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To cite this article: S N A Mohamad Sukri *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1051** 012083

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Green Synthesis of Zinc Oxide-Based Nanomaterials for Photocatalytic Studies: A Mini Review

S N A Mohamad Sukri, K Shameli, E D Mohamed Isa, N A Ismail

Department of Environmental and Green Technology, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia

*Corresponding author: kamyarshameli@gmail.com

Abstract. Due to rapid industrialization, wastewater pollution has become a serious concern that needs to be addressed effectively. Untreated contaminants abundantly discharged into the water bodies have been proven to negatively impact the environment as well as human health. For a long time, zinc oxide (ZnO) has been used to treat these environmental pollutions in a process called semiconductor photocatalysis. In the field of material science, nanosized ZnO synthesized using green route has been used by many researchers as they are usually eco-friendly and cost effective. Even though ZnO nanostructures act as an excellent photocatalyst, there are still a few drawbacks that can limit their efficiency. To overcome these problems, ZnO modifications can be done to produce ZnO-based nanomaterials. In this mini review, we present up-to-date research progress on green synthesized ZnO-based nanomaterials and discusses on the methods used to modify ZnO nanostructures to improve photocatalytic efficiency.

1. Introduction

Over several decades, rapid industrialization and human greed have caused great harm to our mother nature. In order to satisfy high demands from customers, manufacturing plants from various industries have been disregarding the proper treatment of their waste materials before discharging them into our water bodies [1]. Numerous industries including textile, cosmetics, plastic, leather and paper factories regularly release toxic sludge containing harsh pollutants such as organic dyes, synthetic dyes, phenols and detergents into the wastewater [2, 3]. It is proven now that these untreated effluents cause many severe problems to the ecosystem as well as human health. These contaminants can cause skin diseases and might also be carcinogenic [4]. Due to their high solubility and complex structures, immense efforts and complex processes are required to break down the impurities in wastewater treatment plants before they become non-toxic compounds.

In 1972, researchers first proposed the use of semiconductor photocatalysis method as an alternative approach to control groundwater pollution issue [5]. This procedure makes use of light energy to help semiconductor materials degrade pollutants in water or air. Semiconductor materials such as zinc oxide (ZnO), titanium dioxide (TiO₂), iron oxide (Fe₂O₃) and magnesium oxide (MgO) have been studied for their potential in photocatalytic applications for water remediation. Out of all semiconductors, ZnO rises as a strong candidate due to its unique properties and excellent performance



as a photocatalyst. ZnO is a widely known n-type semiconductor with a large band gap of 3.37 eV and high excitation binding energy (60 meV) in room temperature [6]. Besides having high photosensitivity and photostability, ZnO nanostructures can be synthesized at a very low-cost and is considered non-toxic compared to other semiconductors. Therefore, it is extensively used in many other applications such as UV-light emitting diodes, optical gas sensors, solar cells and photodetectors [7].

ZnO nanostructures can be fabricated by chemical, physical or green approach. With increasing awareness on environmental issues, green synthesis has emerged as a desirable method as it aims to produce nanomaterials with none or minimum usage of hazardous chemicals. Instead, different biological sources from plants, fruits, microbes and biopolymers are utilized during green synthesis process. A wide range of techniques including hydrothermal process, microwave decomposition, precipitation and wet chemical method has been adopted to produce ZnO nanostructures of different morphologies [6]. Published works have reported successful ZnO nanostructures production of spherical [6], flower [8], thorn-like [9] and rods shapes [10].

As a semiconductor photocatalyst, ZnO nanostructures have shown brilliant performance in degrading different types of contaminants like synthetic dyes, organic pollutants and pharmaceutical waste. However, there are a few limitations of pure ZnO nanostructures that hold back its maximum potential as an efficient photocatalyst. To overcome these problems, physical, electronic and morphological modifications can be carried out to generate ZnO-based nanomaterials with enhanced photodegradation ability. This mini review will provide a concise insight on improvements of ZnO nanostructures and the current trend of green synthesized ZnO-based nanomaterials for photocatalytic studies.

2. ZnO nanostructures as a semiconductor photocatalyst

Photocatalysis falls under the category of advanced oxidation processes (AOPs) for the purpose of removing harmful pollutants in contaminated water or air through conversion of light energy to chemical energy by semiconductor materials [11]. Throughout the years, photocatalysis has consistently been gaining fame due to its green approach and effectiveness to purify contaminated water.

