

Basics of Photocatalysis and Different Strategy for Enhancing the Photocatalytic Efficiency

¹Yuvaraj M. Hunge, ²Anuja A. Yadav and ³Babasaheb M. Mohite

¹Department of Physics, Savitribai Phule Pune University, Pune, Maharashtra, India

²Department of Physics, The Institute of Science, 15 Madam Cama Road, Mumbai, Maharashtra, India

³Department of Physics, Ajara Mahavidyalaya, Ajara, Kolhapur, Maharashtra, India

Article history

Received: 06-04-2020

Revised: 05-05-2020

Accepted: 19-05-2020

Corresponding Author:

Yuvaraj M. Hunge

Department of Physics,

Savitribai Phule Pune

University, Pune, Maharashtra,

India

Email: yuvihunge@gmail.com

Abstract: This review reports on the basic mechanism of photocatalysis and different ways of enhancing the photocatalytic efficiency. It further examines enhancement of the photocatalytic property using the different combinations of semiconductor oxides (TiO₂, ZnO, stratified WO₃/TiO₂, WO₃/ZnO). TiO₂, ZnO semiconductors have been widely used from the recent few decades in the photocatalytic degradation process, but the main drawback of these materials is able to utilize the UV part of the solar spectrum. So many researchers tried to utilize a major portion of the solar spectrum using different strategies such as doping, applying external bias, stratified films, etc. The main aim of this review is providing different strategies for enhancing the photocatalytic efficiency.

Keywords: Photocatalysis, Degradation, Organic Pollutants

Introduction

In the recent few years, increasing the demand and scarcity of fresh, clean, potable water sources due to the rapid progress of different industry sectors, population growth has become a worldwide subject (Hunge, 2017). In this regard different applied strategies and solutions have been developed to overcome this problem. There are few examples such as the stowing of rainwater for everyday activities and growing the catchment capability for stormwater that could solve the complications in short-term (Shevale *et al.*, 2020). It is found that nearly about 4 billion people worldwide facing the problem of little access to clean and sanitized water supply. According to the WHO millions of people died every year by severe waterborne diseases. Due to more discharge of micropollutants and contaminants into the potable water sources can increase these statistical figures in the short future (Yadav *et al.*, 2019). In this regard to overwhelm the worsening of clean water scarcity, there is a need to develop advanced technologies with low-cost and high photocatalytic efficiency.

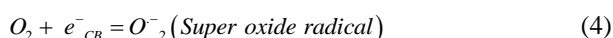
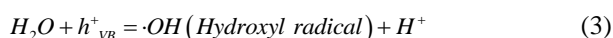
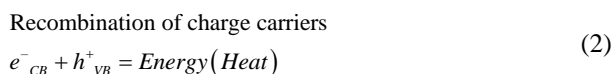
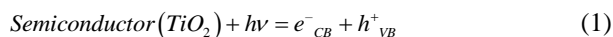
Presently existing wastewater treatment methods such as adsorption or coagulation, membrane filtrations just focus on the contaminants present by shifting them to other phases, but still remain and not being completely removed (Ali *et al.*, 2018). Other commonly used water treatment methods such as

sedimentation, distillation, filtration, chemical and membrane methods involve more operating costs and could produce toxic secondary pollutants into the environment. These highly toxic pollutants are more redundant (Yadav *et al.*, 2018). The most commonly used disinfection process is chlorination. This disinfection method can produce the mutagenic and carcinogenic by-products which are dangerous to human health. In recent decades Advanced Oxidation Processes (AOPs) as the innovative water treatment method for the destruction of organic pollutants present in the wastewater. AOPs are based on the generation of highly reactive radicals like superoxide and hydroxyl (Hunge *et al.*, 2018a). Among these AOPs, heterogeneous photocatalysis employing semiconductor materials (TiO₂, ZnO, Fe₂O₃) has demonstrated that the conversion of organic pollutants into pure water and carbon oxide. Among the semiconductor catalysts, titanium dioxide (TiO₂) has gained more interest in the R&D of photocatalysis technology. The TiO₂ is the most active photocatalyst under the photon energy of 300 nm < 1 < 390 nm and remains stable after the repeated catalytic cycles, whereas ZnO has a similar band gap and properties as compared to that of TiO₂. But these catalyst main drawback is absorbed only ultraviolet part of the solar spectrum. So many researchers focus on how to make the use of the solar spectrum efficiently (Dhodamani *et al.*, 2020). This review focus on the basics of photocatalysis and

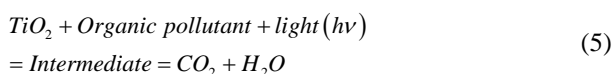
effective utilization of the solar spectrum by applying different strategy. Also it provides an overview of the understanding and development of photocatalytic water treatment methods.

