

Chapter 9

Nanomaterials for the Photoremediation of Pollutants



Mohammad Chahkandi and Mahboobeh Zargazi

Contents

9.1	Introduction	284
9.1.1	General Views of Photocatalytic Remediation	284
9.1.2	Photo-Effective Nanostructures	286
9.2	Principles of Photocatalytic Progress	286
9.2.1	Sunlight Interactions	286
9.2.2	Mechanistic View	287
9.2.3	Thermodynamic	290
9.2.4	Kinetics of Catalytic Reactions	290
9.3	The Mechanistic Aspects of Visible/Sunlight Photoactivity	292
9.3.1	Heterogeneous Coupling	294
9.3.2	Z-Scheme	297
9.3.3	p–n Junction Materials	300
9.3.4	Ion-Exchangeable Semiconductors	301
9.3.5	Photocatalytic Compounds Kind	304
9.4	Future Remarks and Limitations	307
9.5	Conclusions	308
	References	309

Abstract The restricted global fear within contaminated ecosystem has been motivated the impress works to employ the photocatalytic degradation of organic pollutants and pesticides. Generally, stability and water solubility of pesticides cause high impacts on environment due to high resistance in ecosystem. Heterogeneous nano-photocatalyst can be introduced as one of the most appealing technologies bearing great remediation performance because of the high surface area and intense correlated activity. The heterogeneous catalytic nanomaterials have been operated to

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harvest, turn, and supply clean and renewable sunlight energy. It can be performed through entire water splitting and CO production to provide green-sustainable solar fuels alongside of wide ranges of environmental aspects. We reviewed in the presented chapter focusing on the application of effective nanomaterials in environmental remediation about industrial and agricultural effluents. For years TiO₂ photocatalyst has been largely utilized but includes restricted activity just in UV spectrum due to wide band gap. Therefore, it is crucial to development of new effective visible light-sensitive photocatalysts with lower band gap that can be activated by a notable percentage of the solar irradiations. Herein, we try to discuss the basic science drives for performance improving of visible/solar light photocatalysts. First, the corresponding principles which include of thermodynamics, kinetics, and recombination rate are followed. The second section reviews the new effective reported visible-activated photocatalytic compounds considering with proposed photoexcitation mechanisms and reducing the charges recombination. Finally, the main challenges and future prospects for better handling of photocatalytic technology were briefly discussed.

Keywords Nano-photocatalyst · Photocatalytic mechanism · UV-activated · Visible-activated · Semiconductor

9.1 Introduction

9.1.1 *General Views of Photocatalytic Remediation*

During the past centuries, increasing human energy demands have been resolved by fossil combustion-based sources such as oil, coal, and natural gases. The used sources caused different overproductions with known and unknown impacts on environment. Awareness about some other mineral fuel energies like nuclear source are insufficient from waste access and defect of technology points of view (Da Rosa 2012). However, the main adverse effects of mineral fuels on air, water, and soil can be regarded as global warming or impact on climate. Therefore, economic and population growing global societies have urgently asked for new, renewable, inexpensive, and easy affordable clean energy sources (Nuraje et al. 2012; Da Rosa 2012; Asmatulu 2015). The clean energy sources can be mainly achieved from natural sunlight, tides, wind, rain, biomass, and other sources without damaging the earth. The greatest and clean sun energy source has huge magnitude releasing near to 105 terawatts versus world's current energy requirement of 12 terawatts, 0.01% of total amount. Nanotechnology as ongoing technology can suggest approaches to degrading production charges, improving efficiency, and stashing energy, healthy environmental remediation, and so on (Asmatulu et al. 2010, 2011; Luque and Balu 2013; Nuraje et al. 2013). Obviously, industrialization have picked up greenhouse gas emission and particulate dust pollutants, continued over

Table 9.1 Advances oxidation processes for environmental remediation

Type of degradation technology	Example	References
Non-photochemical degradation	Sonochemical	Ghows and Entezari (2013)
	Electrochemical	Li et al. (2007)
	Fenton method (Fenton, electro-Fenton, Sono-Fenton)	Homem and Santos (2011) and Zhang et al. (2019)
	H ₂ O ₂ oxidation	Bokare and Choi (2014)
	Supercritical water oxidation	Yao et al. (2018)
	Solvated electron reduction	Yu et al. (2018)
	Enzymatic treatment	Ahmed et al. (2017)
	Ozonation	Yang et al. (2018)
	O ₃ /H ₂ O ₂ O ₃ /Catalyst	
Photochemical degradation	O ₃ /UV	Homem and Santos (2011)
	O ₃ /UV/H ₂ O ₂	Rivera-Utrilla et al. (2013)
	Photo-Fenton, Photo- Fenton-electro, photo-Sono-Fenton	Barrera-Salgado et al. (2016) and Zhao et al. (2017)
	Photo-activated catalytic oxidation by UV/Visible	Chen et al. (2016) and Opoku et al. (2017)

the decades. Alternative route can be addressed by nanomaterials with photocatalytic degradation ability of greenhouse gases and other emission pollutants (Taherzadeh et al. 2013).

Environmental remediation can be performed by different methodologies, and that one of the widely used is chemical degradation. It can be achieved by different methods such as (1) photocatalytic, (2) Fenton method, (3) ozone/UV radiation/H₂O₂ oxidation, (4) sonochemical, (5) electrochemical, (6) supercritical water oxidation, (7) solvated electron reduction, (8) enzymatic treatment, and (9) the electron beam irradiation (Table 9.1) (Andreozzi et al. 1996, 1999; Jayaweera 2003; Gogate and Pandit 2004a, b; Babuponnusami and Muthukumar 2014). UV light and ozone alone have disinfection applications. The combined O₃/UV/H₂O₂ method progresses through oxidation/photolysis reactions, and generation of free hydroxyl radicals can highly degrade the organic pollutants. However, the secondary treatment for complete neutralization of pollutants should be executed through advanced oxidation processes. Advanced oxidation processes are achieved by complete mineralization of matters to H₂O and CO₂ through in fold of strong vibrant hydroxyl and superoxide radicals. Some of the most prevalent advanced oxidation processing technologies are listed in Table 9.1. One of the effective photodegradation reactions can be progressed using nano-semiconductor and solvated O₂ gas to form the promoter radicals. The principles of photocatalysis process of titania substrates were investigated based on “Honda–Fujishima effect” relating to photoinduced water splitting (Fujishima et al. 2008). Heterogeneous photocatalysts introduce efficient advanced oxidation processes within abatement of chemical pollutions. Advanced oxidation processes are associated with advantages of visible/white light-sensitive

photocatalysts having wide range of absorption spectra from UV to visible wavelengths (Herrmann 1995).

9.1.2 Photo-Effective Nanostructures

The binary and ternary metal oxides are initial photoactive particles used in photocatalytic structural devices such as solar cell, photoremediation, and water splitting. In order of environmental concerns, green, easygoing, and safe-producing methods of nanomaterials are fruitful. The desired techniques should include low temperature and high progress rate, with lowered hazardous agents or by-products. For example, one of the best photocatalysts, TiO₂, is generally synthesized by polymerizable complex approach, sol–gel reaction, and solid-state progress. However, the two first ones offer applicable performance than the last one because of providing small crystallite and particle size and controllable particle shape (Nuraje et al. 2012). Pure TiO₂ photocatalysts have not enough power to hydrogen production through water splitting. Therefore, some modification is needed such as loaded Pt or other metal ions to approach band gap of 3.2 eV or lower activated under UV light (Nuraje et al. 2012; Luque and Balu 2013; Asmatulu 2015). Despite above, ZrO₂ having high 5.0 eV band gap as an UV photocatalyst can split water without assisting of any co-catalyst. Photo-UV catalytic ability of ZrO₂ decreased by loading co-catalysts such as Pt, Au, and RuO₂. In the next sections, the base interaction of photon and photocatalysts, the mechanism, and thermodynamic aspects have been discussed. In the following, different kinds of UV-visible-activated catalysts have been investigated, in details.

9.2 Principles of Photocatalytic Progress

9.2.1 Sunlight Interactions

Green photo-induced nanostructures are considered due to its applicability for sustained energy generation and environmental remediation strategies through interactions with infinite sunlight irradiations. Nanoscale structures with great ratio of surface area to volume resulted in highly increase of sunlight interactions compared to bulk format of materials. Nanostructures can be suggested as ideal entrant for a broad diversity of environmental issues grounded on photocatalysis and photosynthesis (Frank et al. 2004; Kay et al. 2006; Verma et al. 2011; Spinelli et al. 2012; Beard et al. 2014; Yeo et al. 2014). Among whole releasing sun energy, only a few small portion is absorbed by the earth. Therefore, the important photosynthesis reactions are proceedings that can influence on human life as cultivation and forestry. Sunlight as continuous light spectrum includes from high wavelengths of radio to low ones of X, and gamma ray ranges in $1-10^{-13}$ m of wavelength

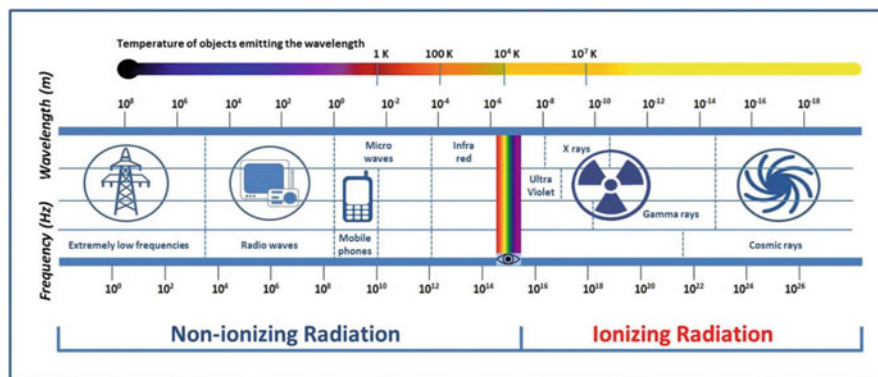


Fig. 9.1 Spectrum of electromagnetic waves. Sunlight as continuous light spectrum includes from high wavelengths of radio to low ones of X, and gamma rays range in $1\text{--}10^{-13}$ m of wavelength. (Saliev et al. 2019)

(Fig. 9.1). The small division of visible wavelengths from violet to red lights is considered in interaction of photocatalyst and visible light.