Among all semiconductors, ZnO has proven to be a robust candidate with many appealing qualities as an efficient photocatalyst. Compared to its competitive rival TiO₂, ZnO photocatalyst is said to have higher electron mobility and better quantum yield [12]. Photocatalytic reaction mechanism starts when electrons (e^-) in the Valence Band (VB) of ZnO semiconductor absorb photons after receiving appropriate energy from a light source. The photo-excited electrons will jump to the Conduction Band (CB) of ZnO, leaving a positively-charged hole (h^+) in the VB. The generated electron-hole pairs (e^-/h^+) will then react with oxygen and water to produce reactive oxygen species (ROS) including hydroxyl radicals and superoxide anions. These active and potent free radicals known to be powerful oxidation agents will later interact with pollutants, breaking down their chemical bonds resulting in complete mineralization [13].

Other than its strong oxidation properties, nano-sized ZnO also has a large surface area over volume ratio that can facilitate higher amounts of pollutant molecules to be adsorbed on the surface of its particles and later degraded into simpler forms. Additionally, reports have claimed ZnO nanostructures to be highly photostable under light irradiation [14]. A study done by M. Kamaraj et al. supports this statement as their synthesized ZnO nanostructures can withstand up to five cycles of photocatalytic experiments without any obvious decrease in its degradation efficiency of Bisphenol-A (BPA) [15]. Other strong points of ZnO nanostructures include its low-cost and non-toxic qualities, which makes it a desirable material to be scaled-up for commercial productions.

2.1. Limitation of ZnO photocatalysts

Even with several noteworthy merits of ZnO nanostructures, there are still a few drawbacks that hinder its performance as an efficient semiconductor photocatalyst. First of all, ZnO nanostructures are considered as UV-light driven semiconductors (UVLD) owing to its wide band gap that can only be activated under UV-radiation [16]. Therefore, its photocatalytic efficiency will be highly compromised when used under sunlight since UV light constitutes only about 10% of the total solar radiation. This low utilization of visible light will also greatly limits their usage in practical and industrial applications as UV light is considered toxic, thus there will be lack of freedom when designing the photocatalytic reactors [11]. Hence, researchers have been working on different ways to modify ZnO photocatalyst in order to extend their optical absorption towards the visible light region so we are able to fully harness the availability of earth-abundant solar light.

Besides that, a major disadvantage of ZnO photocatalyst is the rapid recombination of photoexcited e^-/h^+ pairs [17]. Recombination process happens when an electron falls back from CB into the positively charged hole (h^+) in VB and the e^-/h^+ pair disappears leading to a decrease in quantum efficiency and causing energy wastage [18]. Delaying or inhibiting the fast recombination of e^-/h^+ pairs can improve photocatalytic efficiency dramatically. Other problems with ZnO photocatalyst include difficulty in recovering the nanostructures at the end of a photocatalytic cycle and particle aggregation issue that deter their maximum degradation activity as amount of exposed active sites decreases [19]. To address these concerns, ZnO nanostructures can be fixed or attached to a matrix material for easy recovery while surface coating with organic materials might considerably reduce aggregation problems of pure ZnO.

2.2. Improving photocatalytic activity of ZnO nanostructures

Physico-chemical properties of ZnO are tunable and can be adjusted through physical, electronic and morphological modifications in order to improve photocatalytic activity. These alterations will directly affect various characteristics of ZnO photocatalyst such as crystallite size, band gap energy and defect concentration [20]. Generally, defects and oxygen vacancies in semiconductors are considered as important factors that play huge roles in their performance as photocatalysts. During photocatalysis process, defects and oxygen vacancies act as trapping centers to trap photoexcited electrons thus assisting the process of charge carriers separation to enhance photodegradation activity [21]. Nano-sized ZnO with higher crystallinity and larger surface area reportedly has more frequency of defects compared to its bulk counterpart, resulting in better photocatalytic activity. In this short review, we will focus on several modifications that have been reportedly adopted by green synthesized ZnO-based nanomaterials in recent years.

