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Effect of Photocatalytic Studies of Semiconducting Metal Oxides – A Review

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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

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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[1].

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[2]. ZnO exhibits superior photo catalytic activity owing to its higher efficiency in generating, moving and separating photo induced electrons and holes[3]. Thus, ZnO are widely used in the removal of toxic, harmful or hazardous organic pollutants from sewage in industrial water treatment[4]. 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[5]. 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[6].

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[7]. 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 $^{\bullet}OH$ radicals by oxidation of OH^- anions, (ii) generation of O_2^- radicals by reduction of O_2. Both the radicals and anions can react with pollutants to degrade or otherwise transform them to lesser

harmful byproducts[8,9]. There are many catalysts reported in the literature useful for this exciting process. Among these metal oxide catalysts, CeO_2, is abundant in nature and, has been extensively used as an economic photo catalyst, particularly as heterogeneous photo catalyst since several decades[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[11]. Heterogeneous photo catalysis employing metal oxides such as CeO_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[12]. This sequence of photo catalytic reaction and degradation are shown in Figure 1.

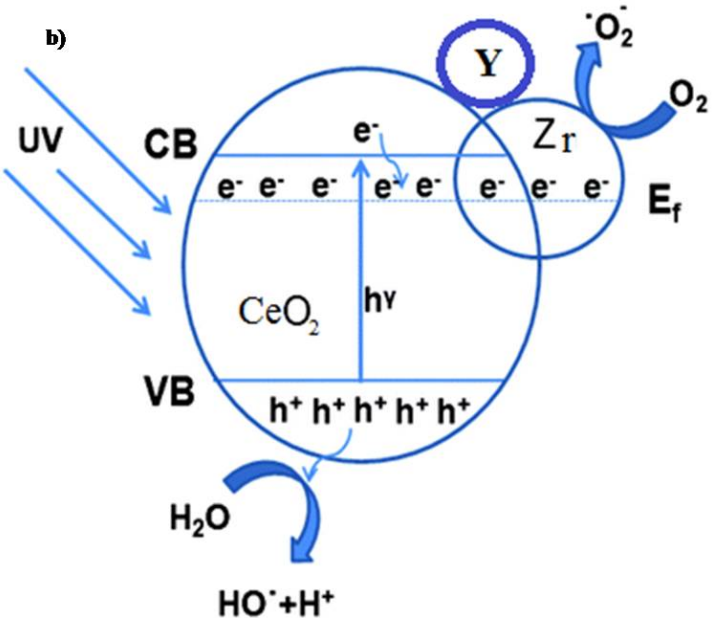

Figure 1. Photocatalytic mechanisms of CeO_2 and its doped materials

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

$$D = A_0\text{-}A_1 / A_0$$

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)

$ZnO + hv\text{--------} h^+ + e^-$

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

Formation of superoxide anion (O_2^-)

$O_2 + e^- \rightarrow O_2^{\bullet -}$

Formation of hydroxyl radicals (OH^-)