Actually, the passed sunlight from atmosphere of the earth interacts with photoactive materials in three ways: reflection, scattering, and absorption. Reflection specified as the fraction of reflected energy calls the reflectivity, R :

$$R = \frac{n_1 - n_2}{n_1 + n_2} \quad (9.1)$$

where n_1 and n_2 are refractive indices of two interface sides of the materials. Refractive index is explained as the ratio of light speed in vacuum against material. Scattering is defined as light orientation changing in randomly manner during the interaction to media that is divided to elastic and inelastic scattering kinds. Absorption happens when energy value of the light adapts the transition energy of the electrons of materials. In clear expression, absorption by an isolated material-bearing electronic density leads to the charge transition of the valence band across the band gap to the conduction band (Neil and Ashcroft 2016). For every transferred electron to conduction band, an unoccupied hole in valence band generates a pair known as e^-h^+ . It must be rephrased that absorption as the basic step of photocatalytic process is necessary for often applications of solar energy (Fig. 9.2).

9.2.2 Mechanistic View

There are 5-main steps involving the heterogeneous photocatalyst occurred from bulk of media toward to the final yield include of surface adsorption, photodegradation reactions, and desorption of conclusive products over the surface to the bulk media (see Fig. 9.3).

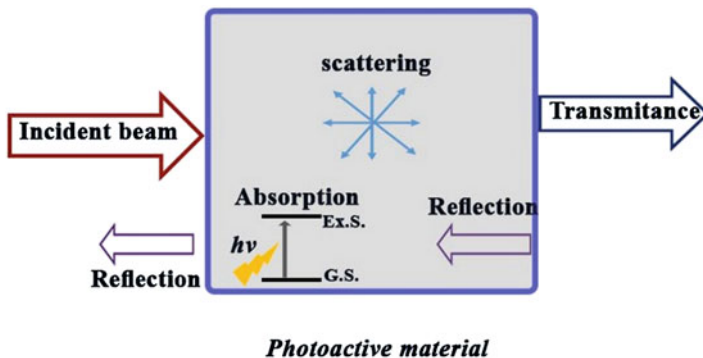


Fig. 9.2 Three ways of interaction of light with the material including reflection, scattering, and absorption. Ex. S. and G. S. represent excitation and ground states, respectively

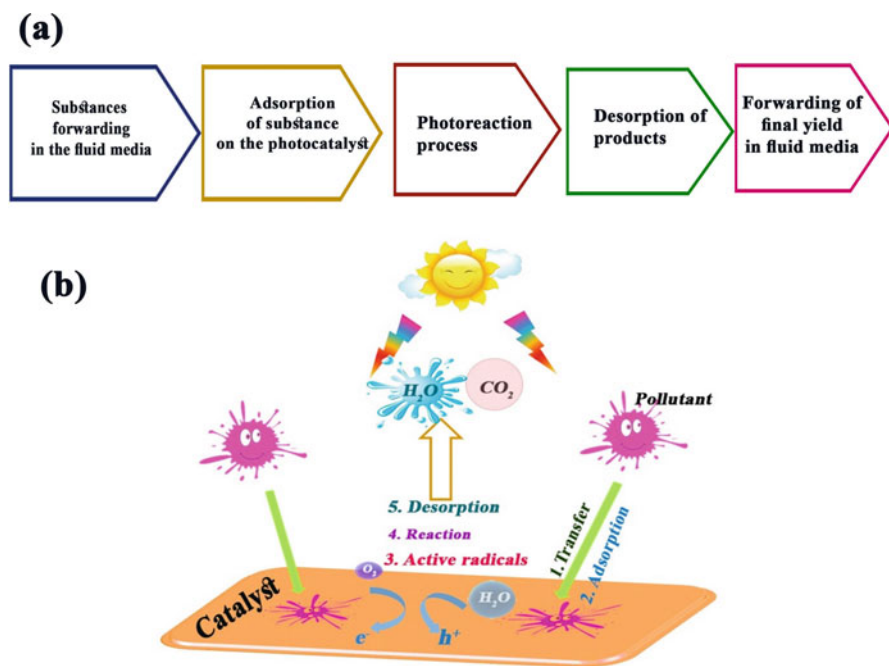


Fig. 9.3 Five possible main steps for interaction of light to the bulk of media and surface of the heterogeneous photocatalyst include surface adsorption, photodegradation reactions, and desorption of conclusive products over the surface to the bulk media

The basic photocatalytic reactions can be explained with six equations (see Fig. 9.4). The absorption of higher-energy photons versus the energy level of photocatalyst band gap is an essential primer step. Equation 9.2: Photon absorption leads to transfer of valence band electrons to conduction band and creation of hole

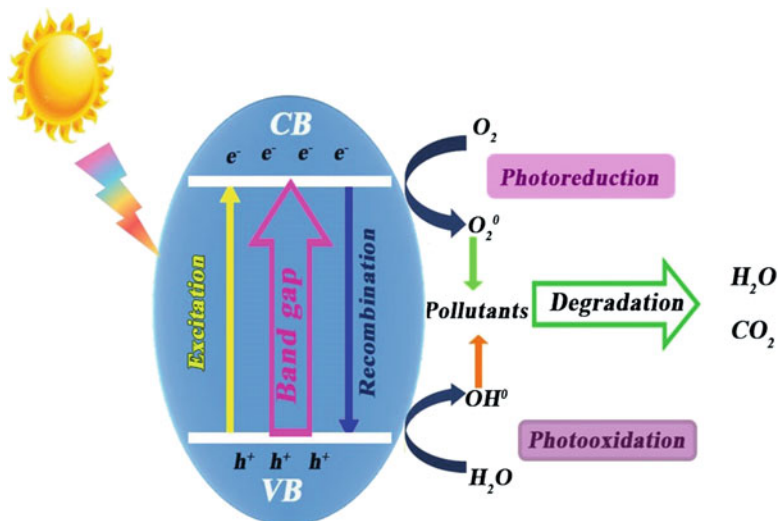
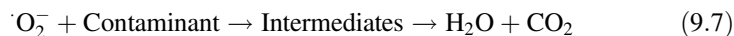
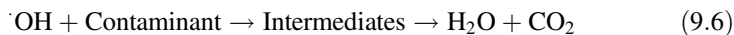
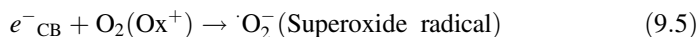
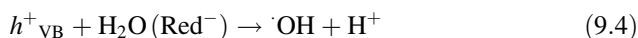


Fig. 9.4 The basic photocatalytic reactions can be explained with six equations: absorption of higher energy photons; transfer of valence band electrons to conduction band; recombination of existing electrons and holes and liberation of heat energy; reaction of produced electrons and involved oxidants; and reaction of holes and reductants. CB and VB stand for conductive band and valence band, respectively

over the valence band. Equation 9.3: The recombination of existing electrons and holes and liberation of energy in heat form is possible. Equations 9.4 and 9.5: Probable reaction of produced electrons and involved oxidants and also reaction of holes and reductants, to build vibrant radicals. Equations 9.6 and 9.7: The following shows degradation of pollution substances to mineralized carbon dioxide and water:



9.2.3 Thermodynamic

The efficiency of catalytic process can be measured by two numeric and energetic methods. The numeric method needs to “inherent quantum efficiency; \emptyset ” definition which means the products value ratio, based on primer photoreaction rate, and to value absorbed photons by system. In practical, in heterogeneous photocatalytic system, a mathematical term named “apparent quantum efficiency; ξ ” is described as the ratio of reaction rate to the intensity of monochromatic light for concentration of i species C_i :

$$\xi_{C_i} = \pm(d[C_i]/dt)_0 / (d[h\nu]_{\text{int}}/dt) \quad (9.8)$$

where $\pm(d[C_i]/dt)_0$ is change of initial rate of species concentration and $(d[h\nu]_{\text{int}}/dt)$ is change of incident photo rate (Hoffmann et al. 1995).

