the Au NPs lead to enhancement of optical and photocatalytic properties of ZnO NRs, aside from being able to inactivate *Escherichia coli*. These materials could serve as great photocatalysts for AOPs as they showed to have a wide range of photon absorption of the solar spectrum and the ability to inactivate bacteria [41].

Goodall et al., showed the photo catalytic performance of ZnO doped with a wide variety of elements, including transition metals, obtaining 56 different samples. All samples were used on the degradation of MB with low doping percentage. Transition metals (Fe, Ag, Mn, V, Ni, Cr, Co, Ti, and Sr) decreased ZnO photoactivity, but an increase was shown by rare earth metals (La, Y, Nd, Er, Gd, and Pr) doping [42].

A series of co-doped ZnO nanostructure was synthesized by Alam et al. using Y and V. The synthetic approach used V_2O_5, $Y(NO_3)_3$ and $Zn(CH_3COOH)_2$ as precursors for the ZnO-V-Y NPs by using a surfactant assisted sol-gel methodology. The doping content of Y varied from 1 to 3%, but for V it remained constant at 1%. Photocatalytic performance was tested by using RhB, MB, and 4-nitrophenol (4-N) under visible light. From all the ZnO-V-Y NPs, the best doping content was found to be 3% Y and 1% V, which notably improved the photocatalytic activity of ZnO. Authors suggest that the introduction of V into ZnO creates impurity level above the VB of ZnO which results on a shift in the spectral response from UV to visible region, but also that the inclusion of Y into ZnO-V retards the recombination of charge carriers since Y is known of being a good electron trapper [43].

Core-Shell Type Structures

Core-shell structures are an attractive way to exploit the properties of ZnO while coupling benefits from other materials, complementing each other. Also, adding a shell-like structure to a main core can be used to protect it from the environmental solution.

It is a fact that ZnO is unstable in acid and alkaline mediums, and a way to protect it against corrosive environments is the use SiO_2as a coat to ZnO in order regain photocatalytic activity in both acid and alkaline solutions. These ZnO/SiO_2 core-shell NPs were successfully synthesized in a two-step methodology [44]. As shown with TEM images, the thickness of the SiO_2 shell is dependent on the molar ratio of both oxides, but considerably thinner than the ZnO core. Photocatalytic performance was also studied using RhB aqueous solution at pH 4.5, 7 and 10. Uncoated ZnO worked best at neutral solution. In contrast, ZnO/SiO_2 NPs showed a better photocatalytic performance in both acidic and alkaline solutions of RhB. This could be explained as the SiO_2 shell could protect the ZnO core from corrosive environments, improving stability and maintaining photocatalytic capability, unlike unprotected ZnO. These results expand the potential application in specific wastewater treatments because the pH variation in some water samples can be extreme.

ZnO/In_2S_3 core/shell nanostructures where synthesized to overcome the e^-/h^+ pair recombination and the narrow range of photon absorption of the solar spectrum. ZnO NRs where used as substrate for the In_2S_3 NPs, which successfully covered the NRs. The core/shell photocatalyst exhibited enhanced photocatalytic activity in the degradation of RhB, which was 5 times higher than $In_2S_3$and 56 times higher than ZnO NRs. This effect can be attributable to the separation of the e^-/h^+ pair due to the formation of heterojunctions between both materials [45].

Biocompatible coatings are also being studied, particularly inulin [46]. A layer of inulin, a biocompatible and biodegradable polysaccharide, was used to cover hematite (α-Fe_2O_3) and brushite ($CaHPO_4$). The interaction of inulin with these materials were weak, but coating the surfaces beforehand with ZnO increased the affinity toward inulin. The new α-Fe_2O_3/ZnO/inulin and $CaHPO_4$/ZnO/inulin core-shell structures were water soluble and stable. This study shows the wide potential in specific tasks in environmental management and the particular physical and chemical advantage of ZnO to bind other materials as polysaccharides.

