Chapter

Supported-Metal Oxide Nanoparticles-Potential Photocatalysts

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Abstract

Recently, nanosized metal oxides play an essential role in the photocatalytic system due to their ability to create charge carriers during the light irradiation. Metal oxide nanoparticles display excellent light absorption properties, outstanding charge transport characteristics, which are suitable in the photocatalytic system for the treatment of wastewater. Most of the photocatalysts found in the literature are in the form of powders. Only a few supported photocatalytic systems have been reported. The advantages of supported photocatalysts, such as that they produce a small pressure drop, have good mechanical stability and are easily separated from the reaction medium, make them superior to conventional powder photocatalysts. In this chapter, the definition of supported-metal oxide nanoparticles as the photocatalyst and their synthesis methodology are detailed discussed.

Keywords: photocatalysis, metal oxides, thin film, semiconductor, substrate

1. Introduction

1.1 General description about photocatalysis

Photocatalysis by semiconductors, such as those indicated above, is a well-established method for degrading organic contaminants in wastewaters. When the photon with energy greater than the band gap of the semiconductor is absorbed by the solid, an electron is excited from the valence band to the conduction band, resulting in an electron-hole pair. These exciting state conduction band electrons and valence band holes have several possible fates [1]:

a. they can combine and disperse the energy as heat while still in the bulk matrix of the crystal;

b. they can become trapped in defect traps;

c. they can migrate to the surface, where they recombine;

d. they may take part in redox reactions with electron donors or acceptors adsorbed onto the surface, which is the desirable pathway if degradation of organic contaminants is to occur.

In aqueous systems, these adsorbed species will correspond to water molecules, hydroxide ions, and oxygen molecules.

It is clear to know that in semiconductors, the generation of electrons and holes depends on the position of the energy levels. Besides, the redox potential of a donor species on the surface of the photocatalyst needs to be more negative (higher in energy) than the valence band position of the semiconductor to fill the electron vacancies. Similarly, acceptor molecules must have a more positive redox potential (lower in energy) than the conduction band. In view of this, one of the advantages of TiO_2 and ZnO compared to other semiconductors is that their electronic structure is such that it allows both the reduction of protons and the oxidation of water [2]. This phenomenon can be appreciated in the redox potential diagram shown in **Figure 1**. Recently, the use of TiO_2 and ZnO as photocatalysts has been thoroughly investigated.

Numerous conditions of a photocatalyst are required to achieve high photocatalytic efficiency. Firstly, the bandgap of the semiconductor must be higher than the redox potential of the $H_2O/OH^{\bullet}$ couple, and the material must be photo-stable. Secondly, the recombination of electron-hole pairs must be minimized. In other words, they need to be kept apart to allow time for the redox reactions to occur. Separation can be achieved by trapping electrons or holes in defects [4] or by using electrically conductive supports [5].

The holes in the photocatalyst valence band can oxidize the adsorbed water or hydroxide ions, while electrons in the conduction band can reduce molecular oxygen to superoxide anions [6]. These processes are summarized in the following equations:

$$\text{Semiconductor} + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O_{ads} \rightarrow OH\bullet_{ads} + H^+ \quad (2)$$

$$h^+ + OH^-_{ads} \rightarrow OH\bullet_{ads} \quad (3)$$

$$e^- + O_2 \rightarrow O_2\bullet^- \quad (4)$$

$$O_2\bullet^- + H^+ \rightarrow HO_2\bullet \quad (5)$$

$$O_2\bullet^- + HO_2\bullet + H^+ \rightarrow H_2O_2 + O_2 \quad (6)$$

The degradation of organic contaminants is commonly attributed to oxidation by hydroxyl radicals. This process is schematically described in **Figure 2**. This has led to the use of the term "Advanced Oxidation Processes," although there is evidence that in some systems, reductive pathways also operate [7].