Efficiency of energy conversion, ϵ , can be evaluated by ξ product to the changes ratio of Gibb’s free energy to effective photon energy, E_p (Ohtani 2010):

$$\epsilon = \xi \cdot (\Delta G/E_p) \quad (9.9)$$

The accurate value of recombination rate of hole and electron cannot be measured by the inherent quantum efficiency.

9.2.4 Kinetics of Catalytic Reactions

The reaction rate of general form of Eqs. 9.6 and 9.7 as $A + B \rightarrow C + D$ is given by:

$$r = -dC_A/dt = k C_A C_B \quad (9.10)$$

where C_A , conduction band, and k are concentrations of A , B , and constant of reaction rate, respectively.

As illustrated in Fig. 9.3, heterogeneous photocatalytic process includes adsorption–desorption and reaction over the surface. It can be supposed that adsorption and desorption of reactants over the surface of catalyst is rapid. However, photocatalytic reaction is obviously the slowest step considered as the rate-determining step generally followed by Langmuir–Hinshelwood or L–H model. It should be formulated as:

$$r = -d[\text{Red}]/dt = -d[\text{Ox}]/dt = k\theta_{\text{Red}}\theta_{\text{Ox}} \quad (9.11)$$

where θ_{Red} means fraction of adsorbed reductant over the catalyst surface and θ_{Ox} means fraction of adsorbed oxidant over the catalyst surface.

Moreover, θ_i can be defined based on K_i , adsorption constant:

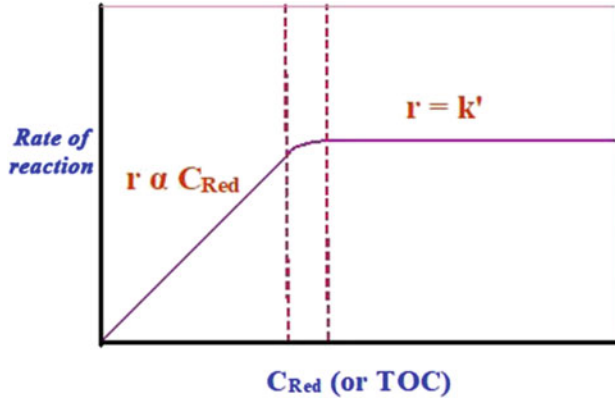


Fig. 9.5 The degradation rates at low concentrations of reductant conforms to first-order kinetics while independent at higher concentrations. C_{Red} stands for concentration of reduction

$$\theta_i = K_i C_i / (K_i C_i + 1) \tag{9.12}$$

Combination of Eqs. (9.11) and (9.12) can be rephrased as:

$$r = k K_{Red} C_{Red} K_{Ox} C_{Ox} / (K_{Red} C_{Red} + 1) (K_{Ox} C_{Ox} + 1) \tag{9.13}$$

Actually, K_i value which is experimentally determined in dark means no photocatalytic reaction. Some simple approximations can reduce the complexity form of Eq. (9.13). The oxidant can be considered as a pure liquid, so $\theta_{Ox} = 1$; or as a fluid solution, based on Henry’s law, $\theta_{Ox} = \text{constant}$. Therefore:

$$r = k' \theta_{Red} = k' K_{Red} C_{Red} / (K_{Red} C_{Red} + 1) \tag{9.14}$$

If $C_{Red} = C_{Red, \max}$, so $\theta_{Red} = 1$ and $r = k'$.

In contrast, if $C_{Red} \ll C_{Red, \max}$, so $\theta_{Red} = K_{Red} C_{Red}$

$$\text{and } r = k' K_{Red} C_{Red} = K_{\text{apparent}} C_{Red} \tag{9.15}$$

Therefore, the degradation rates at low concentrations of reductant conform to first-order kinetics while independent at higher concentrations (Fig. 9.5).

For overall rate estimation as complementary consideration, photomineralization rate of produced intermediates through Eqs. (9.6) and (9.7) can be stated based on total organic carbon; TOC or chemical oxygen demand; COD values (Minero et al. 1996; Malato et al. 2009):

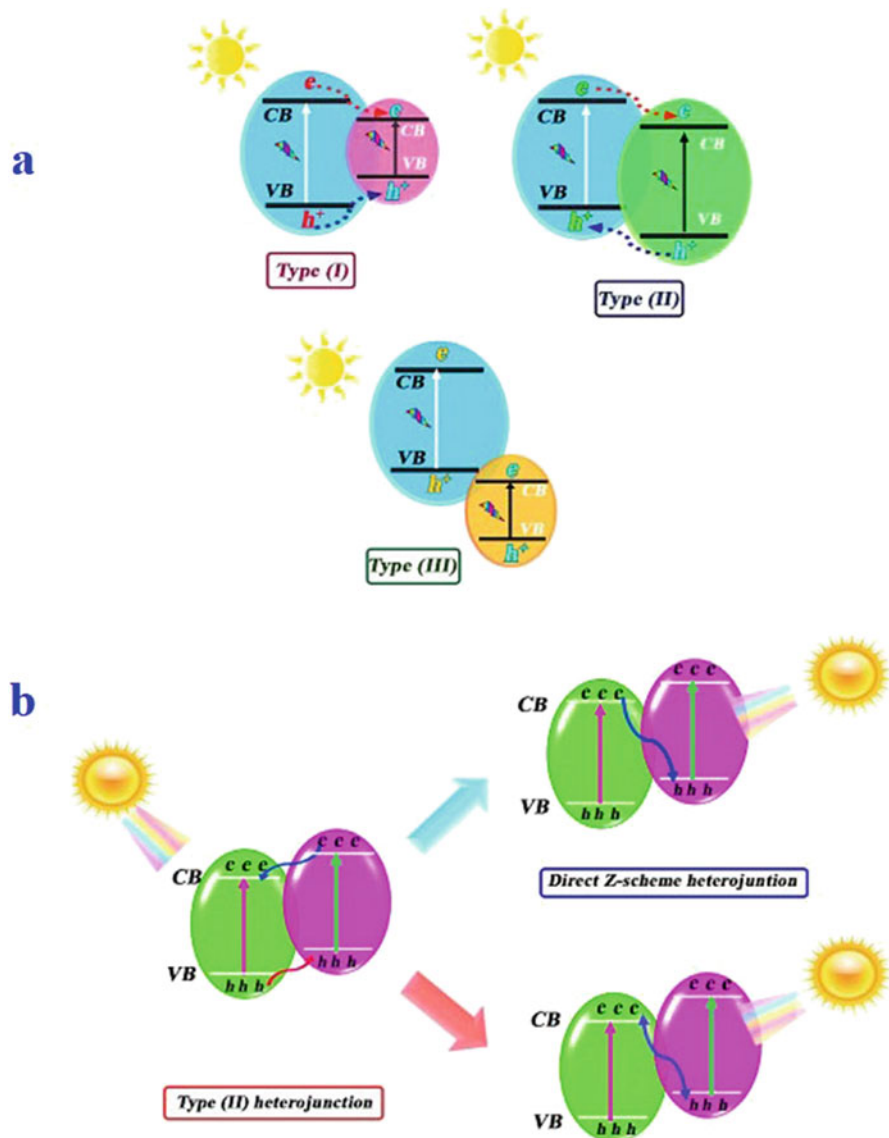
$$r_{TOC,0} = \beta_1 [TOC] / (\beta_2 + \beta_3 [TOC]) \tag{9.16}$$

that $[TOC]_0$ is considered as the prime content of TOC at zero time, $t = 0$.

9.3 The Mechanistic Aspects of Visible/Sunlight Photoactivity

As aforementioned notes, a semiconductor photocatalyst absorbs the energetic photons that lead to the generation of electron–hole pairs with electron photoexcitation through heavy valence band to empty conduction band. As we know, very quick recombination of the generated electron–hole give rise to energy destruction and diminishing of quantum efficiency. Accordingly, novel-improving mechanisms for spare recombination are constantly pursued. The key issue for spare recombination is to stretch the photo-absorption region along with separation performance of electron–hole pairs. Producing of heterojunction kind of crystalline semiconductors is proposed as an operational solution. The effectiveness of a semiconductor within photocatalytic behavior crucially belongs to the energy alignment of the band gap. Interfaces of semiconductor heterojunction can be categorized into three types: straddling gap, type I; staggered gap, type II; and broken gap, type III (Fig. 9.6a). The great improvement can be achieved by conversion of traditional type II into direct Z- and S-schemes. S-scheme is built up as a combination of two n-type semiconductor photocatalysts. (Di et al. 2017; Low et al. 2017; Zhu et al. 2017; Fu et al. 2018, 2019; Tan et al. 2018; Li et al. 2019e) (Fig. 9.6b).

