Effect of Photocatalytic Studies of Semiconducting Metal Oxides – A Review

M.Kavin Micheal\textsuperscript{1}, A.Ayeshamariam\textsuperscript{1,2*}, N.M.I. Alhaji\textsuperscript{3}, S.A.Fowziya\textsuperscript{3}, S. Rajasekar\textsuperscript{4}, D.Nathiya\textsuperscript{3} and M.Jayachandran\textsuperscript{5}

\textsuperscript{1}Department of Physics, Khadir Mohideen College, Adirampattinam, 614701, India
\textsuperscript{2}Research and Development Center, Bharathidasan University, Tiruchirappalli, 620024, India
\textsuperscript{3}Department of Chemistry, Khadir Mohideen College, Adirampattinam, 614701, India
\textsuperscript{4}Department of Physics, Syed Ammal Engineering College, Ramanathapuram, 623501, India
\textsuperscript{5}Department of Physics, Sethu Institute of Technology, Pulloor, Kariyapatti, 626106, India

ABSTRACT

During the process of dyeing in textile industry, about 50\% of the initial dye concentration which is initial is leftover in the spent dye bath in the hydrolyzed form, this result in the colored effluent. Even on very low concentrations, these dye effluents not only cause aesthetic complications, but also show great biotoxicity and possible mutagenic as well as carcinogenic effects. Utmost of the commercial dyes are premeditated to resist photodegradation and many of them are known to be as non-biodegradable in an aerobic biological process. The dye wastewater which is colored in water bodies retards both sunlight penetration and oxygen dissolution, which are essential for water-dwelling organisms is reported as a review here. The catalyst and nanocomposites mechanism for the different materials is discussed here.

KEYWORDS; Dyes, photo catalytic, biotoxicity, Zinc oxide, tungsten oxide and bismuth oxide

*Corresponding author

A. Ayeshamariam

Research and Development Center,
Bharathidasan University,
Tiruchirappalli, 620024, India
Email: aamariam786@gmail.com
INTRODUCTION

Nanoparticles have a high surface to volume ratio which has a dramatic effect on their physico-chemical properties compared to non–nanoscale more bulky forms of the same material. The large surface to volume ratio will allow the development of new and novel industrial catalysts. The increased reactivity and small size of nanoparticles, compared to larger ones, are two important factors, which frequently crop up when studying the function of nanomaterials. When the conventional materials size is reduced to the nanoscale, they become capable of offering new-fangled material with exclusive electrical, optical and mechanical properties.

With increasing environmental problems, it is very important to develop metal/semiconductor heterostructures for high performance photo catalysts due to its unique optical, electrical, and catalytic properties. ZnO exhibits superior photo catalytic activity owing to its higher efficiency in generating, moving and separating photo induced electrons and holes. Thus, ZnO are widely used in the removal of toxic, harmful or hazardous organic pollutants from sewage in industrial water treatment. Meanwhile, the modification of semiconductors with noble metals has attracted significant attention. It is found that catalytic noble metals, such as Ag nanoparticles, can improve the surface states of ZnO nanocrystals. In another word, Ag and oxygen vacancy defects on the ZnO surface can trap the photo generated electrons from the semiconductor, and benefit the separation of photo generated electron–hole pairs, thus enhancing the photo catalytic activity. Ag/ZnO nanocomposites with different structures and morphologies have been prepared by different methods, such as Ag/ ZnO whisker nanocompounds, Ag /ZnO nanorods, Ag/ZnO nanofibers, Ag/ZnO core/shell nanostructures.

DISCUSSION

Metal Oxides and its Photo catalytic Activities

Metal oxides such as oxides of vanadium, chromium, titanium, zinc, tin, and cerium having these characteristics follow similar primary photo catalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes that are able to oxidize organic substrates. In this process, a metal oxide is activated with either UV light, visible light or a combination of both, and photo-excited electrons are promoted from the valence band to the conduction band, forming an electron/hole pair (e− / h+). This photo-generated pair (e− / h+) may be able to reduce and/or oxidize a compound adsorbed on the photo catalyst surface.

The photo catalytic activity of metal oxide comes from two sources: (i) generation of *OH radicals by oxidation of OH− anions, (ii) generation of O2− radicals by reduction of O2. Both the radicals and anions can react with pollutants to degrade or otherwise transform them to lesser
harmful byproducts\textsuperscript{8,9}. There are many catalysts reported in the literature useful for this exciting process. Among these metal oxide catalysts, CeO\textsubscript{2}, is abundant in nature and, has been extensively used as an economic photo catalyst, particularly as heterogeneous photo catalyst since several decades\textsuperscript{10}. The favorable combination of electronic structure, light absorption properties, charge transport characteristics and excited lifetimes of metal oxides have made it possible for their application as an efficient photocatalyst\textsuperscript{11}. Heterogeneous photo catalysis employing metal oxides such as CeO\textsubscript{2} has proved its efficiency in degrading a wide range of distinct pollutants into biodegradable compounds and eventually mineralizing them to harmless carbon dioxide and water\textsuperscript{12}. This sequence of photo catalytic reaction and degradation are shown in Figure 1.