Another interesting core-shell nanostructure V_2O_5/ZnO was synthesized via a combined hydrothermal growth and magnetron sputtering and was supported on a glass substrate [47]. Curiously, after 500°C annealing, the ZnO shell contracted to the tips of each V_2O_5 NRs, giving a lollipop-like structure. This was attributed to the temperature sensitive crystallization and surface diffusion of V_2O_5. This nanomaterial was capable to decompose 2,6-dichlorophenol under visible light, showing promising potential for wastewater treatment and using white light wavelength as light source make this material a cheaper photocatalyst overall.

ZnO has also been covered with zeoliticimidazolate framework-8 (ZIF-8) produces a naturally porous structure, making this material biocompatible with potential use in animal or human applications [48]. These core-shell structures had uniform thickness of around 30 nm composed by ZIF-8 crystalline polyhedrons. An appealing property of these heterostructures is the selective adsorption and permeation effect of the ZIF-8 shell. The ZnO/ZIF-8 also exhibited enhanced selective reduction of Cr (VI) between Cr (VI) and MB, which make this study a niche with its selective photoactivity in mixture aqueous solutions or in Cr (VI) poisoning.

ZnO can also be used as shell for other materials. The synergy of Mn_3O_4/ZnO and Mn_3O_4 were used as photocatalysts in the reduction of Cr (VI) to Cr (III) under sunlight. The optimal ratio of Mn_3O_4/ZnO and Mn_3O_4 was set at 2:1, having removal rates of total Cr and Cr(VI) with 90.5% and 95.4% within 160 min. Authors tested Cr removal at different pH levels, and noting the optimum level at pH = 6. The novel type-II heterojunction inhibited the recombination of photo-excited carriers and had synergistic effect of photocatalysis and adsorption of total Cr removal. This composite exhibited excellent performance for Cr removal, which make a significant contribution to remediating Cr-polluted water bodies [49].

Metallic NWs can also be fabricated for core-shell structures. Worm-like Ag/ZnO core-shell heterostructural composites where fabricated in a two-step polyol method [50]. The Ag NWs were formed by a single-crystal Ag NW and then covered with ZnO particles. The ratio of Ag and ZnO was optimized to be 2.8 atom% of Ag, which had the best photocatalytic performance towards RhB, compared with 0.8 or 4.9 atom% of Ag. Authors calculated the reaction rate Constants k, demonstrating the better photocatalytic activity of Ag/ZnO NWs with $k = 0.0000668\ min^{-1}$, compared to pure ZnO with $k = 0.0034\ min^{-1}$.

Other Structural Modifications

An innovative approach of ZnO nanostructures is a textile modification by growing one-dimensional ZnO NRs onto the textile surface [21]. The modified textile showed to be multifunctional, showing antibacterial activity against *Escherichia coli*, and as a flexible working electrode for the detection of aldicarb pesticide, and finally as a photocatalyst for the degradation of organic dyes such as CR and MB. Result regarding the photocatalytic degradation of the dyes, the Ag-based textile with ZnO NRs showed activity upon UV irradiation and was successfully applied for the degradation of both CR and MB (degradation of 60% and 65% respectively under 200 min).

Another type of hetero-structure of gold-nanoparticle-decorated reduced-graphene-oxide (rGO)-wrapped ZnO hollow spheres have been synthesized [33]. ZnO nPAHS is decorated with Au/rGO, which decreases the charge-transfer time up to $4.1x10^{-12}$s. The Au/rGO/ZnO hybrid shows a higher charge-transfer efficiency of 68.0%, compared with rGO/ZnO of 40.3% and other reported ZnO hybrids. Additionally, the Au/rGO/ZnO exhibit great photocatalytic efficiency due to the reduced recombination of the e^-/h^+ pair, the fast electron-transfer rate and the high charge-transfer efficiency. All different nanostructured ZnO designed so far have high potential to be used in different wastewater treatment and applied mainly to eliminate xenobiotic or recalcitrant organic compounds and even heavy metal reduction as depicted on this review. It is important to note the potential use to reduce the toxicity or pre-degradation of recalcitrant compounds and improve their biodegradation. A summary of the different nanostructured ZnO materials is presented on (Table 3).