The effective developed photocatalysts can be categorized in four main classes: metal oxides (Zhu et al. 2017; Tan et al. 2018; Li et al. 2019e), sulfides (Tada et al. 2011; Zhang et al. 2012, 2016; Bai et al. 2013; Wei et al. 2018b), valuable metal semiconductors (Miao et al. 2013; Cai et al. 2017; Li et al. 2018a; Zhang et al. 2018b), and non-metallic semiconductors (Feng et al. 2018; Wu et al. 2018; Zheng et al. 2018; Qi et al. 2019; Reddy et al. 2019; Wang et al. 2019b). However, each photocatalyst has some disutility such as heavy metal or harmful leaching pollution, expensive, high thermal treatment, and low stability within catalytic reactions. Wang et al. (2008) reported that an applicable synthesized organic conjugated photocatalyst, named graphite carbon nitride (g-C₃N₄), has the capability of visible light absorption with band gap = 2.7 eV and $\lambda > 420$ nm for water splitting. g-C₃N₄ has various advantages such as easy preparation route, high stability, low cost, and visible frequencies sensitivity (Nayak et al. 2015; Jiang et al. 2018a; Li et al. 2019d; Xu et al. 2019b; Zhu et al. 2019). Therefore, recently huge attentions have been grown for preparation of pure g-C₃N₄ (Ma et al. 2018; Wang et al. 2018; Zhao et al. 2018), elemental loading modification (Wang et al. 2017; Bellardita et al. 2018; Da Silva et al. 2018; Deng et al. 2018; Shanker et al. 2018), heterogeneous composites (Tian et al. 2013; Zhou et al. 2014; Ran et al. 2018a), and diverse morphology preparation (Yang et al. 2015; Yu et al. 2016; Shakeel et al. 2019). The notable issue has many defects which exist with pure bulk g-C₃N₄ including small specific surface area (Sun and Liang 2017; Jiang et al. 2018b), low performance in solar irradiation ranges due to low absorption of wavelengths longer than 460 nm (Ye et al. 2015; Naseri et al. 2017; Shen et al. 2018; Zhang et al. 2018a), difficult film forming, and rapid electron–hole recombination (Hao et al. 2018; Jin et al. 2018; Shi et al. 2018) (see Fig. 9.7). Therefore, new composite compounds with specific morphology can



enhance photocatalytic efficiency (Li et al. 2015b, 2017c; Ong et al. 2016) using improved synthetic methods (Che et al. 2017; Li et al. 2017b), design of electrical structure (Ran et al. 2018b; Wei et al. 2018a; Wu et al. 2019), and nanostructure

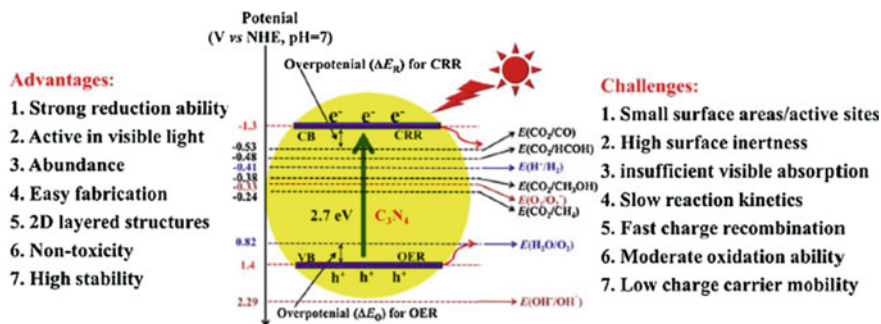


Fig. 9.7 The band gap influencing for redox potential of the appropriate reactions of g-C₃N₄ band edges at pH = 7. (Reprinted with permission of Elsevier from Wen et al. 2017)

manipulation (Dong et al. 2017; Ma et al. 2017; Li et al. 2018b). However, increasing researches about new composite materials of g-C₃N₄ highlight the potentially photocatalytic ability (Li et al. 2019c).

9.3.1 Heterogeneous Coupling

In order to inhibit recombination of formed electron and hole, achieving different surfaces of composited catalyst can be an approach. Therefore, heterostructured catalysts having various potentials of conduction bands and valence bands can be prepared. Through coupling construction, the excited electrons of conduction band having higher energy can move to the coupled catalyst conduction band. Analogously, electrons of valence band state of photocatalyst having higher potential should be excited to the valence band state of the coupled catalyst with lower-energy state (see Fig. 9.8). The progress is equivalent to the hole transferring of valence band with lower potential to the valence band of coupled one having higher potential state. Therefore, recombination rate will be reduced with transferring of generated electron–hole pairs to different surfaces of new coupled photocatalysts, resulting in improving photocatalytic efficiency.

UV-Activated Catalysts

Binary Metal Oxides

The binary metal oxides have mainly metal ions with d^0 configuration, which valence band and conduction band are combined of O 2p orbitals and d metal ones. The general examples are bimetallic TiO₂, Nb₂O₅, ZrO₂, Ta₂O₅, and WO₃, the anatase phase of the first one with lower band gap energy of 3.2 eV, determined as water splitting photocatalyst under UV irradiation. In order of effective photon

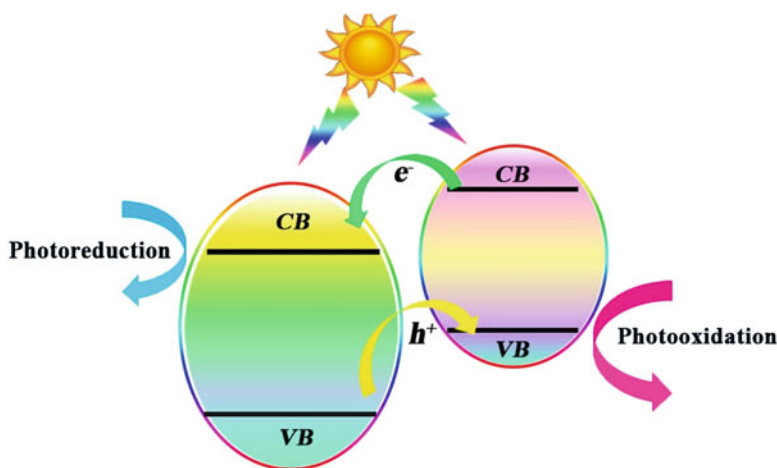


Fig. 9.8 Heterogeneous coupling leads to transfer of photo-prepared electrons and holes between surfaces of coupled photocatalysts and thus inhibition of recombination. CB and VB stand for conductive band and valence band, respectively

absorption of UV range, the band energy gap of photocatalyst should be lower than the UV energy light. The metal oxide having lesser energy of band gap must be reconstructed using cocrystal additives for proper water molecules splitting. TiO_2 with particles loading of Pt, RuO_2 , NaOH, and Na_2CO_3 into photo-cocrystal TiO_2/Pt raises the water splitting activity (Duonghong et al. 1981; Akihiko et al. 1987). Moreover, coupling of TiO_2 with some second semiconductors of metal oxides such as SnO_2 , Ag_xO , and ZrO_2 improves the photocatalytic efficiency. Therefore, the useful formed of heterostructures have higher photocatalytic ability of hydrogen production from an aqueous media including electron donors (Park and Kang 2007; Yuan et al. 2009). Metal oxides based on Nb like Nb_2O_5 with band gap = 3.4 eV can improved photocatalytic hydrogen evolution through coupling of Pt (Chen et al. 2007). The photoactivated splitting efficiency of water by the metal oxides of Ga_2O_3 with band gap = 4.6 eV and CeO_2 with d^{10} electronic configuration of metal ions is highly enhanced when coupled with Zn, Sr, Cr, Ta, Ba, Ca, and RuO_2 (Yanagida et al. 2004; Kadowaki et al. 2007).

Ternary Metal Oxides

Ternary metal oxide based on Ti with interlayered additives of TiO_2 shows efficient splitting reaction of water under UV light. The titanates with layered structures such as $\text{K}_2\text{Ti}_4\text{O}_9$, $\text{Na}_2\text{Ti}_3\text{O}_7$, and $\text{K}_2\text{Ti}_2\text{O}_5$ have enough photoactivity to hydrogen production via splitting reaction of water (Shibata et al. 1987). LaTiO_3 incorporated with NO- and Ba-doped in the presence of additive of alkaline hydroxide show permanent increasing of photocatalytic water splitting (Kim et al. 2005a). SrTiO_3

photocatalytic ability may be improved by some suitable metal cation coupling, such as La and Ga (Qin et al. 2007). Also, perovskite crystallite structure of CaTiO_3 with band gap = 3.5 eV doped with Zr shows higher photocatalytic performance under UV light (Sun et al. 2007). $\text{K}_4\text{Nb}_6\text{O}_{17}$ with layered structure show excellent photosplitting of water in an aqueous methanolic solution. The structure modified with cocatalysts of NiO, Au, Pt, and Cs perform increased photocatalytic activity for H_2 production (Sayama et al. 1998). Tantalate metal oxides like LiTaO_3 with band gap = 4.7 eV, KTaO_3 with band gap = 3.6 eV, and perovskite NaTaO_3 with band gap = 4.0 eV have high water splitting yields that mainly depend on band angles of Ta–O–Ta. Opening the angles near to 180° caused more easily transportation of electron–hole pairs and much reduction of the band gap. Some of W- and Mo-based heterogeneous materials show photoactive performance of water splitting just under UV light such as PbWO_4 with band gap = 3.9 eV and PbMoO_4 with band gap = 3.31 eV (Akihiko et al. 1990).