2.2.1. Doping or coupling with other materials (metal, non-metal, rare earth ions or semiconductor)

In an attempt to generate high performing visible light driven (VLD) photocatalyst, extensive studies have been carried out through doping or coupling of ZnO nanostructures with other materials like metal, non-metal, rare earth ions or other semiconductor materials. The main objective for doping of ZnO photocatalyst with these materials is to expand its visible light absorption spectrum by effectively reducing the band gap value of ZnO. Using a similar concept as surface defects, introduction of new atoms into the structure of ZnO photocatalyst will cause the formation of a new electron state in the band gap that can trap photogenerated charge carriers, resulting in retarded recombination process of e^-/h^+ pairs [5]. Subsequently, quantum efficiency will increase resulting in improved photocatalytic activity.

In the past decade, plasmonic photocatalysis has been gaining more attention as it excels in yielding high photocatalytic performance to degrade different types of contaminants under visible light [22]. In this method, noble metals such as silver (Ag), gold (Au) and copper (Cu) are doped on the ZnO nanostructures to accelerate the rate of production of e^-/h^+ pairs by excited electrons, when radiated with solar or visible light [22]. This is mainly due to the surface plasmon resonance (SPR) characteristics exhibited by these noble metals that have remarkable visible light absorption capability.

Previous literatures have also described doping of non-metal compounds such as carbon dots, silver halides (AgX) and rare earth ions onto ZnO nanostructures. A research by Khaled M. Omer et al. found that loading of phosphorous and nitrogen co-doped carbon quantum dots in the structure of ZnO photocatalyst can further boost its optical properties to be used under weak light LED lamp for degradation of organic pollutants [11]. Furthermore, another study using nitrogen-doped carbon dots claims its incorporation into ZnO nanostructure has successfully enhance solubility of the photocatalyst in aqueous medium [23]. Besides that, a study by Kanitta Phongarthit et al. has provided a comparative analysis on the enhancement of ZnO photocatalytic activity under visible light when coupled with AgX (X=Cl, Br, I) [15]. Alternatively, optimum doping of rare earth ions like europium (Eu^{3+}) and gadolinium (Gd^{3+}) can also facilitate red shift of ZnO nanostructures light absorption as well as help speed up the photodegradation process [24][20].

Another method that is widely used over the years is coupling of ZnO nanostructures with other semiconductors. Several semiconductors that have been successfully coupled with ZnO using green synthesis methods include cadmium oxide (CdO) [25], TiO_2 [26] and nickel ferrite (NiFeO_2) [27]. Intrinsic characteristics of these semiconductors such as their band gap value and magnetic properties can be exploited to create a better performing ZnO-based photocatalyst. Findings have shown that modified semiconductor-ZnO hybrid photocatalysts performed superiorly during photodegradation compared to pure ZnO nanostructures alone.

2.2.2. Surface coating.

Surface coating of metal oxide nanoparticles using biopolymers has continuously progressed to become an important area in polymer nanotechnology lately. Existing reports have described the utilization of chitosan [10], gelatin [28], copolymer [29] and glycine [30] to coat the surface of ZnO nanostructures for photocatalytic as well as biomedical applications. Biopolymers are often preferred as a coating agent as they are usually less toxic and biodegradable in the ecosystem. There are many benefits that can be gained by integrating ZnO photocatalyst with biopolymer.

Seyedeh Hoda Hekmatara et al. in his paper described the coating of their synthesized ZnO photocatalyst with poly citric acid-grafted poly ethylene glycol (PCA-PEG-PCA) copolymer [29]. They reported that coating agent plays a huge role in morphological changes of the synthesized ZnO photocatalyst. Their copolymer coated ZnO photocatalyst exhibited good water solubility, lower particles agglomeration as well as showed significant increment in crystalline quality and degradation efficiency of dyes [29]. Similar results were also recorded by Parita Basnet et al., which concluded that glycine can be used as a structure modifier and agglomeration controller of ZnO photocatalyst [30].

2.2.3. Attachment on matrix material.

Attachment of ZnO nanostructures onto a suitable matrix material has proven to be beneficial towards its photocatalytic performance. Prior works have effectively fix ZnO photocatalysts onto natural zeolite

called clinoptilolite [31] as well as montmorillonite (MMT) clay [22]. Both clinoptilolite and MMT possess excellent adsorption ability due to their high surface area, thus more pollutant compounds can be oxidized resulting in improved photocatalytic efficiency of ZnO photocatalyst. Moreover, impregnation of ZnO nanostructures into a suitable substrate can help increase its stability and reactivity.