$H_2O + h^+$ ------- $H^+ + OH^-$

Neutralization of superoxide anion by protons

$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}$

Formation of hydrogen peroxide and disputation of oxygen

Formation of **degradation products**

R (Organic pollutant) + H_2O_2 + OH^- + $O_2^{\bullet -}$ → depredated products

These processes are called photodegradation processes are shown in Figure 2

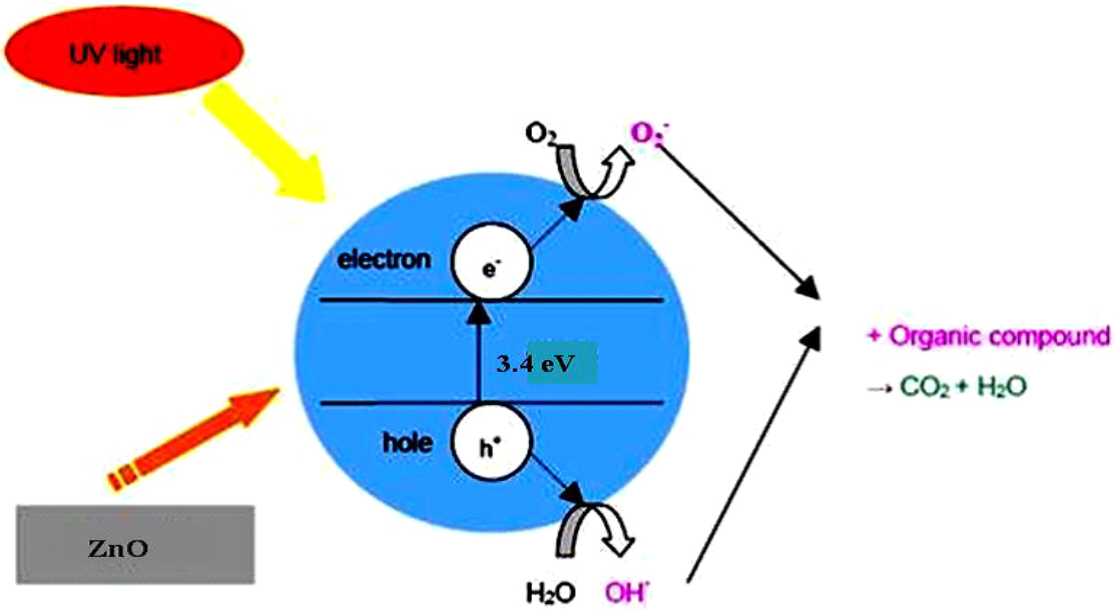

Figure 2 Photocatalytic activity of ZnO mechanism of organic compound by UV light irradiation

The possible reaction mechanism diagram for the degradation of AB 113 using C/$ZnFe_2O_4$ 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 $ZnFe_2O_4$, 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 $\bullet O_2^-$ or caught by Fe^{3+}. The presence of carbon in C/$ZnFe_2O_4$ nanocomposite, the photo induced electrons on the CB of $ZnFe_2O_4$ can be transferred to the carbon because of their fantastic electronic conductivity.

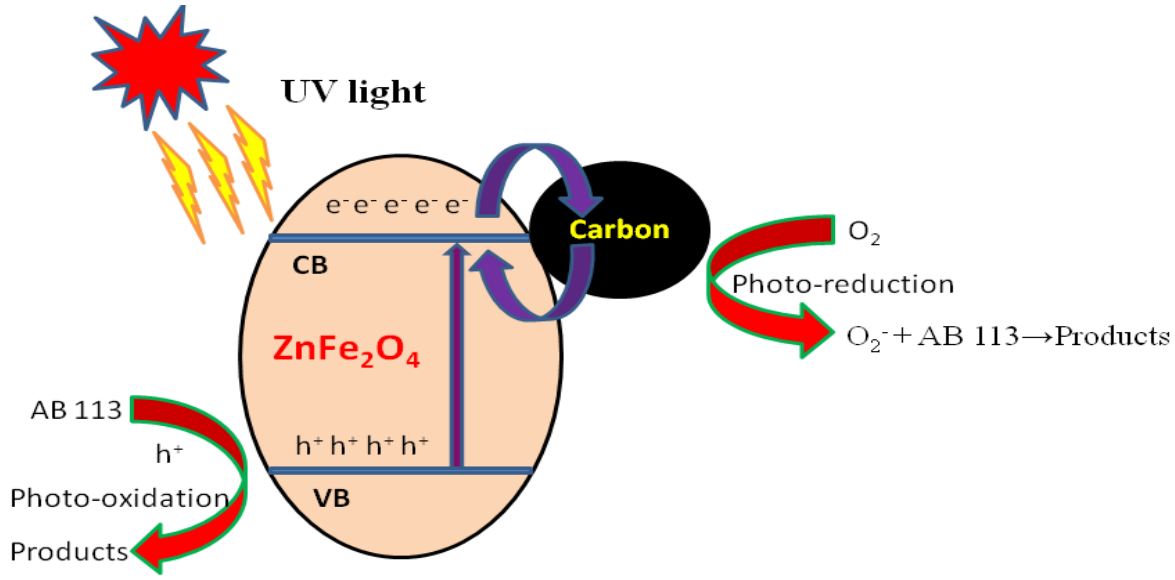

Figure 3. Schematic view of the photocatalytic separation and transfer of photoinduced charges on the C/$ZnFe_2O_4$ photocatalyst under UV light.