Visible Light-Activated Catalysts

The pure metal oxide usually bears some disadvantages of great resistivity and fast recombination pace of photo-produced charges. For example, WO_3 , Bi_2WO_6 , Bi_2MoO_6 , and $\alpha\text{-Fe}_2\text{O}_3$ have band gaps 2.8, 2.8, 2.7, and 2.2 eV, respectively, because positions of low conduction band do not have photoactivity about H_2 evolution (Aroutiounian et al. 2002; Ingler et al. 2004; Satsangi et al. 2008). Therefore, recent investigations try to improve the photoconductivity and low recombination rate of charges. One route is metal or non-metal doping to engineer the band gap energy. The electron donor species with higher levels of band gap than valence band of original photocatalyst, or electron acceptor ones with lower levels of band gap than original conduction band, provide wide ranges of band gap of metal oxides with visible light photoactivity. Coupling of TiO_2 with Pt^{4+} and Ag^+ increases the photocatalytic performance underneath both visible and UV irradiations (Kim et al. 2005b; Rengaraj and Li 2006). Pt^{4+} and Ag^+ metal ions participating in visible light absorption resulted in reducing of recombination rate. Using dye for sensitizing of metal oxides caused in reduction of wide band gap is another approaching method within improving the visible light sensitivity of water splitting. The process progresses with shift of excited electron of HOMO to LUMO of dye molecule and next transferring to conduction band of original photocatalysts. TiO_2 loaded with dye and $\text{K}_4\text{Nb}_6\text{O}_{17}$ show enhanced capability of H_2 evolution. Moreover, numerous coordination compounds Co(II), Zn(II), Pt(II), and Cr(II) with polypyridine, phthalocyanine, alizarine, and metalloporphyrins perform photocatalytic efficiency within H_2 generation (Shimidzu et al. 1985). A new heptazine-based porous organic polymer named POP–HE show intense visible light catalytic activity of oxidative conversion of benzyl alcohol to benzaldehyde. The researchers claimed that POP–HE compound has higher photocatalytic efficiency than graphite carbon nitride (Xu et al. 2019a). Another new research shows that anchoring of Pd nanoparticles to TiO_2 can permanently improve the

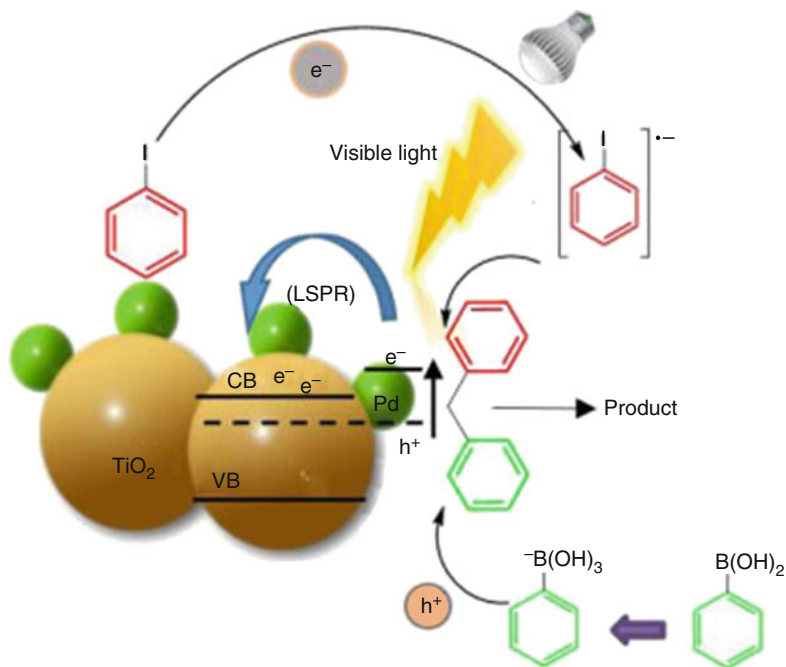


Fig. 9.9 Proposed mechanism of charge separation in Pd/TiO₂ compounds led to enhancement of Suzuki–Miyaura coupling reaction. LSPR represents localized surface plasmon resonance. (Reprinted with permission of Elsevier from Koohgard and Hosseini-Sarvari 2018)

photocatalytic activity of TiO₂ heterogeneous coupled catalyst within Suzuki–Miyaura coupling reaction. The applied synthetic method was resulted in reducing of recombination rate of hole–electron through the shown mechanism in Fig. 9.9 (Koohgard and Hosseini-Sarvari 2018). Li et al. introduced an effective coupled photocatalyst of BiVO₄/Ag₂O with low band gap prepared with impregnation–evaporation technique. BiVO₄/Ag₂O has shown higher photodegradation rate within methyl orange in comparison with pure BiVO₄ as a p–n heterojunction type (Li et al. 2015a). Also another p–n heterojunction semiconductor with BiVO₄ coupled with Cu₂O showed more photocatalytic degradation of methylene blue and colorless organic pollutant of phenol than BiVO₄ (Wang et al. 2013). The discussed and some more of visible light photocatalysts have been listed in Table 9.2.

9.3.2 Z-Scheme

Despite that many pure or couple metal oxides show suitable photocatalytic performance especially water splitting under irradiation of UV or visible light, some weaknesses diminish the quality of process:

Table 9.2 Photocatalysts coupled heterogeneously and the related usage

No.	Photocatalyst	Usage	References
1.	TiO ₂ /Pt/RuO ₂	Water splitting/Rhodamine B	Duonghong et al. (1981)
2.	TiO ₂ /Ag _x O	Hydrogen evolution	Park and Kang (2007)
3.	Nb ₂ O ₅ /Pt	Hydrogen production	Chen et al. (2007)
4.	POP-HE	Benzyl alcohol oxidation	Xu et al. (2019a)
5.	TiO ₂ /Pd	Suzuki-Miyaura coupling	Koohgard and Hosseini-Sarvari (2018)
6.	BiVO ₄ /Ag ₂ O	Methyl Orange	Li et al. (2015a)
7.	g-C ₃ N ₄ / BiOCl _x Br _{1-x}	Rhodamine B and Rhodamine 640	Shi et al. (2014)
8.	Bi ₅ O ₇ I/Bi ₂ O ₃	Malachite Green	Cheng and Kang (2015)

- (a) A low percentage of light absorption up to the photocatalysts band gap
 (b) Returned reaction of water formation

Beyond three interface kinds of heterojunction semiconductors, only type II bears acceptable photocatalytic activity. The conversion of type II with a direct Z-scheme mechanism can more increase the efficiency and suggests the solution for the abovementioned disadvantages. The system includes two photocatalysts coupled through redox charges carrying. The mentioned system is a biomimetic mechanism occurred in the photosynthesis reactions for transferring of the photo-induced electron of H₂O to nicotinamide adenine dinucleotide phosphate. The formed couple of heterojunction includes several photocatalysts species as the relevant redox potentials of the generated charges are held at higher capacity. Therefore, a recombination reaction of a small amount of electron–hole pairs causes them to be sacrifice that makes the excited charges with higher energies leave behind (see Fig. 9.10). The interesting mechanism provides the capability for visible photons with relatively low energies to promote an efficient degradation process. Since Z-scheme mechanism donates the mentioned benefits to a single photocatalyst having wide band gap, the respected studies have been greatly increased. Some of them are summarized in Table 9.3. One of notable study reports Pt-loaded in ZrO₂–TaON and Pt-loaded in WO₃ that demonstrate permanent photocatalytic H₂ generation from water with high apparent quantum yield at 420 nm. ZrO₂ extends the lifetime of the photogenerated charges and inhibition of the recombination because of modification of TaON n-type semiconductor (Maeda et al. 2010). A modified silver chromate with graphene oxide as binary Ag₂CrO₄–GO photocatalyst has shown notable degradation of methylene blue and phenol under visible light (Xu et al. 2015). The energy levels of conduction band and valence band for single Ag₂CrO₄ and graphene oxide were measured ca. 0.47 V and 2.27 V vs. NHE and ca. –0.75 V and 1.75 V vs. NHE, respectively. The photogenerated electrons of the conduction band of silver chromate combine with cavities of valence band from graphene oxide resulted in leaving of conduction band electrons of graphene oxide with higher potential and more negatively potential than the –0.28 V as potential value of O₂^{*}/O₂. In some recent studies, the effective Z-scheme heterojunctions