Among *Advanced Oxidation Processes*, the photocatalytic processes are focused on the conversion of highly toxic organic to either less toxic organic compounds or CO_2 and H_2O [8]. When the photocatalytic reaction is implemented in the presence of O_2, the catalyst plays two main roles: to scavenge the photogenerated electrons and to produce active oxygen species [9]. We already know that metal oxides can respond to both UV-light and visible light, depending on the energy band gap of the materials. Newly, the photocatalytic process used visible light is widely employed for environmental cleanup [10].

Recently, many metal oxides (TiO_2, ZnO, SnO_2, and WO_3) have been widely used for the photocatalysis process. This is due to their abundance in nature,

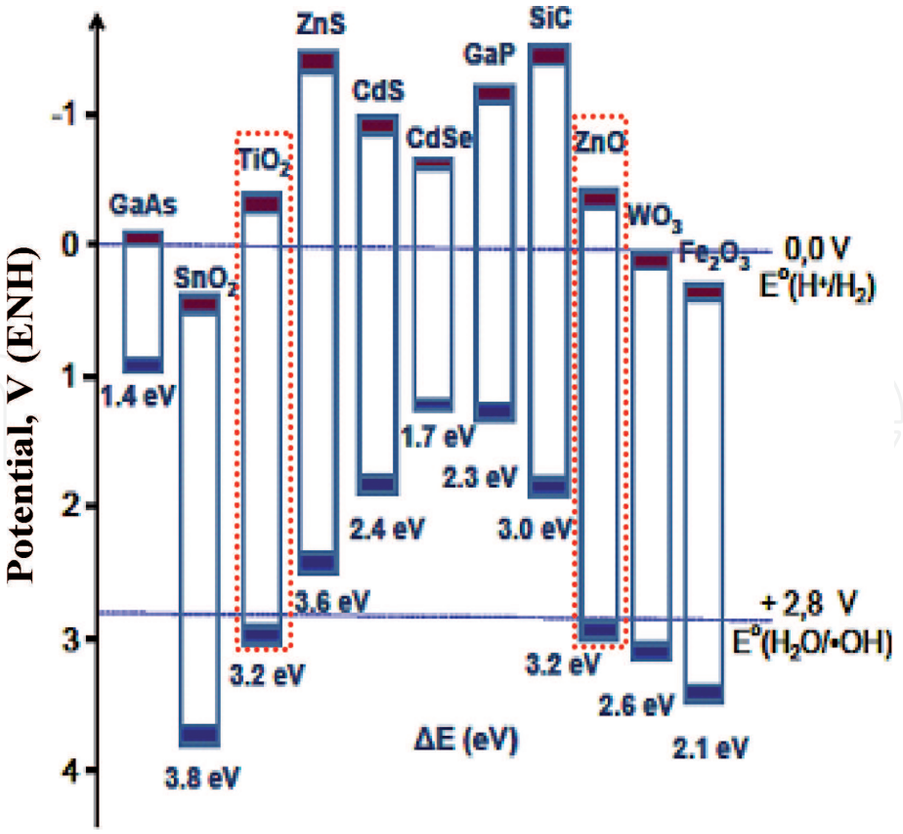

Figure 1.
Band gaps (eV) and redox potentials for several semiconductors referred to the normal hydrogen electrode (NHE). Reproduced from Ania et al. [3].

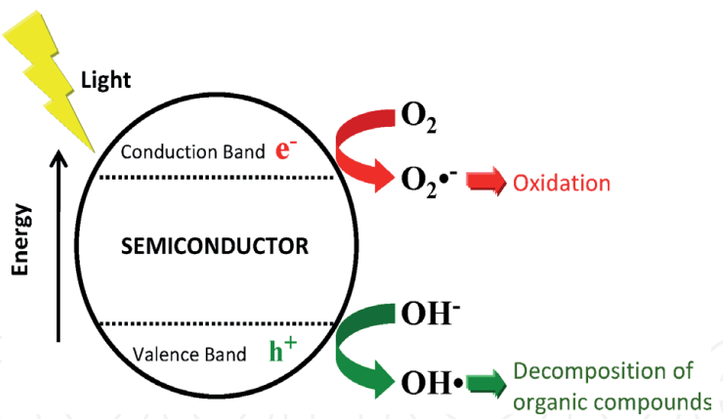

Figure 2.
Schematic diagram showing the processes involved in semiconductor photocatalysis. Reproduced from Gratzel et al. [2].