Fundamental and Mechanism of Photocatalysis

Heterogeneous photocatalysis comes under AOPs. Basically photocatalytic degradation mechanism involves the interaction between the semiconductor materials with a photon of light. It generates the charge carriers and then the formation of radicals. It involves the absorption of photons having energy ($h\nu$) equal to or greater than the bandgap energy (E_g) of semiconductor material and then there is a transfer of electrons (e^-) from its valence Band (VB) to conduction Band (CB), thus there is a simultaneous generation of a hole in the valence band (Hunge *et al.*, 2019a). For example in the case of TiO_2 , when the TiO_2 particle is irradiated with adequate photon having energy equal to or greater than band gap energy $h\nu$ usually 3.2 eV for anatase phase and 3.0 eV rutile phase. The light wavelength for such photon energy usually corresponds to $1 < 400$ nm, thus creating the electron-hole pairs. The series of redox reactions that occurs at the surface of semiconductor material are as follow (Hunge and Yadav, 2018):



In heterogeneous photocatalysis, the liquid phase organic impurities are degraded to its corresponding intermediates byproducts and then further mineralized into carbon dioxide and water:



The overall photocatalysis reactions are divided into four independent steps, (i) Mass transfer of the organic impurity in the liquid stage to the TiO_2 , (ii) Adsorption of the organic impurity on stimulated TiO_2 surface. (ii) Redox reaction for the adsorbed phase on the TiO_2 surface. (iv) Desorption of the intermediate product from the TiO_2 surface. In photocatalysis, the

photocatalytic activity depends on the ability of the catalyst to create electron-hole pairs and then generation radicals, which are able to undergo several reactions (Hunge *et al.*, 2019b). The main drawback of this process is low efficiency due to the recombination of charge carriers, so there needs to develop some strategy to overcome this drawback. Some strategies are discussed below.

Graphene Based Composites

Graphene is the most promising carbon material for photocatalysis application due to its good properties such as high surface area, good electrical conductivity and chemical stability. The faster electron transfer capability of GO has motivated researchers to fabricate the graphene based semiconductor materials and inspecting their application in different fields like gas sensors, photocatalysis etc. (Hunge *et al.*, 2020).

Photoelectrocatalysis

Photocatalysis can be enhanced by applying an external potential to the semiconductor photoelectrode known as photoelectrocatalysis. In photoelectrocatalysis photocatalysts are deposited onto the conducting transparent electrodes and in order to increase the rate of a chemical reaction by applying an external bias to a semiconductor electrode which is simultaneously irradiated by a stream of photons. However, technique, would make the treatment in a practical application much easier and have potential to enhance charge separation by applying a potential to serve higher degradation performance (Hunge *et al.*, 2018b).

Doping of Metal Ions

The photocatalytic efficiency of semiconductor material is decided by its band position. The bandgap of semiconductor material is minimized by introducing a new band between conduction and valence bands. This can be achieved by doping of metal ions (Hunge *et al.*, 2018c).

By Surface Sensitization

This is another way to improve the photocatalytic efficiency. Surface sensitization is done by noble metals like Ag, Au, Pt etc. (Wen *et al.*, 2015).

Coupling of Two Semiconductors

It is also one of the trending methods for improving photo efficiency. A suitable combination of two semiconductor materials restricts the recombination of charge carriers (Hunge *et al.*, 2018d).

Sonocatalytic Degradation Technique

Sonocatalytic degradation process is an alternative way for the degradation of organic compounds. The

sonocatalytic method is similar to photocatalysis excluding the use of ultrasound as the energy source. Sonocatalytic process involves two major phenomena, one is sonoluminescence and another one hot spots formed by acoustic cavitation in a liquid can produce glows with a wide range of wavelengths, high temperatures up to 5000 K and high pressure up to 1000 atm that causes splitting of the water molecule, into the oxygen and hydrogen peroxide (H_2O_2). In addition there is the formation of highly reactive radicals like hydroxyl radical ($\bullet OH$) and superoxide radical ($\bullet O_2^-$), that contain unpaired electron and attack on the organic impurity. These radicals are helpful for sonocatalytic degradation (Hunge *et al.*, 2019b).

Conclusion

This review, present the basic mechanism of photocatalysis and different strategy for enhanced photocatalytic degradation efficiency. The advanced oxidation process proved to be a green path for the degradation of organic pollutants. By avoiding the recombination of charge carriers and can improve efficiency. Also utilize a maximum portion of the solar spectrum for photocatalysis application.

Acknowledgement

Dr. YMH and Dr. AAY are thankful to the Science and Engineering Research Board (SERB), New Delhi, for awarding National Postdoctoral Fellowship (N-PDF) award F. No. PDF/2017/000691 and No. PDF/2017/0001419.

Author's Contributions

Yuvaraj M. Hunge: Supervised the work carried out and reviewed the manuscript.

Anuja A. Yadav: Analyzed the work.

Babasaheb M. Mohite: Prepared the manuscript draft and data collection.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all other authors approved the manuscript and no ethical issue involved.