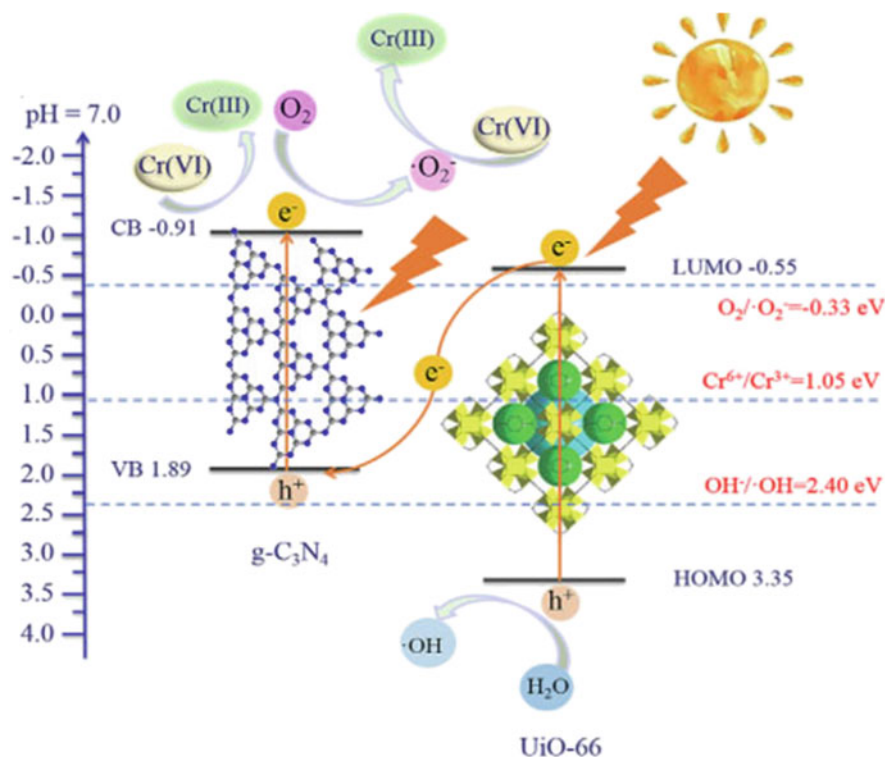


Fig. 9.10 A mechanistic view of photocatalytic Cr(VI) reduction mechanism of g-C₃N₄/UiO-66. HOMO energy of UiO-66 which is smaller than OH⁻/[·]OH pairs caused to form [·]OH with oxidation of OH⁻ or H₂O. CB and VB stand for conductive band and valence band, respectively. (Reprinted with permission of Elsevier from Yi et al. 2019)

within visible light photocatalytic performance have been prepared by loading of cuprous oxide, graphite carbon nitride, bismuth oxide, cadmium sulfite, and metal organic frameworks (Li et al. 2019a; Yi et al. 2019; Hu et al. 2020; Wang et al. 2020; Xu et al. 2020). A new interesting one is a heterojunction of g-C₃N₄/UiO-66 (BG_xU_y) prepared by 3D UiO-66 and 2D g-C₃N₄ sheets through ball milling method. The superior improvement of Cr(VI) reduction upon white light irradiation was shown in comparison with both of single contents. Yi et al. (Yi et al. 2019) reported a facile fabrication of 2D/3D Z-scheme g-C₃N₄/UiO-66 heterojunction with enhanced photocatalytic Cr(VI) reduction performance under white light (see Fig. 9.10).

Table 9.3 Photocatalysts of Z-scheme modified and their summarized reaction

Sr. No.	Photocatalyst	Usage	References
1.	Pt-loaded WO ₃ & Pt-loaded ZrO ₂ /TaON	Water splitting	Maeda et al. (2010)
2.	Ag ₂ CrO ₄ -GO	Methylene Blue and Phenol	Xu et al. (2015)
3.	Cu ₂ O/Bi ₂ MoO ₆	Decontamination of Sulfadiazine and Ni(II)	Xu et al. (2020)
4.	CdS/polyimide (PI)	Hydrogen evolution	Hu et al. (2020)
5.	α -Fe ₂ O ₃ /d-C ₃ N ₄ and α -Fe ₂ O ₃ /g-C ₃ N ₄	Tetracycline	Wang et al. (2020)
6.	BiOBr/Bi ₁₂ O ₁₇ Br ₂	Resorcinol degradation and NO removal	Li et al. (2019a)
7.	Tungsten trioxide/polyimide (PWO/PI)	Imidacloprid	Meng et al. (2018)
8.	Er ³⁺ :Y ₃ A ₁₅ O ₁₂ @NiGa ₂ O ₄ -MWCNTs-WO ₃	Methylene Blue and Hydrogen evolution	Tang et al. (2019)

9.3.3 p–n Junction Materials

Other improved photocatalysts as dual semiconductors reported in literature are heterojunctions of two p-type and n-type semiconductors. The considered photocatalysts including trivalent and pentavalent additives, respectively, resulted in electron–hole generation in the electronic states of semiconductor (Beydoun et al. 2000; Spasiano et al. 2013). The designed p–n junctions of photocatalysts allow the charge transfer between two semiconductor contents through the direct contact. The structure provides the advantage of separation of charge carriers along with reduction of electron–hole pair recombination. The charge transfer mechanism in a general p–n junction type is illustrated in Fig. 9.11. Through the connection of two types of p–n semiconductors, a small content of electron from n-type is transferred to p-type. Therefore, the resulted hole in interfacial establishes an inner electric field where the n-type extends the positive charge and vice versa for p-type. The formed inner electric field prohibits to flux of the remaining hole and electron into the related negative and positive fields. Therefore, the effective charge separation and reduced recombination rate can be achieved.

The position of valence band of g-C₃N₄ as 1.89 eV vs. NHE is more in comparison with OH⁻/^{*}OH standard potential with 2.40 eV vs. NHE, so photo-excited holes on g-C₃N₄ will not respond with OH⁻/H₂O to form ^{*}OH. It can be rephrased that HOMO energy of UiO-66 with 3.35 eV vs. NHE is smaller than OH⁻/^{*}OH pairs with 2.40 eV vs. NHE, caused to form ^{*}OH with oxidation of OH⁻ or H₂O.

Lee et al. (Kim et al. 2017; Chae et al. 2019) introduced some p–n junction having photocatalytic behavior or usable in diodes/solar cells with semiconductor combination, viz., p-poly(3-hexylthiophene)/n-ZnO and p-Co₃O₄/n-ZnO. For the first one

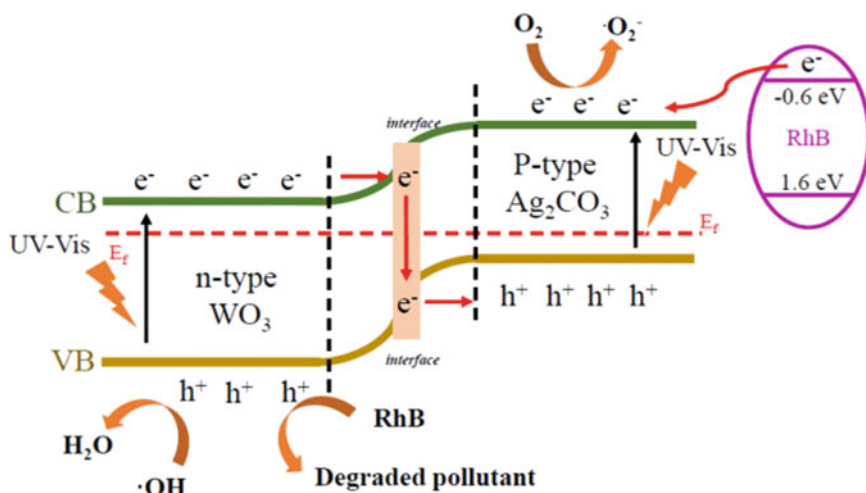


Fig. 9.11 Photoexcited electron–hole separation in n–p heterojunction $\text{WO}_3\text{-Ag}_2\text{CO}_3$ at photocatalytic degradation process of Rhodamine B. CB and VB stand for conductive band and valence band, respectively. RhB stands for Rhodamine B. (Reprinted with permission of Elsevier from Gao et al. 2019)

Table 9.4 *p-n* heterojunction photocatalysts and the summarized usage

Number	Photocatalyst	Usage	References
1.	$\text{TiO}_2/\text{Cu(II)}$	Production of Benzaldehyde	Spasiano et al. (2013)
2.	$\text{TiO}_2/\text{Fe}_3\text{O}_4$	Photodissolution	Beydoun et al. (2000)
3.	$p\text{-WO}_3/n\text{-Ag}_2\text{CO}_3$	Rhodamine B	Gao et al. (2019)
4.	$p\text{-P3HT}/n\text{-ZnO}$	Rhodamine 6G	Chae et al. (2019)
5.	$p\text{-Co}_3\text{O}_4/n\text{-ZnO}$	Light-Emitting Diode	Kim et al. (2017)

through self-grown organic content over ZnO surface, the hybrid *p-n* junction was prepared. It shows the catalysis activity for Rhodamine 6G degradation (Chae et al. 2019) and the next one prepared from aqueous media at low temperature and growing of ZnO over Co_3O_4 having light-emitting diode property (Kim et al. 2017). Some of more recent introduced *p-n* heterojunction photocatalyst are collected in Table 9.4.