Bian et al[13] fabricated β-Bi_2O_3/$Bi_2O_{2.33}$@$Bi_2O_2CO_3$ ternary composite has been synthesized using self-assembled $Bi_2O_2CO_3$ nanosheets by slow thermal decomposition. A result indicates that β-Bi_2O_3/$Bi_2O_{2.33}$@$Bi_2O_2CO_3$ composite exhibits superior photocatalytic activity than that of pure $Bi_2O_2CO_3$ towards the degradation of RhB and MB under the visible light irradiation. The mechanism of 3D hierarchical β-Bi_2O_3/$Bi_2O_{2.33}$@$Bi_2O_2CO_3$ under visible light irradiation is shown in Figure 3. The Bi_2O_3/$Bi_2WO_{6-x}F_{2x}$ heterojunction powders were prepared via a microwave hydrothermal method using NH_4F/Bi_2WO_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_2O_3/$Bi_2WO_{6-x}F_{2x}$compound prepared at 220 °C showed superior photo catalytic activity duo to the crystal growth and formation of the p-n junction between t-type Bi_2O_3 and n-type Bi_2WO_6[13]. Liu et al[14] reported that a novel Bi_2O_3/$FeVO_4$ heterojunction semiconductor prepared by co-precipitation method. The photo catalytic activities were evaluated through the photo-deprevation of MG under the irradiation of visible light. It is concluded that Bi_2O_3/$FeVO_4$ composite had abundant developed photo catalytic activity than unadulterated Bi_2O_3 or $FeVO_4$. He et al[15] reported that Z-scheme photo catalysts supported Bi_2O_3/g-C_3N_4 was prepared by room-temperature in-situ fabrication. The Z-scheme supported Bi_2O_3/g-C_3N_4 composite unveiled better visible-light photo catalytic activity for phenol degradation than unadulterated Bi_2O_3 and g-C_3N_4, owing to the Z-scheme charge migration[16].

g-C_3N_4 BASED WO_3 COMPOSITE PHOTOCATALYSTS

Wang et al. fabricated the WO_3/g-C_3N_4 composite photo catalysts with different content of g-C_3N_4 and achieved an enhanced visible-light photo catalytic activity for WO_3/g-C_3N_4compoundin the direction of the degradation of Rhedamine B (RhB) when compare to that pure WO_3 and g-C_3N_4[17]. Cui et al. prepared Z-scheme WO_3/g-C_3N_4 composite photo catalysts with addition of dissimilar content of WO_3 into g-C_3N_4. Then, the visible -light photo catalytic performance of the WO_3/g-C_3N_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_3N_4 and other composites[18]. Liu et al. developed a novel WO_3/g-C_3N_4 composite photo catalysts 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_3N_4 composite exhibits an outstanding adsoption and photocatalytic activity than in the bare WO_3 and g-C_3N_4. The probable Z-scheme mechanism for photocatalytic degradation of MB over WO_3/g-C_3N_4 composite is also displayed in Figure 4. This enhanced photocatalytic activity of WO_3/g-C_3N_4 is may be attributed the

increased adsorption and efficient charge separation. Hence, the WO_3/g-C_3N_4 is an excellent material for environmental remediation.

