In: Environmental Degradation: Causes and Remediation Strategies
DOI: 10.26832/aesa-2020-edcrs-09

CHAPTER [9]

ZnO nanostructures and nanocomposites as promising photocatalysts for the remediation of wastewater pollution

Satinder Pal Kaur Malhotra

ICFAI Tech School, ICFAI University Dehradun,
Rajawala Road, Selaqui, 248197, Uttarakhand, India

ABSTRACT

Recently, hierarchical 3D nanostructures have attracted attention due to their multiple advantages, such as large surface area, porous structures, as well as enhanced light harvesting ability. Zinc oxide is a promising photocatalyst alternative to TiO_2 used for environmental remediation of wastewater pollutants due to its high photosensitivity, non-toxic nature, low cost, and environmental friendliness. ZnO can be crystallized in three forms under different conditions i.e., wurtzite, zinc-blende, and rock-salt structures. ZnO exhibits a higher quantum efficiency and has a similar bandgap as TiO_2 as it has a larger number of inherent active defect sites on the surface, which makes it capable of absorbing a larger fraction of the solar spectrum. Various approaches have been used to efficiently utilize the solar radiation and to enhance the efficiency of zinc oxide photocatalyst. These techniques enhance the photocatalytic performance ZnO under visible light by shifting the bandgap energy, suppressing the recombination rate of electron-hole pairs, increasing charge separation efficiency. In future there is a need of developing green, scalable, low-cost and highly efficient hierarchically ZnO nanostructures and nanocomposites photocatayst for remediation of wastewater pollution. In this chapter the emphasis has been on the advantages, fabrication methods, and photocatalytic applications of hierarchical ZnO nanostructures for the degradation of organic contaminants present in wastewater.

KEYWORDS Fabrication, Hierarchical nanostructure, Photocatalysis, Zinc oxide

Satinder Pal Kaur Malhotra, Email: malhotrasatinder@gmail.com

Introduction

Over the past few decades, industrial effluents discharged into rivers and oceans have been the major sources of water pollution. Conventional methods used to treat organic effluents such as physical, biological or chemical are ineffective as they are non-destructive, since they just transfer organic compound from water to another phase, thus causing secondary pollution and requiring further treatment (Janotti and Van de Walle, 2009; Malhotra *et al*., 2019; Kumar *et al*., 2019). Heterogeneous photocatalysis is a promising technique to control environmental pollution harnessing cheap solar energy whereby toxic organic compounds can be effectively degraded into completely into green by-products i.e., H_2O, CO_2, and mineral acids without bringing secondary pollution, through a process called photocatalysis using semiconducting nanostructures. In recent years, various semiconductors with hierarchical nanostructures have been fabricated to achieve efficient photocatalysts owing to their multiple advantages, such as high surface area, porous structures, as well as enhanced light harvesting. (Li *et al*., 2016). Zinc oxide is a promising photocatalyst alternative to TiO_2 used for environmental remediation of wastewater pollutants due to its high photosensitivity, non-toxic nature, low cost, and environmental friendliness (Chen *et al*., 1998; Reynolds *et al*., 1999).

ZnO as a photocatalyst

In the field of photocatalysis, titanium dioxide (TiO_2) is undoubtedly the material most extensively studied (Huang *et al*., 2008; Mahendra *et al*., 2008). Due to the high price and rareness in existence of TiO_2 its large-scale application in industrial wastewater treatment operations is very non-economic (Daneshvar *et al*., 2004). Zinc oxide is a promising photocatalyst used for environmental remediation of wastewater pollutants than TiO_2 due to its high photosensitivity, non-toxic nature, low cost, and environmental friendliness. ZnO exhibits a higher quantum efficiency and has a similar bandgap as TiO_2 as it has a larger number of inherent active defect sites on the surface, which makes it capable of absorbing a larger fraction of the solar spectrum (Qiu *et al*., 2008; Chen *et al*., 2009; Yogendra *et al*., 2011).

Crystal structure of ZnO

ZnO can be crystallized in three forms under different conditions i.e., wurtzite, zinc-blende, and rock-salt structures (Ozgur *et al*., 2005; Moezzi *et al*., 2012). ZnO hexagonal wurtzite is thermo-dynamically the most stable at ambient conditions and hence most common among the three structures. Cubic zincblende, however, can be stabilized by growing ZnO on cubic substrates.

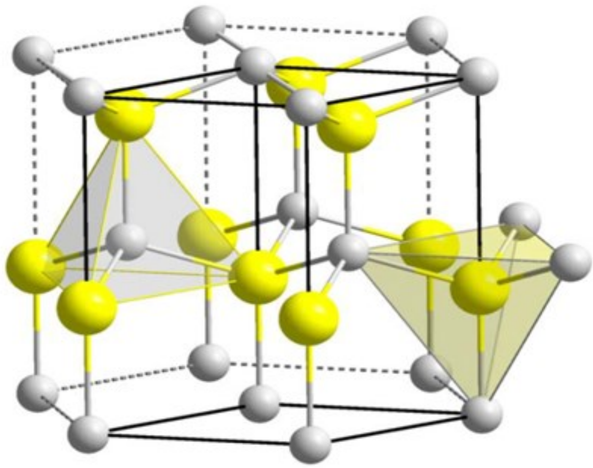

Figure 1. Wurtzite of ZnO.