![Figure 1. Photocatalytic mechanisms of CeO$_2$ and its doped materials](image)

**MECHANISM OF PHOTOCATALYTIC ACTIVITIES IN SEMICONDUCTING OXIDES**

When photo catalyst ZnO absorbs Ultraviolet radiation from sunlight or illuminated light source, it will produce pairs of electrons and holes. The electron in the valence band becomes excited state due to the illumination of light. The excess energy of this excited electron promoted the electron to the conduction band of ZnO therefore creating the negative-electron and positive hole pair. This stage is referred as the semiconductor’s “Photo excitation” state. The energy difference between valence band and conduction band is known as the “Band gap”. In order for Photo catalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. The hole has the potential to oxidise water that may be on the surface of the material resulting in the formation of hydroxyl radical. Hydroxyl radicals are themselves very powerful oxidizers and can easily oxidize
any organic species that happens to be nearby, ultimately carbon dioxide and water. The electrons in
the conduction band the electron has no hole to recombine with since it has no oxidized surface
bound water. It quickly looks for an alternative and rapidly reduce oxygen to form the superoxide
anion. Increase in photo catalytic activity is probably due to prevention of electron-hole
recombination. These processes are called photodegradation process and the photodegradation
efficiency is given by equation as

\[
D = \frac{A_0 - A_1}{A_0}
\]

Where, \( A_0 \) is the initial concentration and \( A_1 \) is the final Concentration.

**PHOTODEGRADATION PROCESS**

Formation of excitons by absorption of photons by photo catalyst (ZnO)

\[
\text{ZnO} + h\nu \rightarrow h^+ + e^-
\]

Electrons (e-) are produced in conduction band and holes (h+) are produced in valence band

Formation of superoxide anion (O\(_2^\cdot\))

\[
O_2 + e^- \rightarrow O_2^\cdot
\]

Formation of hydroxyl radicals (OH\(^-\))

\[
\text{H}_2\text{O} + h^+ \rightarrow H^+ + OH^-\]

Neutralization of superoxide anion by protons

\[
O_2^- + H^+ \rightarrow HO_2^\cdot
\]

Formation of hydrogen peroxide and disputation of oxygen

Formation of degradation products

R (Organic pollutant) + H\(_2\)O\(_2\) + OH\(^-\) + O\(_2^\cdot\) \rightarrow \text{depredated products}

These processes are called photodegradation processes are shown in Figure 2
The possible reaction mechanism diagram for the degradation of AB 113 using C/ZnFe$_2$O$_4$ photo catalyst under UV light is proposed in Figure 3. Upon UV light illumination, the photo generated electrons could be excited from the VB to the CB of ZnFe$_2$O$_4$, by creating holes on the VB. Without carbon, majority of electron–hole pairs rapidly recombine and just few electrons could be caught by O$_2$ to create •O$_2^{-}$ or caught by Fe$^{3+}$. The presence of carbon in C/ZnFe$_2$O$_4$ nanocomposite, the photo induced electrons on the CB of ZnFe$_2$O$_4$ can be transferred to the carbon because of their fantastic electronic conductivity.
Bian et al.\textsuperscript{13} fabricated $\beta$-Bi$_2$O$_3$/Bi$_2$O$_{2.33}$@Bi$_2$O$_2$CO$_3$ ternary composite has been synthesized using self-assembled Bi$_2$O$_2$CO$_3$ nanosheets by slow thermal decomposition. A result indicates that $\beta$-Bi$_2$O$_3$/Bi$_2$O$_{2.33}$@Bi$_2$O$_2$CO$_3$ composite exhibits superior photocatalytic activity than that of pure Bi$_2$O$_2$CO$_3$ towards the degradation of RhB and MB under the visible light irradiation. The mechanism of 3D hierarchical $\beta$-Bi$_2$O$_3$/Bi$_2$O$_{2.33}$@Bi$_2$O$_2$CO$_3$ under visible light irradiation is shown in Figure 3. The Bi$_2$O$_3$/Bi$_2$WO$_{6.3}$F$_{2x}$ heterojunction powders were prepared via a microwave hydrothermal method using NH$_4$F/Bi$_2$WO$_6$ at different temperature at 220° and 240 °C. The photocatalytic activities of the composite were also examined via the degradation of RhB under the illumination of visible light.