Besides that, a common problem often faced by ZnO photocatalyst is the agglomeration of particles in suspension, especially when used in high concentrations [32]. Additionally, difficulty to separate ZnO powder and recover them in a reaction system at the end of a photocatalysis process is also an issue that needs to be addressed. By attaching the ZnO photocatalyst onto an appropriate material, these concerns can be tackled efficiently while indirectly enhancing their photodegradation activity.

3. Green Synthesis of ZnO-Based Nanomaterials

With the purpose of developing a safer approach towards nanomaterials production, researchers have been emphasizing the importance of green synthesis methods as opposed to other chemical and physical routes. Chemical and physical methods to synthesize nanomaterials usually always require rigorous experimental conditions, complicated steps, usage of high-tech equipments as well as hazardous chemicals [24]. On the other hand, green synthesis methods are often favored as it is facile, cost-effective, energy saving and utilizes sustainable resources. Therefore, the methods can be easily scaled up with minimum toxic by-products released into our ecosystem [33].

Over the last five years, a wide range of ZnO-based nanomaterials has been fabricated through green synthesis methods for photocatalytic studies. The ZnO-based nanomaterials were synthesized from a variety of sources such as plants, fruits, microorganisms, biopolymer, natural zeolite or pure compounds. Photocatalytic abilities of the nanomaterials to oxidize different target pollutants under UV, visible or solar light irradiation were also investigated and analysed. A list of data to summarize the research carried out was prepared and presented as shown in **Table 1**.

As compared to other green source, it can be observed that fruits or plants mediated synthesis is the most frequently adopted method to generate ZnO-based photocatalyst. Plants or fruits extract can act as reducing agents and stabilizer to replace the use of harmful chemicals during synthesis process [34]. This is due to the presence of a variety of phytochemical compounds in these extract. Other advantages of using plants or fruits mediated synthesis include its abundant availability and low-cost. Therefore, it is sustainable which makes it easier for mass scale production of nanomaterials. A couple of works have also reported the green synthesis of ZnO-based photocatalyst using microorganisms like *Escherichia coli* (*E. coli*) bacteria and algae. When induced with environmental stress, these microorganisms will release enzyme, protein and other bio-active molecules as a response to protect themselves [35]. These stress-induced compounds will later interact with metal ions and consequently reducing them to produce nanomaterials. Other ZnO-based photocatalysts were reported to have been successfully synthesized using biopolymer, zeolite and pure compounds such as bioflavonoid rutin, ascorbic acid, and glycine. Biopolymers and zeolite typically act as capping agents or matrix materials for improving structures of ZnO-based photocatalyst. Meanwhile, pure compounds usually play a role as reducing agents for facilitating the growth of nuclei to form nanomaterials.

Table 1. Green synthesized ZnO-based nanomaterials from various sources for degradation of different pollutants.

S. No	ZnO-based nanomaterials	Synthesis medium	Size (nm)	Target pollutant	Ref.
Plants or fruits:					
1.	Ag/ZnO	Co-reduction method using aqueous extract of oak fruit hull (Jaft)	19.2	Basic violet 3 dye under visible light	[36]
2.	AgZnO	Phytosynthetic route using <i>Psidium guajava</i> leaf extract	27-117	Methylene blue (MB) under sunlight irradiation	[37]
3.	ZnO/Ag core shell	Solution combustion method using <i>Calotropis gigantean</i> leaves extract	100-150	MB dye under UV light	[38]
4.	Ag/ZnO-MMT	Simple green method using <i>Urtica dioica</i> leaf extract	Ag: 2-4 ZnO: 15-20	MB dye under visible light	[22]
5.	Eu-doped ZnO	Phytomediated combustion route using <i>Aloe vera</i> gel as fuel	25-45	Rhodamine B dye under natural sunlight	[20]
6.	Gd loaded ZnO	Simple single step synthesis using <i>Caralluma fimbriata</i> extract	29-32	Indigo Carmine (IC) under UV and sunlight irradiation	[24]
7.	ZnO@ZnHCF	Facile green route using <i>Azadirachta indica</i> plant leaves extract	~100	Bisphenol-A (BPA) under sunlight	[39]
8.	ZnO-CDs	CDs prepared from powder coffee using low temperature hydrothermal route	CDs: 3-4 ZnO: 15-20	MB dye under irradiation with weak LED white light	[11]
9.	ZnO/TiO ₂	Solid state reaction route and modified sol-gel method using leaf extract of <i>Ocimum basilicum L.</i>	50	Textile dye Blue RGB under sunlight and UV irradiation	[26]
10.	ZnO@N-C hybrid	Simple hydrothermal method using peach fruit juice	25	MB degradation under UV light	[23]
Microbes or algae:					
11.	Ag/ZnO	Simple enzymatic method in the presence of <i>E. coli</i> nitrate reductase enzyme	1040	Reactive Black B under visible light	[40]
12.	CdO-ZnO	Simple chemical precipitation method using seaweed (macro algae)	20-50	Reactive Blue 198 dye and phenol pollutants under sunlight irradiation	[25]
Others (biopolymer, zeolite, pure compounds)					