ZnO will exist in the rock salt structure only at relatively high pressures (Ozgur *et al*., 2005). The hexagonal wurtzite structure possesses lattice spacing a = 0.325 nm and c = 0.521 nm, the ratio c/a * 1.6 that is very close to the ideal value for hexagonal cell c/a = 1.633. Each tetrahedral Zn atom is surrounded by four oxygen atoms and vice versa (George *et al*., 2009). ZnO is generally an intrinsically n-type semiconductor with the presence of intrinsic defects such as oxygen vacancies (V_O), zinc interstitials (Z_{ni}), and zinc vacancies (V_{Zn}), which will affect its optical properties and electrical behavior (Boukos *et al*., 2012). It has been noted that a greater V_O can provide more electron charge carriers (Figure 1).

Classification of ZnO nanostructures

In the past decade, many different strategies have been employed to synthesize ZnO nano-materials rich in morphologies due to the availability of cheap and versatile routes of fabrication of zinc oxide nanostructures. From the point of dimensionality, zero-dimensional (0D) ZnO includes quantum dots, one-dimensional (1D) which includes nanorods, nanofibers, nanowires, nanotubes, and nanoneedles, while two-dimensional (2D) and three-dimensional (3D) nano-materials include nanosheets and nanoflowers, respectively. Processes leading to three dimensional (3D) hierarchical ordered structures are still not perfectly understood and therefore attract attention from the research community. As the photocatalytic activity of semiconductors generally depends on crystal size, surface area, morphology and native defects, the abundancy in morphologies makes ZnO representative material in the research field of photocatalysis.

Synthesis of 3D ZnO hierarchical nanostructures

Different synthesis methods have been used to obtain 3D ZnO hierarchical nanostructures which include physical, chemical and biological methods (Banerjee *et al*., 2012). Among the various methods used to synthesize ZnO nanostructures, solution phase synthesis is widely used for the synthesis of 3D ZnO hierarchical nanostructures as it is the simple and less energy consuming. Through this synthesis route, the morphology of the nanostructures can be easily controlled by manipulating the experimental factors such as type of solvents, starting materials and reaction conditions (Banerjee *et al*., 2012). Solution-based methods used to synthesize ZnO nanostructures include hydrothermal, sol-gel, precipitation, microemulsion, solvothermal, electrochemical deposition process, microwave, polyol, wet chemical method, flux methods and electrospinning. Solution phase synthesis has attracted increasing interest for the synthesis of 3D ZnO hierarchical nanostructures due to their advantages, such as low cost, low temperature (<200°C) required for synthesis, scalability, and ease of handling.

Advantages of hierarchical ZnO nanostructures and nanocomposites

High surface area and porous structures

The photocatalytic activity of semiconductor is affected by its specific surface area (Yuan *et al*., 2003; Wang *et al*., 2005; Zhang *et al*., 2007). Hierarchical nanostructures with a high surface area (Yu *et al*., 2009; Cai *et al*., 2010; Cheng *et al*., 2011) showed better photocatalytic properties than low dimensional ZnO nanostructures, such as nanoparticles, nanorods, nanosheets, nano-tetrapods, etc. (Guo *et al*., 2011). High surface areas offered by hierarchical ZnO nanostructures make them a popular choice in solar photocatalysis, as more pollutant could be easily adsorbed and a higher rate of degradation can be achieved, enhancing the photocatalytic activity (Mukhopadhyay *et al*., 2015).

Enhanced Light scattering of photocatalyst

Hierarchical porous and hollow nanostructures increase the light-harvesting ability of photo-catalysts. The interconnected pores in their structures increase the number of light traveling paths and thereby facilitate their light-harvesting ability (Wang *et al*., 2005). The mesoporosity structures not only act as distribution channels increasing absorption of visible light but also create an ideal environment for mass transportation of electrons. Due to these facts 2D ZnO nanoflowers and porous 3D hierarchical ZnO nanostructures possess better light scattering properties when compared to ID nanorods. Sinha *et al.* (2010) showed hierarchical ZnO hollow spheroids exhibited enhanced photocatalytic in dye degradation due to efficient utilization of light through the multiple reflections of light in their hollow structures.

Synergistic nano-building blocks and multi-components

Hierarchical nanostructures are composed of 3D self-assembly of primary structure e.g., nano-particle, nanorod, nanotube or nanosheets in nanoscale. 3D hierarchical structures inherit the excellent properties of the single nano-sized building blocks and also possess superior photo-catalytic performance due to charge transfer and separation among the well-organized nanoscale building blocks (Han *et al*., 2015; Ko *et al*., 2011).