The Bi$_2$O$_3$/Bi$_2$WO$_{6.3}$F$_{2x}$ compound prepared at 220 °C showed superior photo catalytic activity due to the crystal growth and formation of the p-n junction between t-type Bi$_2$O$_3$ and n-type Bi$_2$WO$_6$\textsuperscript{13}. Liu et al.\textsuperscript{14} reported that a novel Bi$_2$O$_3$/FeVO$_4$ heterojunction semiconductor prepared by co-precipitation method. The photocatalytic activities were evaluated through the photo-deprivation of MG under the irradiation of visible light. It is concluded that Bi$_2$O$_3$/FeVO$_4$ composite had abundant developed photo catalytic activity than unadulterated Bi$_2$O$_3$ or FeVO$_4$. He et al.\textsuperscript{15} reported that Z-scheme photo catalysts supported Bi$_2$O$_3$/g-C$_3$N$_4$ was prepared by room-temperature in-situ fabrication. The Z-scheme supported Bi$_2$O$_3$/g-C$_3$N$_4$ composite unveiled better visible-light photo catalytic activity for phenol degradation than unadulterated Bi$_2$O$_3$ and g-C$_3$N$_4$, owing to the Z-scheme charge migration\textsuperscript{16}.

**g-C$_3$N$_4$ BASED WO$_3$ COMPOSITE PHOTOCATALYSTS**

Wang et al. fabricated the WO$_3$/g-C$_3$N$_4$ composite photocatalysts with different content of g-C$_3$N$_4$ and achieved an enhanced visible-light photo catalytic activity for WO$_3$/g-C$_3$N$_4$ compound in the direction of the degradation of Rhedamine B (RhB) when compared to that pure WO$_3$ and g-C$_3$N$_4$\textsuperscript{17}. Cui et al. prepared Z-scheme WO$_3$/g-C$_3$N$_4$ composite photo catalysts with addition of dissimilar content of WO$_3$ into g-C$_3$N$_4$. Then, the visible-light photo catalytic performance of the WO$_3$/g-C$_3$N$_4$ composites were investigated which is used to degrade of RhB and observed that composites with 25 wt.% WO$_3$ content has an efficient photo catalytic activity than the pure WO$_3$, pure g-C$_3$N$_4$ and other composites\textsuperscript{18}. Liu et al. developed a novel WO$_3$/g-C$_3$N$_4$ composite photocatalysts and studied their adsorption and photocatalytic activity for the photodegradation of MB visible-light illumination. The observed results were found to be showed that the 30 wt% WO$_3$/g-C$_3$N$_4$ composite exhibits an outstanding adsorption and photocatalytic activity than in the bare WO$_3$ and g-C$_3$N$_4$. The probable Z-scheme mechanism for photocatalytic degradation of MB over WO$_3$/g-C$_3$N$_4$ composite is also displayed in Figure 4. This enhanced photocatalytic activity of WO$_3$/g-C$_3$N$_4$ is may be attributed the
increased adsorption and efficient charge separation. Hence, the WO$_3$/g-C$_3$N$_4$ is an excellent material for environmental remediation.

![Diagram](image)

**Figure 4.** Possible Z-scheme mechanism for the photodegradation of MB over WO$_3$/g-C$_3$N$_4$ composite under visible-light irradiation$^{19}$

**SILVER COMPOUNDS BASED WO$_3$ COMPOSITE PHOTOCATALYSTS**

Wang et al. developed the Ag$_3$PO$_4$/WO$_3$ hybrid photo catalyst for investigated its visible-light photo catalytic ability towards the degradation of methylene blue (MB). Also, they observed that the Ag$_3$PO$_4$/WO$_3$ hybrid achieved an progressive photo catalytic activity than pure Ag$_3$PO$_4$ and WO$_3$$^{20}$. Recently, Cao et al. prepared the novel AgIO$_3$/WO$_3$ composites from hydrothermal and chemical precipitation method with different amount of AgIO$_3$. The photo catalytic performance these AgIO$_3$/WO$_3$ composites were investigated towards the deprivation of RhB under the visible-light irradiation. It revealed that 50% AgIO$_3$/WO$_3$ composites possesses a highest photo catalytic performance than the pure AgIO$_3$ and WO$_3$. This may be due to the fast separation and migration of photo generated electron-hole pairs at the interface of AgIO$_3$ and WO$_3$$^{21}$.