stability in many conditions, and the capability to create charge carriers when they were exposed under UV or visible light. The advantageous combination of the electronic structure, light absorption capacities, and excited lifetimes of metal oxides have provided of metal oxides has provided them possible for their application as photocatalyst. The photocatalysis employing metal oxides such as TiO_2, ZnO, SnO_2, and WO_3 has demonstrated their efficiency in the degradation of various harmful pollutants into carbon dioxide and water.

The vast majority of the photocatalysts studied are in powder form with all the difficulties in handling and recovering that implies. Consequently, supported photocatalysts are nowadays an important research area.

2. Supported TiO_2 photocatalysts

When the light is irradiated to the surface of the semiconductor, its absorption of photons provokes the photocatalytic reaction at the surface of the catalyst. Among many semiconductor materials, titanium dioxide (TiO_2) nanoparticles have been widely studied for photocatalytic applications over the last two decades [11, 12]. TiO_2 is relatively inexpensive, insoluble in water, and non-toxic. It can provide photogenerated holes with high oxidizing power because of its wide bandgap (3.2 eV) [13].

The common mechanism of the photocatalytic process of TiO_2 material consists of the interfacial redox reactions of the generated holes and electrons when the TiO_2 materials are irradiated by light with appropriate energy (**Figure 3**) [14, 15].

Most of the photocatalysts found in the literature are in the form of powders. Only a few supported photocatalytic systems have been reported, even though they have clear advantages from a practical point of view [16–18]. The most important benefit is that the separation of the supported photocatalysts from the reaction medium is simple, which minimizes the power requirements. In addition, they can be adapted to operate in flow-type continuous reactors [19–21]. Most recently, research was described by Fernández et al. [21]. They reported two methods of deposition of TiO_2 powders on different substrates (glass, quartz, and stainless steel) and evaluated the photocatalytic activities of these supporting materials through the degradation of organic compounds (**Figure 4**).

The authors demonstrated the influence of coating methodology and photocatalytic activities. The results showed that titania deposited on quartz displays a similar photocatalytic activity to that of the powder form. Therefore, the result opens a new feature for a new advantage route to immobilize catalyst for flow reactor or batch reactor. Because filtration step to recover the catalyst always causes many drawbacks in water treatment.

Then some authors [22, 23] developed a new type of supported photocatalyst that consists of mixtures of noble metal nanoparticles and commercially available TiO_2 nanoparticles (P25, Degussa-Evonik) deposited by dip-coating procedure on quartz substrate. The photocatalytic activity of the immobilized catalyst was evaluated by the degradation of malic acid. A comparison of the photocatalytic activity between supported TiO_2 with the powder TiO_2 Degussa P-25 shows slightly lower catalytic activity. This phenomenon could be explained by the total surface exposed of the catalyst to the light during the irradiation. However,