Problems associated with photocatalytic applications of ZnO

First, the recombination of photogenerated electron-holes pairs which deteriorates the charge transport leading to low reaction efficiency at the ZnO photocatalyst surface. Another problem associated with ZnO photocatalyst is its limited light harvesting efficiency. ZnO has a large bandgap (3.37 eV) which restricts its light absorption only in ultraviolet region and thus, limits the practical applications of ZnO photocatalysts for solar light harvesting. Therefore, intense efforts have been made to improve the photocatalytic activity of ZnO under solar illumination by minimizing the bandgap energy and inhibiting the recombination of photogenerated electron-hole pairs.

Fabrication of hierarchical ZnO nanostructures and nanocomposites

The development of visible-light active zinc oxide photocatalyst is one of the key challenges in the field of semiconductor photocatalysis. Various techniques have been used to improve the -photocatalytic efficiency of ZnO such as coupling of ZnO with either wide band or narrow band semiconductors, surface modification of ZnO with noble metals, metals/non-metal doping of ZnO, etc., which are discussed below:

Coupling ZnO with other semiconductors

Coupling ZnO-based composites with either wide band or narrow band semiconductors serve as an attractive alternative for enhancing the photoactivity. Chiang and Lin (2012) have shown that the increased charge separation was due to an extended lifetime of charge carriers by inter-particle electron transfer between the conduction bands of nanocomposites leading to a larger number of electrons involved in a photo-degradation reaction. Nur *et al*. (2007), showed that highly active photocatalysts can be obtained by coupling two semiconductors having different band gaps. Coupling of different semiconductor oxides can reduce the band gap,

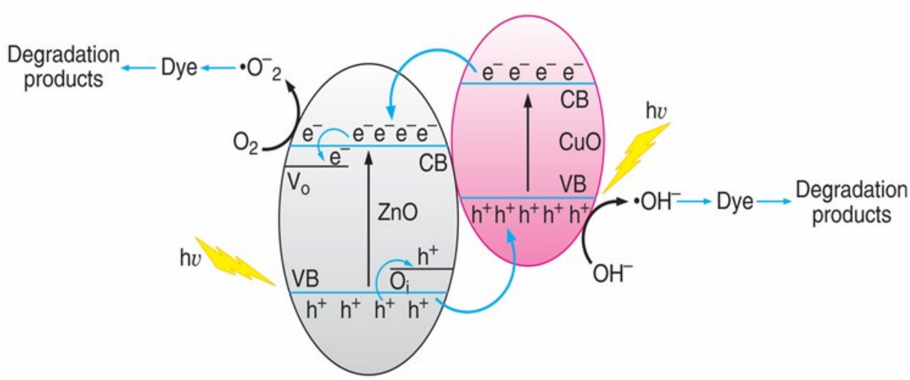

Figure 2. Schematic diagram of the ZnO-CuO nanocomposite showing the charge transfer process.

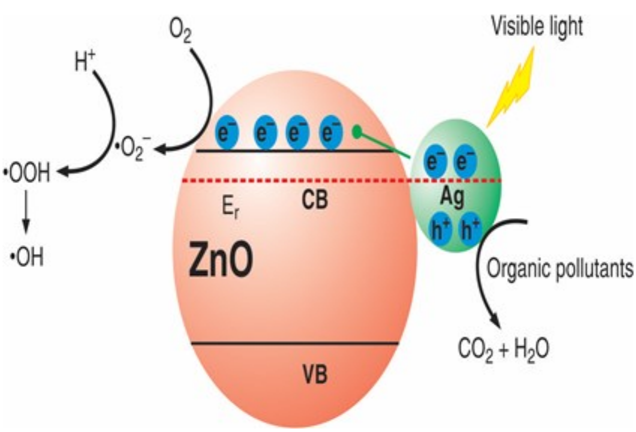

Figure 3. Schematic diagram of the Ag-ZnO nanocomposite showing charge transfer process

extending the absorbance range to visible region leading to electron–hole pair separation under irradiation due to photoinduced electrons that are transferred away from the photocatalyst. When ZnO-CuO nanocomposite is irradiated by photons, electrons flow to the conduction band of ZnO while the holes flow to the valence band of CuO and efficient charge separation is maintained (Li *et al.*, 2010). For example, Xiao *et al*. (2014) prepared branched hierarchical ZnO nanorod-TiO_2 nanotube array heterostructures via a two-step assembly method. Various combinations of wide band semiconductors, such as a TiO_2 nanobelt/ZnO nanorod hierarchical nanostructure (Pan *et al.*, 2013), branched hierarchical TiO_2/ZnO hierarchical nanostructures (Athauda *et al.*, 2012), ZnO-SnO_2 hollow spheres (Wang *et al.*, 2007) were developed, which showed an enhanced photocatalytic property (Figure 2).