References

Ali, T., Y.M. Hunge and A. Venkatraman, 2018. UV assisted photoelectrocatalytic degradation of reactive red 152 dye using spray deposited TiO_2 thin films. *J. Mater. Sci.: Mater. Electron.*, 29: 1209-1215. DOI 10.1007/s10854-017-8023-y

Dhodamani, A.G., A.V. More, S.B. Mullani, S.P. Deshmukh and V.B. Koli *et al.*, 2020. Structural refinement and optoelectronic properties of $Mo_xTi_{1-2x}O_{2-\delta}1-y(RGO)_y$ nanocomposites and their photovoltaic studies with natural pigments as sensitizers. *Chem. Select*, 5: 218-230. DOI: 10.1002/SLCT.201903606

Hunge, Y.M., 2017. Sunlight assisted photoelectrocatalytic degradation of benzoic acid using stratified WO_3/TiO_2 thin films. *Ceram. Int.*, 43: 10089-10096. DOI: 10.1016/j.ceramint.2017.05.028

Hunge, Y.M. and A.A. Yadav, 2018. Basics and advanced developments in photocatalysis – a review (Mini review). *Int. J. Hydrol.*, 2: 539-540. DOI: 10.15406/ijh.2018.02.00122

Hunge, Y.M., A.A. Yadav and V.L. Mathe, 2018a. Oxidative degradation of phthalic acid using TiO_2 photocatalyst. *J. Mater. Sci.: Mater. Electron.*, 29: 6183-6187. DOI: 10.1007/s10854-018-8593

Hunge, Y.M., A.A. Yadav, S.B. Kulkarni and V.L. Mathe, 2018b. A multifunctional ZnO thin film based devices for photoelectrocatalytic degradation of terephthalic acid and CO_2 gas sensing applications. *Sensors Actuators B: Chemical*, 274: 1-9. DOI: 10.1016/j.snb.2018.07.117

Hunge, Y.M., A.A. Yadav, B.M. Mohite, V.L. Mathe and C.H. Bhosale, 2018c. Photoelectrocatalytic degradation of sugarcane factory wastewater using WO_3/ZnO thin films. *J. Mater. Sci.: Mater. Electron.*, 29: 3808-3816. DOI: 10.1007/s10854-017-8316-1

Hunge, Y.M., A.A. Yadav and V.L. Mathe, 2018d. Ultrasound assisted synthesis of WO_3-ZnO nanocomposites for brilliant blue dye degradation. *Ultrason. Sonochem.*, 45: 116-122. DOI: 10.1016/j.ultsonch.2018.02.052

Hunge, Y.M., A.A. Yadav and V.L. Mathe, 2019a. Photocatalytic hydrogen production using TiO_2 nanogranules prepared by hydrothermal route. *Chem. Phys. Lett.*, 731: 136582-136586. DOI: 10.1016/j.cplett.2019.07.010

Hunge, Y.M., A.A. Yadav, S. Liu and V.L. Mathe, 2019b. Sonochemical synthesis of CZTS photocatalyst for photocatalytic degradation of phthalic acid. *Ultrason. Sonochem.*, 56: 284-289. DOI: 10.1016/j.ultsonch.2019.04.003

Hunge, Y.M., A.A. Yadav, A.G. Dhodamani, N. Suzuki and C. Terashima *et al.*, 2020. Enhanced photocatalytic performance of ultrasound treated GO/TiO_2 composite for photocatalytic degradation of salicylic acid under sunlight illumination. *Ultrason. Sonochem.*, 61: 104849-104855. DOI: 10.1016/j.ultsonch.2019.104849

- Shevale, V.B., A.G. Dhodamani and S.D. Delekar, 2020. Catalytic reclamation of silver present in photographic waste using magnetically separable $\text{TiO}_2@ \text{CuFe}_2\text{O}_4$ nanocomposites and thereof its use in antibacterial activity. ACS Omega, 5: 1098-1108. DOI: 10.1021/acsomega.9b03260
- Wen, J., X. Li, W. Liu, Y. Fang and J. Xie *et al.*, 2015. Photocatalysis fundamentals and surface modification of TiO_2 nanomaterials. Chinese J. Catalysis, 36: 2049-2070. DOI: 10.1016/S1872-2067(15)60999-8
- Yadav, A.A., Y.M. Hunge and S.B. Kulkarni, 2019. Synthesis of multifunctional FeCo_2O_4 electrode using ultrasonic treatment for photocatalysis and energy storage applications. Ultrason. Sonochem., 58: 104663-104668. DOI: 10.1016/j.ultsonch.2019.104663
- Yadav, A.A., Y.M. Hunge, V.L. Mathe and S.B. Kulkarni, 2018. Photocatalytic degradation of salicylic acid using BaTiO_3 , Photocatalyst under ultraviolet light illumination. J. Mater. Sci.: Mater. Electron., 29: 15069-15073. DOI: 10.1007/s10854-018-9646-3