9.3.4 Ion-Exchangeable Semiconductors

The wide range of ion-exchangeable compounds with layered structures can be classified into oxides and hydroxides. The ion-exchangeable compounds bear zigzag lepidocrocite sheet type intercalated with counter ions of hydrates protons arrive with high capability of solar energy utilization. As above discussed, adequate

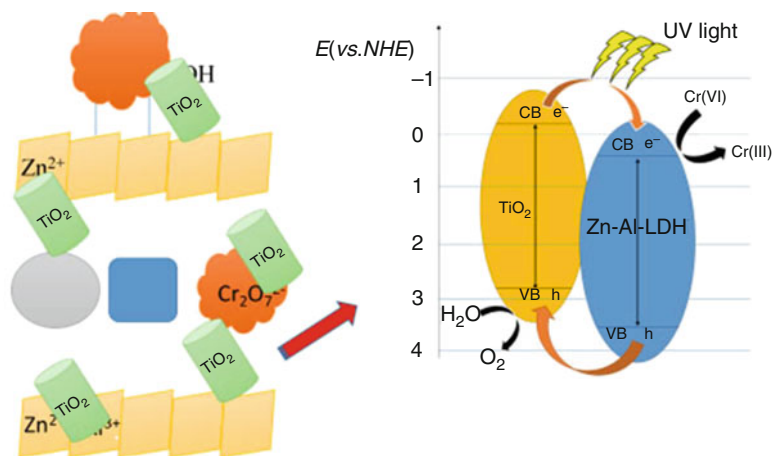


Fig. 9.12 Photocatalytic reduction of Cr(VI) using Zn-Al-layered double hydroxide and TiO₂ composites. CB and VB stand for conductive band and valence band, respectively. (Reprinted with permission of Elsevier from Yang et al. 2019)

separation of electron–hole with low recombination rate is a key involving factor of performance of photo-remediation, water splitting, and general photocatalytic applications. An advanced method to gain the purpose of adequate separation of electron–hole is structural manipulation of layered materials with interstitial inserting of heteroatoms to engineering charge transfer procedure (Zong et al. 2011; Gao et al. 2013; Xiong et al. 2016; Cui et al. 2017; Li et al. 2017a; Cao et al. 2018). Further alternative structure is two-dimensional layered double hydroxide having general formula of $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-1})_{x/n} \cdot m\text{H}_2\text{O}$. The negatively charged A anion is accommodated betwixt of positive-charged M layers of two various divalent and trivalent metal ions (Chen et al. 2019; Jo et al. 2019; Li et al. 2019b; Wang et al. 2019a; Yang et al. 2019). Generally, the main applicable researching fields on ion-exchangeable materials can be highlighted as dye degradation, removal of toxic gaseous like NO, toluene, and so on, water splitting, light-emitting diode, solar cell, Cr(VI) reduction, CO₂ transformation to carbonic fuel like methane, and so on (Zong et al. 2011; Gao et al. 2013; Xiong et al. 2016; Cui et al. 2017; Lee et al. 2017; Li et al. 2017a, 2018c, 2019b; Cao et al. 2018; Chen et al. 2019; Yang et al. 2019; Jo et al. 2019; Wang et al. 2019a). The reported ion-exchangeable layered sheets having negatively charged particles intercalated between layers with positive charge have different species like carbonate/Zn, ZnNi and ZnCu hydroxides, carbonated/Bi₂WO₆, TiO₂/polyvinyl alcohol, alkaline metal ions/carbon nitride, NO₃⁻/g-C₃N₄, and so on. As obviously illustrated in Fig. 9.12, the titania nanoparticles were uniformly intercalated in the layered double hydroxide of Zn–Al. The combination of TiO₂/Zn–Al–layered double hydroxide is the main reason for enhancing performance of transformation of photogenerated electron–hole and separation for reduction of Cr(VI) (Yang et al. 2019).

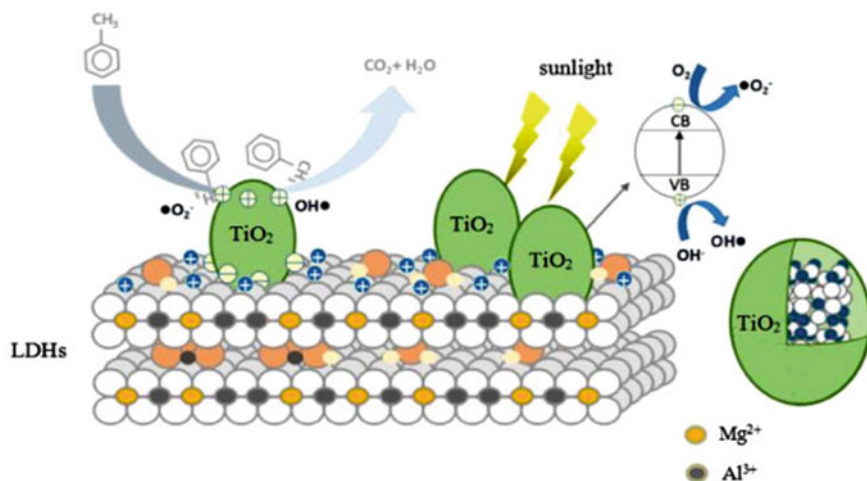


Fig. 9.13 A proposed photocatalytic mechanism of $\text{TiO}_2@$ layered double hydroxide under simulated sunlight. CB and VB stand for conductive band and valence band, respectively. LDH represent layered double hydroxide. (Reprinted with permission of Elsevier from Wang et al. 2019a)

Lee et al. (Lee et al. 2017) claimed to fabrication of sandwich structures bear transparent pliable light-emitting diodes with capable usage in wearable electronic instruments with transparent textiles. Lee et al. (Lee et al. 2017) used electrospinning method to intercalating light-emitting diodes of $\text{ZnO}@$ graphene quantum dots in transparent nanofiber textile to safeguard QLED devices versus the degradation. Lee et al. (Lee et al. 2017) attended the obtained results can inspire new-generation methods of wearable electronic cloths and so on.

Moreover, Wang et al. (2019a) reported a new synthesized $\text{TiO}_2@$ layered double hydroxide having permanent photocatalytic degradation of gaseous toluene under true sunlight irradiation. Actually, TiO_2 was formed through hydrolyzation of tetrabutyl titanate over initially designed MgAl -layered double hydroxide substrate. Large surface area of designed substrate, acceptable separation of generated hole and electron charges, and existence of necessity amount of OH^\bullet and $^\bullet\text{O}_2^-$ radicals are the main reasons of highly observed photocatalytic efficiency. For more information see proposed mechanism in Fig. 9.13.

Along with photodegradation of organic pollutants like dyes, the ion-exchangeable intercalated and layered double hydroxides show the ability for hydrogen and oxygen generation and energy production. Some of the interested recently reported results have been listed in Table 9.5.

Table 9.5 Ion-exchangeable photocatalysts having layered structure and their summarized applications

Number	Photocatalyst	Application	References
1.	Li/g-C ₃ N ₄	Rhodamine B	Zhang et al. (2019)
2.	PbS-CdS/Ti ₆ O ₁₃	Reactive Black 5	Sehati and Entezari (2017)
3.	g-C ₃ N ₄ NT/rGO	Rhodamine B	Wei et al. (2019)
4.	RGO@ZnAlTi-LDO	Cr(VI) reduction	Ye et al. (2019)
5.	Nd/CoAL LDH	Acid Red 14/Ciprofloxacin/Ibuprofen	Khodam et al. (2018)
6.	CoNiSe ₂ LDH	Hydrogen evolution	Yang et al. (2019b)
7.	NiFeSP/Nickel Foam	Hydrogen evolution	Xue and Sun (2019)
8.	CoOx/ZnS@CdS/Ni	Hydrogen production	Xin et al. (2018)

9.3.5 Photocatalytic Compounds Kind

Numerous photocatalysts have prepared and examined the activity toward environmental purification. Many of them show high performance under UV irradiation. Finally, there have been continual tries to development and improvement of visible light photocatalytic efficiency. The related efforts necessitate more studies of physicochemical properties of powerful photocatalysts.

TiO₂ as one of known powerful photocatalyst can be modified to achieve higher than promising results of photocatalytic activity. The sophistication include loading of TiO₂ with carbon, fullerene, graphite, activated carbon, different forms of grapheme oxide, nanosheets, single-walled carbon nanotubes, multiple-walled carbon nanotube, and so on (Wu et al. 2010; Cong et al. 2011; Meng and Oh 2012; Mohammadi and Sabbaghi 2014; Rong et al. 2015). However, some alternative modifications have been attended on the incorporation of metallic and nonmetallic elements (such as S, I, N, La, and Fe) in related structure (Li et al. 2011; Collazzo et al. 2012; Niu et al. 2013). Loaded TiO₂ over MWCNT using a modified sol-gel technique was shown better activity of TiO₂/MCNT composite within photodegradation of Reactive Black 5 dye in comparison with function of single TiO₂ (Hamid et al. 2014). Except modifications of titania, the photocatalysts can be widely classified as oxides, oxyhalides, and sulfides of metals and non-metals. In addition, their combinations and composite compounds have been investigated on different substrates. Actually, the catalytic performances of modified titania compounds for contaminant photodegradation for irradiation of UV-visible-solar light were examined. Table 9.6 was subdivided with numerous recent reported photocatalysts having high efficient performance.