Noble metal loading

Plasmonic photocatalyst is usually prepared by incorporating noble metal nanoparticles such as Au, Ag, Pt, etc., onto the ZnO semiconductor to improve its photocatalytic performance under both UV and visible light illuminations. Fermi levels of these noble metals are lower than that of ZnO, which results in the effective transfer of the photogenerated electrons from the conduction band of ZnO to metal particles, which serves as a passive sink for electrons and therefore it hinders the recombination of electron-hole pairs. The enhanced photoactivity of plasmonic photocatalysis is due to Schottky contact and localized surface plasmon resonance (LSPR) (Zhang *et al*., 2013). The Schottky contact formed at the interface between noble metal and the semiconductor enhances the migration of photogenerated electrons and holes in opposite directions. The electron-hole recombination is reduced and the charge transfer would be facilitated by the noble metal anchored at the surface. LSPR improves the photocatalytic activity by extending light absorption of semiconductor to longer wavelengths, increasing the scattering of visible-light. Since LSPR takes place at the surface of the anchored noble metal and the size of the noble metal nanoparticles is very small, it enables the fast electrons or holes transfer to the surface. Ahmad *et al*. (2011) synthesized hierarchical flower-like ZnO-Au nanostructures via an electrochemical method. Nanoplate-built ZnO hollow microspheres decorated with Au nanoparticles were produced by Xia *et al*. (2015) through solvothermal route. The enhanced photocatalytic activity of Ag-ZnO indicates that the Ag NPs anchored at the surface of p-ZnO behave like an electron sink, which could increase the separation of the photogenerated electron-hole pairs and inhibit their recombination (Figure 3).

Non-metal doping

Recent studies (Figure 4) have demonstrated that non-metal dopants such as nitrogen, carbon, sulfur and fluorine can shift the bandgap of ZnO upwards and narrow the bandgap energy to the ultraviolet-visible region and thus, enhance solar energy utilization of ZnO photocatalyst (Liu *et al*., 2011). Due to their smaller band gaps, ZnO hierarchical photocatalysts doped N and C have been found to exhibit better absorption of light in both visible and ultraviolet regions (Yu *et al.*, 2016). Liu *et al*. (2011) reported better photocatalytic decomposition of the RhB dye by hierarchical flower-like C-doped ZnO superstructures in aqueous solutions than ZnO due to their enhanced solar light absorption.

Coupling of nanocarbon component to ZnO

ZnO hierarchical structures have been synthesized (Figure 5) by combining it with reduced graphene oxide (r-GO) and carbon nanotube (CNT) due to their good conductivity and large surface area. The heterojunction of ZnO with carbon nanotubes (CNTs) can enhance the performance of nano-composites by acting as electron scavenging agents (Fan *et al*., 2012) while

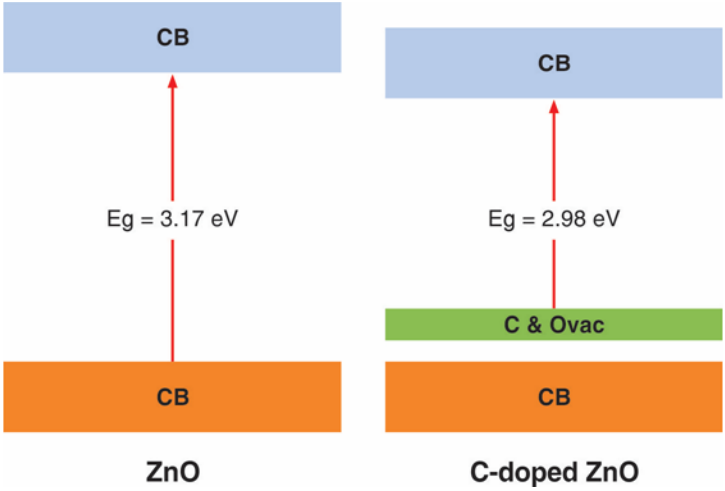

Figure 4. Schematic band structures of ZnO and C-doped ZnO crystals. (Adapted from Ahmad et al., 2015).