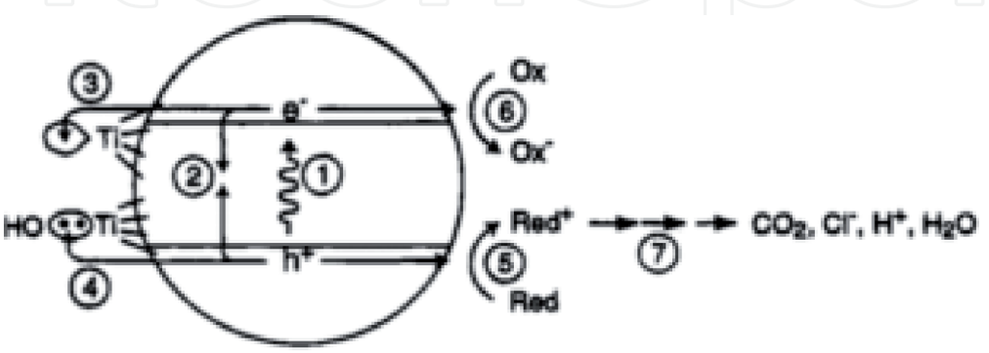

Figure 3.
The mechanism of photocatalysis process of TiO_2. Reproduced from Hoffman et al. [15]. (1) The formation of the electrons and holes by photon absorption. (2) The recombination of the generated electrons and holes. (3) The electron trapping of Ti (IV) at the conduction band to form Ti (III). (4) The hole trapping of titanol group at the valence band. (5) The oxidative pathways at the conduction band. (6) The reductive pathways at the valence band. (7) Photocatalytic oxidation reactions to form harmless compounds.

the result could be compensated by the advantage of eliminating the recovering catalyst after the treatment.

Lately, several works also reported the preparation of thin TiO_2 film on quartz substrates (**Figure 5**) by coating the TiO_2 sol using rotary evaporator [24], by dip-coating [25], by spin coating [26].

Recently, Borges et al. [27] supported commercial TiO_2 (Degussa P25) on glass spheres as a photocatalyst to treat the wastewater (**Figure 6**).

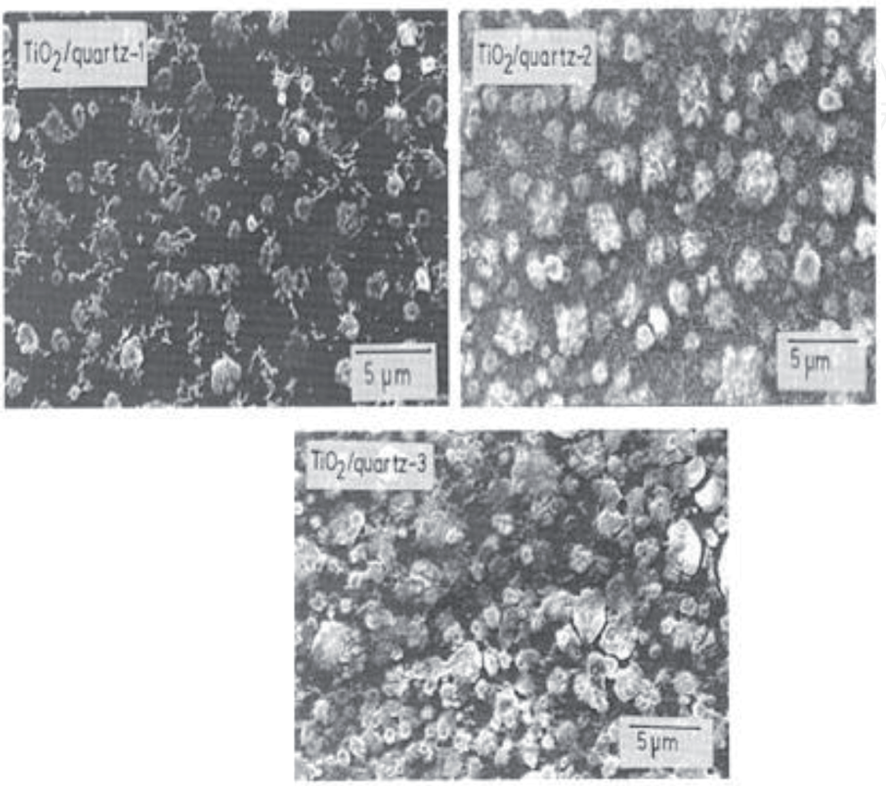

Figure 4.
SEM micrographs for the three TiO_2/quartz samples. Reproduced from Hoffman et al. [15].