13.	NiFe ₂ O ₄ @ZnO	Sol-gel method using tragacanth gel	35-45	Direct Blue 129 and Reactive Blue 21 dyes	[27]
14.	Ag-ZnO	Solution combustion method using <i>Azadirachta indica</i> gum	15	MB degradation under UV light	[41]
15.	PCA-PEG-PCA-capped ZnO	Facile method using water-soluble, biocompatible copolymer	25-50	Methyl Orange (MO) and MB dye removal with UV radiation	[29]
16.	ZnO-nanoclinoptilolite	Overnight stirring of clinoptilolite powder with zinc precursor followed by calcination process	45-50	MB dye under visible light irradiation	[31]
17.	CS-ZnO	Green chemistry approach using bioflavonoid rutin	20-150	MB and Congo Red (CR) Dye under sunlight	[10]
18.	Ag/ZnO/3D graphene	Graphene hydrogel prepared using ascorbic acid (vitamin C) as the reducing agent	ZnO: ~400 Ag: 30-80	MB dye solution under UV and visible light	[42]
19.	Gly@ZnO	Use of amino acid glycine as capping agent	10-30	Rhodamine B (RhB) dye under solar light	[30]

3.1. Photocatalytic performance of green ZnO-based nanomaterials

Large majority of green synthesized ZnO-based nanomaterials listed in this mini review exhibit outstanding photocatalytic performance against different target contaminants under certain light radiation. M. Chandrasekhar et al. found that doping ZnO nanostructures with optimum Eu dopant concentration produced excellent photocatalyst that have 94% degradation efficiency on RhB dye under sunlight irradiation [20]. Similar results can also be observed in a study by Preeti Mishra et al. that reported IC dye decolorization were found to be more effective under sunlight irradiation (98%) compared to UV light (90%) for Gd loaded ZnO nanomaterials [24]. Furthermore, research paper by Khalid M. Omer et al. showed dramatic photocatalytic enhancement of ZnO-CDs against MB as 80% of the dye was degraded under irradiation with a weak LED white light compared to 10% for ZnO under the same circumstances [11]. These findings show effective improvement of ZnO nanostructures to successfully extend its optical absorption capability towards visible light region for better utilization of the solar light.

Manviri Rani and Uma Shanker in their published literature about ZnO and zinc hexacyanoferrate (ZnHCF) claims that the ZnO@ZnHCF nanocomposite showed improvement in surface area and decrease in band gap value [39]. They explained the reason is due to the synergism of ZnO nanostructures and intercalative feature of ZnHCF. During photocatalytic studies, they found that ZnO@ZnHCF nanocomposite has much higher adsorption ability and faster degradation activity of BPA compared to bared ZnHCF [39]. They also investigated the reusability properties of the nanocomposites and found that it can be used up to ten cycles [39].

4. Conclusion

ZnO nanostructures have generally been accepted as one of the best photocatalyst to exist until now. Though it possesses many good qualities to be used as a semiconductor photocatalyst, there are still

several flaws that hinder its true potential in photocatalysis process. Modifications of ZnO nanostructures using green synthesis methods can be done to produce ZnO-based nanomaterials with improved physical, electrical and morphological properties. Based on the current trends, it seems that green synthesized ZnO-based nanomaterials have tremendous potential to rise as a superior photocatalyst in treating contaminated water. Nevertheless, more in-depth research is still required to understand and develop high performing ZnO-based photocatalyst using sustainable green sources in an effort to solve water pollution concerns. At the same time, there is also a need to test photodegradation of ZnO-based photocatalyst on a wider range of pollutants other than dyes.

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