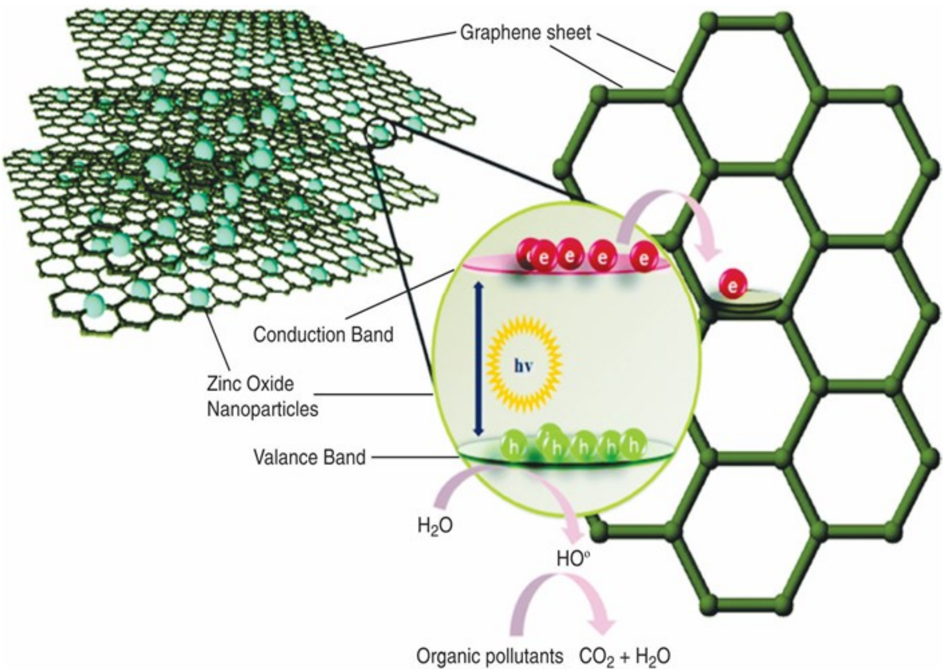

Figure 5. Mechanism of electron transfer from conduction band of zinc oxide to graphene sheets

heterostructure of ZnO/GO has greater carrier transport efficiency due to the graphene encapsulation, specific surface area and electrical transport properties (Li *et al*., 2012) Luo *et al*. (2012) preapred rGO-hierarchical ZnO hollow sphere composites via ultrasonic method to enhance the photocurrent and photocatalytic activity due to the conjunction between rGO and ZnO could be attributed to electronic interaction between the components. Zhang *et al*. (2006) prepared a ZnO-CNT heterostructure via hydrothermal method in which ZnO nanowires were grown on carbon nanotube (CNT) arrays serve as the nucleation sites for the growth of the ZnO nanowires.

Metal doping

Recently, metals like transition metals, rare earth metals and other metals have shown advantages in tuning the morphology of ZnO in photocatalytic applications. Metal doping of ZnO can improve the photoactivity of catalyst by increasing the trapping site of the photo-induced charge carriers and thus decreasing the recombination rate of photoinduced electron-hole pairs (Rezaei *et al*., 2013). In order to decrease the bandgap energy of photocatalysts, metal dopants such as Ce, Nd, Cu and Al have been used in in dye degradation.

Photocatalytic degradation of organic contaminants

When the ZnO semiconductor is excited by solar light greater than its bandgap energy, an electron is excited from the filled valence band (VB) to an empty conduction band (CB), creating an electron-hole pair (e^-/h^+). The electron-hole pairs move to the ZnO photocatalyst surface and take part in redox reactions (Figure 6). The H^+ reacts with water and OH^- ions to produce hydroxyl radicals while e^- reacts with oxygen to produce superoxide radical anions then hydrogen peroxide which further reacts with superoxide radicals to form hydroxyl radicals. The resulting hydroxyl radicals, which are powerful oxidizing agents, attack the pollutants adsorbed on the surface of ZnO to rapidly produce intermediate compounds that get mineralized to green products such as CO_2, H_2O and mineral acids.

The photoexcitation of ZnO semiconductor by UV light irradiation, followed by the formation of electron-hole pairs can be expressed below (Rauf *et al*., 2009; Rajamanickam *et al*., 2016):

$$ZnO + hv \rightarrow ZnO\ (e^-_{(CB)}) + (h^+_{(VB)})$$

The photogenerated holes are involved in oxidation reaction and electrons are involved in reduction reaction, as illustrated by the following reactions:

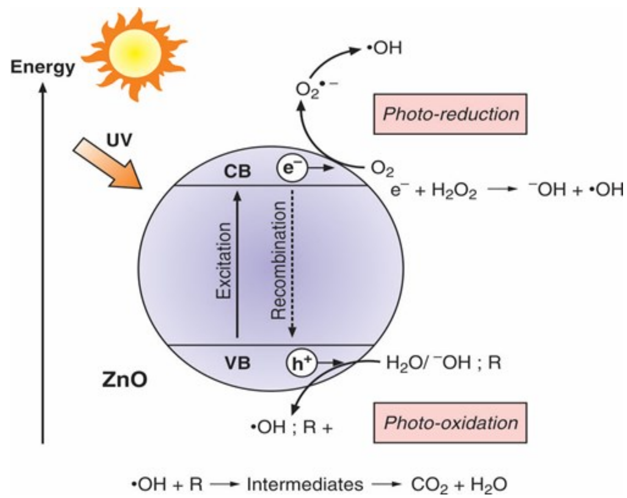

Figure 6. A schematic diagram illustrating the principle of photocatalysis

Photooxidation reactions:

$$ZnO(h^+_{(VB)}) + H_2O \rightarrow ZnO + H^+ + OH•$$

$$ZnO(h^+_{(VB)}) + OH^- \rightarrow ZnO + OH•$$

Photoreduction reactions:

$$ZnO(e^-_{(CB)}) + O_2 \rightarrow ZnO + O_2•^-$$

$$O_2•^- + H^+ \rightarrow HO_2•$$

$$HO_2• + HO_2• \rightarrow H_2O_2 + O_2$$

$$ZnO(e^-_{(CB)}) + H_2O_2 \rightarrow OH• + OH^-$$

$$H_2O_2 + O_2•^- \rightarrow OH• + OH^- + O_2$$

$$H_2O_2 + hv \rightarrow 2OH•$$

$$\text{Organic pollutants} + OH• \rightarrow \text{Intermediates}$$

$$\text{Intermediates} \rightarrow CO_2 + H_2O$$

During the photocatalytic process, free electrons/holes, and reactive oxidizing species (ROS) such as $HO_2^•$, $HO^•$ and $O_2^{•-}$ react with the surface adsorbed impurities including inorganic, organic compounds, and biological species (bacteria, virus *etc.*) leading to their decomposition. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle or at the surface within nanoseconds after the generation of electrons and holes by photon illumination and the energy is usually dissipated as heat. The electrons on the surface semiconductors can react with oxygen to form superoxide anion and prevents the recombination of electron-hole pairs.

Conclusions

ZnO nanostructures have been shown to be a promising photocatalyst for visible light photodegradation process of organic pollutants due to its low production cost, non-toxic and ability to absorb larger fraction of solar spectrum. Hierarchical ZnO nanostructures have been fabricated to achieve efficient photocatalysts due to their multiple advantages, such as large surface area, porous structures, as well as enhanced light harvesting ability. Various methods that have been attempted to enhance photoresponse of ZnO nanostructures such as coupling of two semiconductors, surface modification of ZnO with noble metals, and doping with metals/ non-metals. These techniques enhance the photocatalytic performance ZnO under visible light by shifting the bandgap energy, suppressing the recombination rate of electron-hole pairs, increasing charge separation efficiency. In future there is a need of developing green, scalable, low-cost and highly efficient hierarchically ZnO nanostructures and nanocomposites photocatalyst for remediation of wastewater pollution.

References

Ahmad, M., Shi, Y., Nisar, A., Sun, H., Shen, W., Wei, M. and Zhu, J. (2011). Synthesis of hierarchical flower-like ZnO nanostructures and their functionalization by Au nanoparticles for improved photocatalytic and high-performance Li-ion battery anodes. *Journal of Materials Chemistry*, 21: 7723.

Alshammari, A.S. Chi, L., Chen, X. Bagabas, A., Kramer, D., Alromaeha A. and Jiang, Z. (2015). Visible-light photocatalysis on C-doped ZnO derived from polymer-assisted pyrolysis. *RSC Advances,* 5: 27690.

Athauda, T.J., Neff, J.G., Sutherlin, L., Butt, U. and Ozer, R.R. (2012). Systematic Study of the Structure–Property. *Mater.* Relationships of Branched Hierarchical TiO_2/ZnO Nanostructures. *ACS Appl Interfaces,* 4: 6917-6926.

Banerjee, P., Chakrabarti, S., Maitra, S. and Dutta B.K. (2012). Zinc oxide nano-particles – sonochemical synthesis, characterization and application for photo-remediation of heavy metal. *Ultrasonics Sonochemistry,* 19: 85-93.

Boukos, N., Chandrinou C. and Travlos, A. (2012). Zinc vacancies and interstitials in ZnO nanorods. *Thin Solid Films*, 520: 4654 -7.

Cai, W., Yu, J. and Jaroniec, M. (2010). Template-free synthesis of hierarchical spindle-like -Al2O3 materials and their adsorption affinity towards organic and inorganic pollutants in water. *Journal of Materials Chemistry,* 20: 4587.

Chen, J., Li, C., Song, J.L., Sun, X.W., Lei, W. and Deng, W.Q. (2009). Bilayer ZnO nanostructure fabricated by chemical bath and its application in quantum dot sensitized solar cell. *Applied Surface Science*, 255: 7508-7511.

Chen, Y., Bagnall, D.M., Koh, H., Park, K., Hiraga, K., Zhu, Z. and Yao, T. (1998). Plasma assisted molecular beam epitaxy of ZnO on c-plane sapphire: Growth and characterization. *Journal of Applied Physics,* 84: 3912.

Cheng, B., Le, Y., Cai, W. and Yu, J. (2011). Synthesis of hierarchical Ni(OH)2 and NiO nanosheets and their adsorption kinetics and isotherms to Congo red in water. *Journal of Hazardous Materials,* 185: 889-897.

Chiang, Y.J. and Lin, C.C. (2012). Preparation of coupled ZnO/SnO_2 photocatalysts using a rotating packed bed. *Chemical Engineering Journal,* 181: 196-205.

Daneshvar, N., Salari, D. and Khataee, A. (2004). Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. *Journal of Photochemistry and Photobiology A: Chemistry*, 162: 317-322.

Fan, H., Zhao, X., Yang, J, Shan, X., Yang, L. and Zhang, Y. (2012). ZnO–graphene composite for photocatalytic degradation of methylene blue dye. *Catalysis Communications,* 29.