Wang et al. prepared met stable hexagonal WO$_3$ (h-WO$_3$) from a hydrothermal reduction method with glycerol and then, the Ag$_3$PO$_4$/h-WO$_3$complexes were prepared by a modest precipitation method. They found that the Ag$_3$PO$_4$/h-WO$_3$ photo catalyst was showed an outstanding photo catalytic activity for degradation of methyl orange (MO) under the visible-light illumination than the Ag$_3$PO$_4$/h-WO$_3$. Also, the Ag$_3$PO$_4$/h-WO$_3$ composites exhibited a good stability compared with the pure Ag$_3$PO$_4$ which clear that the obtained h-WO$_3$ played a vital role in the degradation process$^{22}$. Wang et al. synthesized a novel visible-light-driven AgI/WO$_3$ nanocomposites using facile
precipitation method. The photocatalytic activities of the AgI/WO₃ nanocomposites were premeditated by the deprivation of tetracycline hydrochloride (TC) under the visible-light illumination. They found that an optimized 20%-AgI/WO₃ revealed a highest photocatalytic performance than that of pure AgI and WO₃. Also, the stability test indicates that the better photostability of AgI/WO₃ nanocomposite. The possible photodegradation mechanism meant for the enhanced photocatalytic activity of AgI/WO₃ towards to the TC degradation is shown in Figure 5²³.

![Figure 5. Possible photocatalytic mechanism for the degradation of TC over AgI/WO₃ nanocomposite photocatalysts under the visible-light illumination²³](image)

<table>
<thead>
<tr>
<th>Nano catalyst</th>
<th>Applications/ Degradation</th>
<th>light source</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>amido black/acridine orange.</td>
<td>UV–visible</td>
<td>24</td>
</tr>
<tr>
<td>CeO₂</td>
<td>cytotoxicity/lung cancer cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO₂</td>
<td>MB</td>
<td>UV and sunlight</td>
<td>25</td>
</tr>
<tr>
<td>CeO₂</td>
<td>acid orange 7</td>
<td>solar light</td>
<td>26</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Azo dye acid orange 7</td>
<td>visible light</td>
<td>27</td>
</tr>
<tr>
<td>CeO₂</td>
<td>gas-phase purification of C₆H₆</td>
<td>UV–visible</td>
<td>28</td>
</tr>
<tr>
<td>CeO₂/Tb₂O₃ NTs</td>
<td>MB</td>
<td>visible light</td>
<td>29</td>
</tr>
<tr>
<td>CeO₂–CNT</td>
<td>Metal ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO₂ hierarchical NRs</td>
<td>MO</td>
<td>White light, 500 W Xe lamp</td>
<td>30</td>
</tr>
<tr>
<td>CeO₂ hierarchical NWs</td>
<td>MO</td>
<td>White light, 500 W Xe lamp</td>
<td>31</td>
</tr>
<tr>
<td>CeO₂ microspheres</td>
<td>AO 7</td>
<td>White light, 500 W Xe lamp</td>
<td>32</td>
</tr>
<tr>
<td>Ordered meso-CeO₂</td>
<td>AO 7</td>
<td>Visible (λ&gt;420 nm), 1000 W Xe lamp</td>
<td>33</td>
</tr>
<tr>
<td>Flower-like CeO₂</td>
<td>AO 7</td>
<td>UV light (λ=365 nm), 2mWcm⁻²</td>
<td>21</td>
</tr>
<tr>
<td>CeO₂ NCs</td>
<td>RhB</td>
<td>350 nm&lt;λ&lt;500 nm, 3.5mWcm⁻²</td>
<td>34</td>
</tr>
<tr>
<td>meso-CeO₂ NRs</td>
<td>K₂Cr₂O₇</td>
<td>UV light, 500 W Hg lamp</td>
<td>35</td>
</tr>
</tbody>
</table>
CONCLUSION

This review explains the optical absorption and optical energy gap which is dependent on its Photocatalytic properties. Extensive investigations have been explored by several research groups on the fundamental aspects of development, modification and utilization of metal oxide based heterostructured materials as photo catalysts for deprivation of the organic pollutants. In this present review, we have concise the topical developments in metal oxide based heterostructures for photocatalytic applications towards environmental remediation. The major challenges concentrated on numerous studies which are related with an advancement of metal oxides based visible-light driven photo catalysis for the environmental remediation applications.

REFERENCES


13. Bian, Y., Ma, Y., Shang, Y., Tan, P. and Pan, J., Self-integrated β-Bi$_2$O$_3$/Bi$_2$O$_5$. 33@Bi$_2$O$_2$CO$_3$ ternary composites: Formation mechanism and visible light photocatalytic activity. Applied Surface Science, 2018; 430: 613-624,


41. Sharma, Aditya, Mayora Varshney, Jaehun Park, Tae Kyun Ha, Keun Hwa Chae, and Hyun Joon Shin. "Bifunctional Ce$_{1-x}$Eu$_x$O$_2$ (0 ≤ x ≤ 0.3) nanoparticles for photoluminescence and photocatalyst applications: an X-ray absorption spectroscopy study." Physical Chemistry Chemical Physics, 2015; 17(44): 30065-30075.


43. Qing, R., Photocatalysis of cerium-zirconium dioxide solid solution nanoparticle free radical scavengers (Doctoral dissertation, University of Florida), 2009.