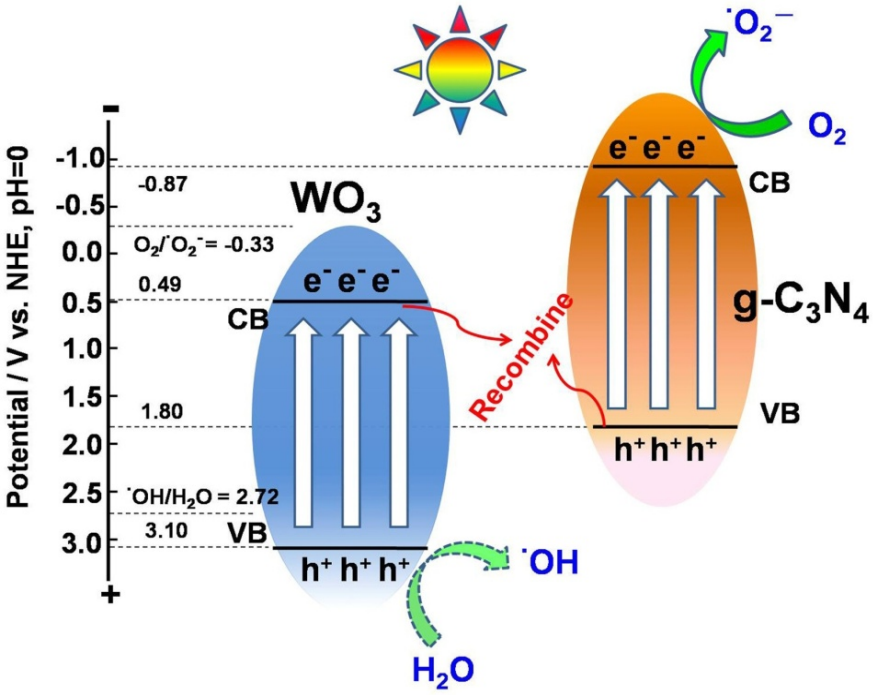

Figure 4. Possible Z-scheme mechanism for the photodegradation of MB over WO_3/g-C_3N_4 composite under visible-light irradiation[19]

SILVER COMPOUNDS BASED WO_3 COMPOSITE PHOTOCATALYSTS

Wang at al. developed the Ag_3PO_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_3PO_4/WO_3 hybrid achieved an progressive photo catalytic activity than pure Ag_3PO_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 $AgIO_3$ andWO_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_3PO_4/h-WO_3complexes were prepared by a modest precipitation method. They found that the Ag_3PO_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_3PO_4/h-WO_3. Also, the Ag_3PO_4/h-WO_3 composites exhibited a good stability compared with the pure Ag_3PO_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/WO_3 nanocomposites were premeditated by the deprivation of tetracycline hydrochloride (TC) under the visible-light illumination. They found that an optimized 20%-AgI/WO_3 revealed a highest photocatalytic performance than that of pure AgI and WO_3. Also, the stability test indicates that the better photostability of AgI/WO_3 nanocomposite. The possible photodegradation mechanism meant for the enhanced photocatalytic activity of AgI/WO_3 towards to the TC degradation is shown in Figure 5[23].