George, S., Pokhrel, S., Xia, T., Gilbert, B., Ji, Z., Schowalter, M., Rosenauer, A., Damoiseaux, R., Bradley, K.A. and Ma¨dler, L. (2009). Use of a rapid cytotoxicity screening approach to engineer a safer zinc oxide nanoparticle through iron doping. *ACS Nano*, 4(1): 15-29.

Guo, M.Y., Ng, A.M.C., Liu, F., Djuriši´c, A.B., Chan, W.K. and Su, H. (2011). Effect of Native Defects on Photocatalytic Properties of ZnO. *The Journal of Physical Chemistry A,* 115: 11095-11101.

Han, C., Chen, Z., Zhang, N., Colmenares, J.C. and Xu, Y. (2015). Hierarchically CdS Decorated 1D ZnO Nanorods-2D Graphene Hybrids: Low Temperature Synthesis and Enhanced Photocatalytic Performance. *Advanced Functional Materials***,** 25: 221-229.

Huang, X., Leal, M. and Li, Q. (2008). Degradation of natural organic matter by TiO_2 photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Research*, 42: 1142-1150.

Janotti, A. and Van de Walle, C.G. **(**2009). Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics,* 72: 126501.

Ko, S.H. Lee, D., Kang, H. Nam, K. Yeo, J., Hong, S., Grigoropoulos, C.P. and Sung, H. (2011). Nanoforest of Hydrothermally Grown Hierarchical ZnO Nanowires for a High Efficiency Dye-Sensitized Solar Cell. *Nano Letters,* 11: 666-671.

Kumar, V., Kumar, R., Singh, J. and Kumar, P. (2019). Contaminants in Agriculture and Environment: Health Risks and Remediation, Volume 1, Agro Environ Media, Haridwar, India, pp. 1-283, https://doi.org/10.26832/AESA-2019-CAE

Li, B. and Wang, Y. (2010). Facile synthesis and photocatalytic activity of ZnO–CuO nanocomposite. *Superlattices and Microstructures*, 47: 615-623.

Li, B., Liu, T., Wang, Y. and Wang, Z. (2012). ZnO/graphene-oxide nanocomposite with remarkably enhanced visible-light-driven photocatalytic performance. *Journal of Colloid and Interface Science,* 377: 114-21.

Li, X., Yu, J. and Jaroniec, M. (2016), Hierarchical photocatalysts. *Chemical Society Reviews,* 45: 2603-2636.

Liu, S., Li, C. and Yu, J., (2011). Improved visible-light photocatalytic activity of porous carbon self-doped ZnO nanosheet-assembled flowers. *CrystEngComm,* 13: 2533-2541.

Liu, Y., Hu, Y., Zhou, M., Qian, H. and Hu, X. (2012). Microwave-assisted non-aqueous route to deposit well-dispersed ZnO nanocrystals on reduced graphene oxide sheets with improved photoactivity for the decolorization of dyes under visible light. *Applied Catalysis B: Environmental*, 125: 425-31.

Luo, Q., Yu, X., Lei, B., Chen, H., Kuang, D. and Su, C. (2012). Reduced Graphene Oxide-Hierarchical ZnO Hollow Sphere Composites with Enhanced Photocurrent and Photocatalytic Activity. *The Journal of Physical Chemistry C,* 116: 8111-8117.

Mahendra, Q., Li, S., Lyon, D.Y., Brunet, L., Liga, M.V., Li, D. and Alvarez, P.J. (2008). Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. *Water Research*, 42: 4591-4602.

Malhotra, S.P.K. and Kumar T. (2017). Enhanced photocatalytic activity of Ag nanostructures. *Journal of Mountain Research,* 12: 67-72.

Malhotra, S.P.K. and Mandal, T.K. (2019). Zinc Zinc oxide nanostructure and its application as agricultural and industrial material. In: Kumar, V., Kumar, R., Singh, J. and Kumar, P. (eds) Contaminants in Agriculture and Environment: Health Risks and Remediation, Volume 1, Agro Environ Media, Haridwar, India, pp. 216-226, https://doi.org/10.26832/AESA-2019-CAE-0171-016

Moezzi, A., McDonagh, A.M. and Cortie, M.B. (2012). Zinc oxide particles: synthesis, properties and applications. *Chemical Engineering Journal,* 185: 1-22.

Mukhopadhyay, S., Das, P.P., Maity, S., Ghosh, P. and Devi, P.S. (2015). Solution grown ZnO rods: Synthesis, characterization and defect mediated photocatalytic activity. *Applied Catalysis B: Environmental*, 165: 128-138.

Nur, H., Misnon, I.I., Wei and L.K. (2007). Stannic oxide-titanium dioxide coupled semiconductor photocatalyst loaded with polyaniline for enhanced photocatalytic oxidation of 1- octene. *International Journal of Photoenergy*, 1-6.

Ozgur, U., Alivov, Y.I., Liu, C., Teke, A., Reshchikov, M., Dogan, S., Avrutin, V., Cho, H. and Morkoc, S.J. (2005). A comprehensive review of ZnO materials and devices. *Journal of Applied Physics,* 98(4): 041301.