Table 9.6 Routine classification of effective visible/solar light photocatalysts

Number	Class	Photocatalyst	Irradiation	Dye/pollutant	Light time	Destruction	References
1.	Bi_2S_3	Bi_2S_3 coated on Stainless steel mesh	Natural sunlight	Cr (VI)/Rhodamine B	60 min	Photodegradation of single mode of 10 ppm Cr(VI) and binary mixture of 10 ppm Cr(VI) and 5 ppm RhB	Chahkandi and Zargazi (2019)
2.	BiFeO_3	Coated on SS mesh	Natural sunlight	Phenol	30 min		Zargazi and Entezari (2019a)
3.	Bi_2WO_6	Coated on SS mesh	Natural sunlight	4-Nitrophenol/ chlorophenol	140 min		Zargazi and Entezari (2019b)
4.	Bi_2WO_6	Flower like powder	Natural sunlight	Rhodamine B/Methylene Blue	30 min		Zargazi and Entezari (2018)
5.	$\text{g-C}_3\text{N}_4$	Heptazine-based $\text{g-C}_3\text{N}_4$	Natural sunlight	Water splitting	–	High efficient visible light photocatalyst of C_6N_7 monolayer for water splitting	Liu et al. (2019)
6.	BiOC	$\text{Ag@Ag}_2\text{O/BiOC}$	150 W xenon	Rhodamine B	120 min	Heterojunction of $\text{Ag@Ag}_2\text{O/BiOC}$ as efficient photodegradation of 10 ppm RhB	Zhao et al. (2019)
7.	BiOBr	p-n junction of $\text{Bi}_4\text{Tl}_3\text{O}_{12}/\text{BiOBr}$	$\lambda > 400$ nm	Ciprofloxacin/ tetracycline	180 min	p-n junction of $\text{Bi}_4\text{Tl}_3\text{O}_{12}/\text{BiOBr}$ as photodegradation of 20 ppm CIP/TC	Shen et al. (2019)
8.	$\text{BaTa}_2\text{O}_6/\text{Ir,L a}/\text{SrTiO}_3/\text{Ir}$	Z-scheme BaTa_2O_6 and SrTiO_3 doped with Ir and La	300 W Xe lamp	Water splitting	–	Z-scheme $\text{BaTa}_2\text{O}_6/\text{Ir,L a}/\text{SrTiO}_3/\text{Ir}$ as effective for H_2 and O_2 evolution	Kudo et al. (2019)

(continued)

Table 9.6 (continued)

Number	Class	Photocatalyst	Irradiation	Dye/pollutant	Light time	Destruction	References
9.	Fluorescein	Fluorescein	10 W blue LED lamp	Synthesis of benzimidazoles		Benzimidazoles synthesis from aromatic aldehydes and o-phenylenediamines	Li et al. (2019f)
10.	FeOCPc	FeOCPc@Ni	Sunlight lamp (220 V, 8 W, white light LED)	Methyl orange and p-nitrophenol	30 min	Degradation of 97.91% and 97.99% of MO and PNP by (FeOCPc@Ni)	Ma et al. (2019)
11.	RGO	Silver doped RGO	350–370 nm	Oxidative coupling of benzylamines	12 h	Plasmonic photocatalyst of silver for benzylamines coupling	Kumar et al. (2019)
12.	Amine functionalised ZnCr LDH–MCM-41	Au/Pd alloy on an amine functionalised ZnCr LDH–MCM-41	300 wt xenon lamp	One-pot imine synthesis	45 min	Au/Pd bimetallic alloy loaded amine (APTES) functionalised LDH (Layered double hydroxide)–MCM-41 composite for imine synthesis	Sahoo et al. (2019)
13.	MOF	Pt/[Zn2(BODIPY)(BPDC)2]·H2O	420 nm	Hydrogen production	–	Visible photocatalyst of pillared-paddlewheel type metal-organic framework decorated with Pt nanoparticles for efficient H2 generation	Yang et al. (2019a)
14.	BVO4	Z-scheme ZnRh2O4/Au/BiVO4	Xenon lamp $\lambda > 400$ nm	Liberation of H2 and O2	–	Hierarchical structure of efficient photocatalyst of ZnRh2O4/Au/BiVO4 for production of H2 and O2	Takashima et al. (2019)

9.4 Future Remarks and Limitations

During the twentieth century and for future enhancing outlook, one of the main universal fears should be environmental remediation aspects. The required energy for remediation and environmental have close dependence about numerous issues having interplaying effects. The ultimate goal of green remediation for minimizing the greenhouse gas emissions needs most spending efforts. The well-known different nanomaterials have been introduced to achieve detection and elimination of pathogens. The respected nanomaterials can act through applicable routes with high sensitivity, lower cost, in-line and real-time detection, lower turnaround times, and more throughput and transportability in environmental purification. Among them, nanomaterials of metal oxide and metal especially chemical-functionalized ones can be utilized for removal of aqueous and aerial organic pollutants. Further improvements have to be exerted in selective and complete photocatalytic remediation through degradation of contaminants to non-toxic products to changing of pH and concentration of chemical staffs and cost optimization. TiO_2 has been considered one of the most effective ones because of its stability and some other advantages. However, several efforts have been and are being followed to decrease the major failure of TiO_2 to enhance usage in a huge area of solar light for more asked applications. The original importance of sophistication of proper band gap and chemistry of surface/interface addressed the required researches. The appropriate studies are (i) usage of metals–non-metals having general suitable characters as semiconductor, surface plasmon resonance, and so on, (ii) introduction of novel composite compounds; (iii) study of the effect of dopants–additives–sensitizers; (iv) finding the catalytic mechanism; (v) production of thin films of photocatalysts within titania, alumina, stainless steel, and molecular sieves; (vi) enhancing the effective surface area of photocatalyst; (vii) development of more sensitive photocatalyst in natural sunlight against of fictional light; and (viii) applying of diverse synthesis methods such as hydrothermal, co-precipitation, electrochemical, sol–gel, and so on. Another important challenge regarded to designing of appropriate photoreactor and the commercial concerns. Despite the great contents of mercantile contaminants needing remedy, the running conditions of technology should not be enough. However, at first an effective multiphasic impact of pollutant, oxygen, solar light, and photocatalyst is required. In order to commercialize of scale implementation for reliable scale-up, the specification of eminent factors and simulation of a reliable rate declaration are necessary. Investigations are still pursuing to improve quantum yield and maximize the impact of substances and photons regarding fluctuations in solar irradiation. Nonetheless, designing of photoreactors are followed according to alternative and approximate kinetic statements. Main designs of a photoreactor are performed for concentrating collector–reactor, compound parabolic collector–reactor, and non-concentrating collector one (Blanco et al. 2009; Braham and Harris 2009; Spasiano et al. 2015). Of the related more routine designs, compound parabolic collector–reactor includes more advantages about utilizing both of beam and reactive components and is resulted as the most modern

and applicable design (Tanveer and Tezcanli Guyer 2013). However, even the perfected design involved with some process limitations include (i) more effective performance for oxidative process like dyes with low concentration, (ii) sensitivity to mutability in solar intensity, (iii) complete contact of catalyst and effluent and then asking for separation of catalyst and treated effluent, and (iv) far from of headed commercialization. Resolving the last case along with commercial livability needs a facile, cost-effective, sustainable, and safety operation. To achieve the respected goals and minimize the pertinent limitations, it seems employing of proper UV-visible light photocatalysts is promised.

9.5 Conclusions

One can state that the best technique and material for pesticide removing can be chosen according to all involved parameters such as pH, temperature, quantity of contaminated environments, kind of matrix, and solubility of pesticides. The applied physicochemical process of pesticides remediation is permanently based on the forms of usage energy to degradation of the related pollutants, along with photolysis, ultrasound, and the other alternative methods. For purpose of pesticides remediation, metal oxide photocatalysts like TiO_2 using Fenton reactions joined to light, electric current, and ultrasound can highly extend the destruction of pesticides especially in aqueous phase. However, the current study was furnished the fundamental issues of the photocatalytic process. The most important ones contents are appropriate mechanism, thermodynamics, kinetics and recombination of reaction, suggested mechanism of an active photocatalyst, and the impact of effective factors on photocatalytic performance. Typical heterogeneous photocatalysis progresses by generation of electron–hole pairs commenced through band gap agitation of particle of a semiconductor. Adsorption of a photon with required potential equal or greater than band gap as the initial necessity of photocatalytic reactions resulted in electron transition from valence band to conduction band. Desired thermodynamically catalytic process can be evaluated based on intrinsic, apparent, and official quantum yield and efficiency of conversion. Conclusive measurement of total carbon content of the contaminants in terms of TOC or COD can be used to quantity determination of the photoreaction rate in a pseudo-L–H model. Since visible light active photocatalysts have small band gap energy, arresting of charge recombination is needful. The main mechanisms of effectual excitation and charge pair separation have been noted and discussed with clear examples. The governed parameters influencing on photocatalytic activity have been studied at length, completed with accounted results in literature. The parameters are (i) intrinsic photocatalyst type related to contents and band structure, (ii) irradiation energy effect on the number of generated electron–hole pairs, (iii) kind and character of pollutants having different functional groups, (iv) scattering and blockage of adventure light that can restrict the amount of loaded catalyst into the system, (v) pH of media and substrate, and (vi) value and property of dopant in composited catalyst–substrate influenced on surface

chemistry. However, a plenary path across for achieving optimized factors should be figured out. For applicable scale-up of photocatalysis process, an impact face of the photocatalyst and contaminant/goal, irradiation light, and O₂ should be provided. Finally, the most attended conclusions can be derived from the presented review chapter as:

1. Effective photocatalysis using natural sunlight energy and without any new generated footprint can decolorized/degrade the industrial effluent including paints and/or organics.
2. Manipulation of a photocatalyst band gap by hetero-coupling with the purpose of extending of absorption of visible region of spectrum.
3. Investigation of effective parameters can be useful to improve the photocatalytic performance.

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