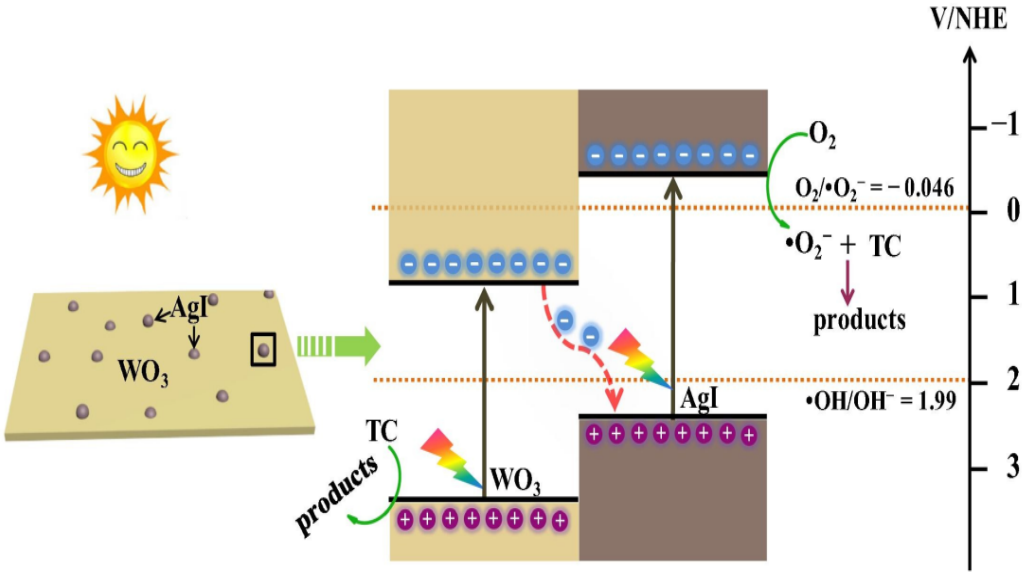

Figure 5. Possible photocatalytic mechanism for the degradation of TC over AgI/WO_3 nanocomposite photocatalysts under the visible-light illumination[23]

Table -1 Applications of semiconducting oxides of CeO_2 and its dopant in Photocatalytic activities

Nano catalyst	Applications/ Degradation	light source	Ref
CeO_2	amido black /acridine orange.	UV–visible	24
CeO_2	cytotoxicity/lung cancer cells		25
CeO_2	MB	UV and sunlight	26
CeO_2	acid orange 7	solar light	26
CeO_2.	Azo dye acid orange 7	visible light	27
CeO_2.	gas-phase purification of C_6H_6	UV–visible	27
CeO_2/Tb_2O_3 NTs	MB	visible light	28
CeO_2-CNT	Metal ions		29
CeO_2 hierarchical NRs	MO	White light, 500 W Xe lamp	30
CeO_2 hierarchical NWs	MO	White light, 500 W Xe lamp	31
CeO_2 microspheres	AO 7	White light, 500 W Xe lamp	32
Ordered meso-CeO_2	AO 7	Visible (λ>420 nm), 1000 W Xe lamp	33
Flower-like CeO_2	AO 7	UV light (λ=365 nm), 2mWcm^{-2}	21
CeO_2 NCs	RhB	350 nm<λ<500 nm, 3.5mWcm^{-2}	34
meso-CeO_2 NRs	$K_2Cr_2O_7$	UV light, 500 W Hg lamp	35

CeO_2 NPs	CR	350 nm<λ<500 nm, 3.5mWcm^{-2}	36
CeO_2 lamellar	MB	UV light, 120 W uviol lamp	37
Octahedral CeO_2	MO	UV	38
CeO_2 NTs	MO	UV	38
CeO_2 nanocrystals	C3H8	White, 500 W Xe lamp	39
CeO_2 nanocrystals	C3H6	White, 500 W Xe lamp	39
Y:CeO_2	IC	UV, 450 W Hg lamp	40
Y:CeO_2	RhB	UV, 450 W Hg lamp	41
CeO_2/Tb_2O_3 NPs	MB	Visible, 50 W Xe lamp	21
CeO_2/Tb_2O_3 NTs	MB	Visible, 50 W Xe lamp	22
Eu:CeO_2	MO	UV, 100 W Hg lamp	23
CeO_2/Y_2O_3	Rh-B	UV light	42
CexZr1-xO_2	Procion® Red MX-5B	UV light	42
Y:CeO_2	IC 32	UV, 450 W Hg lamp	43
(Ce-Pr-Nd)VO_4ND	MB/RhB/RhBL/OG/RBBL	UV	43
($Ce_{0.9}La_{0.1}O_{1.95}$–CeO_2	Pb removal	UV	44
$Zr_xCe_{1-x}O_2$	bromophenol blue dyes	Solar	45
Sm-Gd-CeO_2	MB	UV	46

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 photo catalytic 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.

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