Pan, K., Dong, Y., Zhou, W., Pan, Q., Xie, Y., Tian, G. and Wang, G. (2013). Facile Fabrication of Hierarchical TiO_2 Nanobelt/ZnO Nanorod Heterogeneous Nanostructure: An Efficient Photoanode for Water Splitting. *ACS Applied Materials & Interfaces,* 5: 8314-8320.

Qiu, R., Zhang, D., Mo, Y., Song, L., Brewer, E. and Huang, X., (2008). Photocatalytic activity of polymer-modified ZnO under visible light irradiation. *Journal of Hazardous Materials,* 156: 80-85.

Rajamanickam, D. and Shanthi, M. (2016). Photocatalytic degradation of an organic pollutant by zinc oxide–solar process. *Arabian Journal of Chemistry*, 9: S1858-S1868.

Rauf, M.A. and Ashraf, S.S. (2009). Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. *Chemical Engineering Journal*, 151: 10-8.

Reynolds, D.C., Loo, D.C. and Jogai, B. (1999). Valence-band ordering in ZnO. *Physical Review B,* 60: 2340-2344.

Rezaei, M. and Habibi-Yangjeh, A. (2013). Simple and largescale refluxing method for preparation of Ce-doped ZnO nanostructures as highly efficient photocatalyst. *Applied Surface Science,* 265: 591-596.

Sinha, A.K., Basu, M., Pradhan, M., Sarkar, S. and Pal, T. (2010). Fabrication of Large-Scale Hierarchical ZnO Hollow Spheroids for Hydrophobicity and Photocatalysis. *Chemistry: A European Journal,* 16: 7865-7874.

Wang, W.W., Zhu, Y.J. and Yang, L.X. (2007). ZnO–SnO_2 Hollow Spheres and Hierarchical Nanosheets: Hydrothermal Preparation, Formation Mechanism, and Photocatalytic Properties. *Advanced Functional Materials,* 17: 59-64.

Wang, X., Yu, J., Ho, C., Hou, Y. and Fu, X. (2005). Photocatalytic Activity of a Hierarchically Macro/Mesoporous Titania. *Langmuir,* 21: 2552–2559.

Xia, W., Mei, C., Zeng, X., Fan, G., Lu, J., Meng, X. and Shen, X. (2015). Nanoplate-Built ZnO Hollow Microspheres Decorated with Gold Nanoparticles and Their Enhanced Photocatalytic and Gas-Sensing Properties. *ACS Applied Materials & Interfaces,* 7: 11824-11832.

Xiao, F., Hung, S., Tao, H., Miao, J., Yang, H. and Liu, B. (2014). Spatially branched hierarchical ZnO nanorod-TiO_2 nanotube array heterostructures for versatile photocatalytic and photoelectrocatalytic applications: Towards intimate integration of 1D-1D hybrid nanostructures. *Nanoscale*, 6: 14950-14961.

Yogendra, K., Naik, S., Mahadevan, K.M. and Madhusudhana, N. (2011). A comparative study of photocatalytic activities of two different synthesized ZnO composites against Coralene red F3BS dye in presence of natural solar light. *Journal of Environmental Sciences Research,* 19: 1-11.

Yu, W., Zhang, J. and Peng, T. (2016). New insight into the enhanced photocatalytic activity of N-, C- and S-doped ZnO photocatalysts. *Applied Catalysis B: Environmental,* 181: 220-227.

Yu, X., Yu, J., Cheng, B. and Jaroniec, M. (2009). Synthesis of Hierarchical Flower-like AlOOH and TiO2/AlOOH Superstructures and their Enhanced Photocatalytic Properties. *The Journal of Physical Chemistry C,* 113: 17527-17535.

Yuan, Z.Y., Ren, T.Z. and Su, B.L. (2003). Hierarchically Mesostructured Titania Materials with an Unusual Interior Macroporous Structure. *Advanced Materials,* 15: 1462-1465.

Zhang, L., Wang,W., Zhou, L. and Xu, H. (2007). Bi_2WO_6 Nano- and Microstructures: Shape Control and Associated Visible-Light-Driven Photocatalytic Activities. *Small,* 3: 1618–1625.

Zhang, W. (2006). Growth of ZnO nanowires on modified well-aligned carbon nanotube arrays. *Nanotechnology*, 17: 1036-1040.

Zhang, X., Chen, Y.L., Liu, R.S. and Tsai, D.P. (2013). Plasmonic photocatalysis. *Reports on Progress in Physics,* 76: 046401.

*****

Cite this chapter as: Malhotra, S.P.K. (2020). ZnO nanostructures and nanocomposites as promising photocatalysts for the remediation of wastewater pollution. In: Environmental Degradation: Causes and Remediation Strategies, Volume 1, Eds. Kumar, V., Singh, J. and Kumar, P., pp. 120-132, https://doi.org/10.26832/aesa-2020-edcrs-09