Structure Type	Name	Synthesis	Photocatalytic performance	Ref
Nanostructures	ZnO NPs	Biosynthesis using *Aloe babadensis* miller leafs	--	[30]
	ZnO NPs	Biosynthesis using *P. trifoliata*	Claisen-Schmidt condensation of 3,4-dimethyl benzaldehyide with acetophenone. 80% yield	[22]
	ZnO NRs on textile	Seed growth on Ag-based textile	60% Photodegradation of MB and CR in 200 min using the modified textile. Also had antibacterial activity.	[21]
	ZnO nanofiber mats	Electrospinning	Full degradation of naphthalene and anthracene dyes using UV light in 30, 20 and 12 min with 5, 10 and 20 mg of ZnO nanofibers respectively.	[2]
Hollow nanostructures	ZnO hollow sphere	Reflux	Photodegradation of MB under black-light irradiation of 56%	[33]
	ZnO hollow microblocks	Calcination of Zn coordination compound	Degradation of CR with efficiency of 96.7% in 3 h using a light source of λ = 546.8 nm.	[34]
Core-Shell nanostructures	ZnO/SiO_2	Chemical	Total photoreduction of RhB under 35 min at pH 7. Almost full photoreduction of RhB, 95% and 98% under 100 min at pH 10.5 and 4.5 respectively	[44]
	α-Fe_2O_3@ZnO,	Hydrolysis and	--	[46]
	α-Fe_2O_3@ZnO/inulin and ZnO/inulin	Chemical with ultrasonic bath		
	Ag/ZnO	Polyol process	High RhB degradation, comparing different of Ag at%	[50]
	ZnO@ZIF-8	Sol-gel (using 2-methylimidazole)	Selective removal of Cr (VI) in a mixture of Cr (VI)/MB (almost full removal in 70 min).	[48]
	ZnO/In_2S_3	Chemical	Degradation of RhB. 83.7% was degraded in 100 min.	[45]
	Mn_3O_4@ZnO and Mn_3O_4	Hydrothermal method and atomic layer deposition (ZnO layer)	Reduction of Cr(VI) to Cr(III) of 92% in 70 min in sunlight and pH = 6.0	[49]
	V_2O_5@ZnO lollipop-like structures	Hydrothermal growth and magnetron sputtering	Degradation of 2-6-dichlorophenol, around 60% in 6 hours (under different synthesis conditions)	[47]
Doped nanostructures	ZnO-Fe NPs	Chemical	Dye degradation and color removal of an azo dye under different conditions.	[37]
	ZnO-S NWs	Hydrothermal growth and thiourea doping	--	[38]
	Zn-V-Y NPs	Assisted sol-gel method	Degradation of RhB, MB and 4-N in 3 h using visible light of about 89%, 89% and 43.4% respectively.	[43]
	ZnO-X NPs	Hydrothermal flow synthesis	Dye degradation of MB under UV irradiation. Most rare earth ions increased photoactivity than ZnO.	[42]
	(X = Ce, Fe, Sr, La, Y, Mn, Ag, Ga, Nd, V, Ni, Cr, Co, Ti, S, Er, Gd, Pr)			

Decorated nanostructures	Composite TiO_2/ ZnO decorated with ZnO	Solvothermal method	Dye degradation of RhB, 75% in 60 min. Isomeration of norbornadiene (k = 0.591 h^{-1})	[36]
	rGO/ZnO NPs and Au/rGO/ZnO NPs	Solvothermal method + ultrasonic bath	Photodegradation of MB of 64% and 70% under black-light irradiation of rGO/ZnO NPs and Au/rGO/ZnO NPs respectively	[33]
	ZnO-X nanocrystals	Anti-solvent approach	Degradation of MB in 180 min under UV irradiation. Degradation rate of 45, 75, and 80%	[40]
	(X = Au, Ag, Pd)		with Au, Ag, and Pd doping respectively.	
	ZnO-Ag NRs	Microwave Assisted Deposition-Precipitation method	Degradation of MB with visible/UV irradiation. 90% of degradation in 120 min (0.1 g L^{-1} MB)	[41]

Table 3: Structure type, synthesis and photocatalytic performance details for ZnO nanostructures.

Toxicity Concerns of ZnO

Since ZnO has not shown any toxicity to human cells, it has been used in cosmetics and sun blocker formulations as NPs [51].Nan scaled particles improve skin retention, UV attenuation properties and especially public acceptance in comparison with non-nanosized materials [52].It has been demonstrated that ZnO can undergo photocatalytic reactions while exposed to UV light and generating several ROS ($O_2^{\bullet}$, H_2O_2 and $HO^{\bullet}$) [53], which can cause cellular damage and environmental toxicity. For many species, including fish [54] and algae [55], nanosized ZnO is extremely toxic [51]. ZnO has a similar toxicity as TiO_2, which is also used as an ingredient for sunscreen lotions. It is ascribed that the toxicity is due to two effects: the oxidative stress due the ROS generated and the release of Zn^{2+} ions [24,51]. However, nanosized ZnO is known for its antibacterial activity over many bacterial species [7,24,51,56]. ZnO toxic properties are being studied in both bulk and nanoscale formulations. Literature reports that antimicrobial properties are improved as size is decreased up to nanometer range, as nanosized ZnO can interact with both outside and inside of cells [57].

This particular property however, needs to be considered because its release to the environment can affect microbial population in water and soil systems. Microbial colonies play an important role to the environment by biodegrading different types of organic matter [58].and act as nitrogen fixers for plants. In this case, it is a priority to control its release to the environment or reduce the toxicity of the nanostructures in some way.

Future Challenges

It is a fact that conventional methods are not enough to eliminate all pollutants and need improved with other processes such as photocatalysis in order to degrade recalcitrant compounds. While it has attractive advantages over other types of water treatment methods, photocatalysis faces several challenges that need to overcome. First of all, photocatalysis degradation must be performed using polluted water and using contaminants of interests rather than scavenger agents or proxies [59]. Then, a better understanding of degradation mechanisms is required, along with the mechanism of the interaction between ZnO and pollutants.

Second, the development of ZnO nanostructures must be improved for specific cases. Therefore, the efficiency is dependent on the photocatalysts structure; studies must focus on techniques to synthesize adequate ZnO nanostructures in terms of particle size, surface area and lifespan of charge carrier [59]. A good opportunity is the research on ZnO with both metallic and non-metallic doping, fixing ZnO in rigid surfaces and other NPs, and exploration on adequate morphologies.

Performance of ZnO needs to be optimized, as this process alone has technical issues. The method is limited by the clarity of the water being treated, as UV light must be able to reach the ZnO. Also, in order to be implemented on water treatment plants, ZnO photocatalysis must be paired with other treatment processes, limiting its usage. Photocatalysis can be ineffective in the long-term as its limited by the water chemistry and the presence of co-contaminants. There is also a need of developing mathematical models for photocatalytic systems, which may help on predicting kinetics and will help to optimize conditions of the process.

Research on the potential toxicity of nanoscaled ZnO should be enhanced. While ZnO NPs have good biocompatibility to human cells, wild-life suffers from the poor management of these materials. Antibacterial mechanisms are not well understood, and investigations should be focus on the comprehension of the phenomenon. Favoring its reuse or recovering and avoid its inclusion to the environment and water bodies.

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