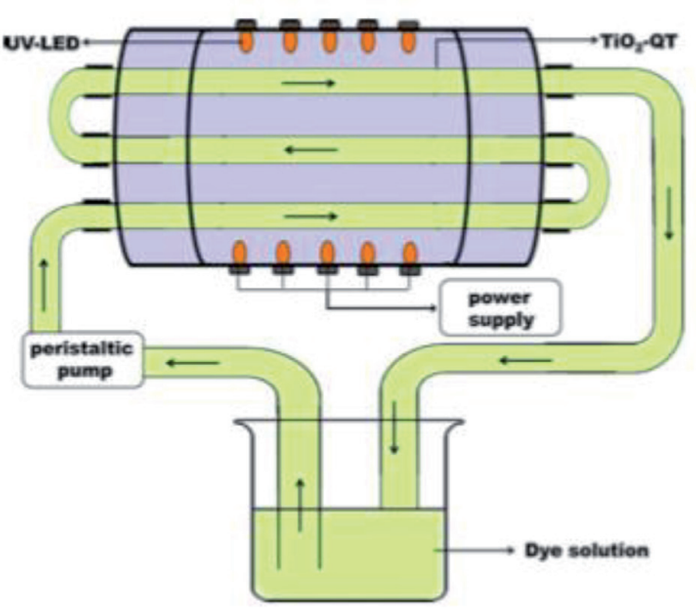

Figure 5.
Schematic representation of photocatalytic reactor using TiO_2 supported on quartz. Reproduced by Natarajan et al. [25].

Figure 7 shows the surface morphology substrate of the glass spheres without TiO_2 particles. **Figure 7b** shows the TiO_2 supported on the substrate and the homogeneous distribution of TiO_2 on the surface of the glass sphere. The authors showed that photocatalytic treatment in photoreactor displays more advantages than in batch system for high volumes of industrial wastewater.

Later, several authors also used poly-vinylidene fluoride (PVDF) dual layer hollow fiber membrane as a support to immobilize TiO_2 to treat pharmaceutical compound in wastewater (**Figure 8**) [28, 29].

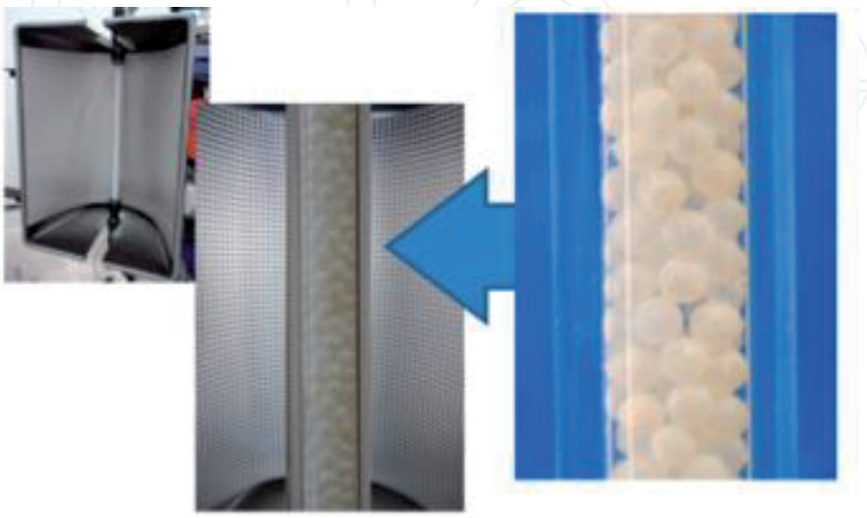

Figure 6.
Packed-bed photoreactor system and glass spheres photocatalytic bed in photoreactor. Reproduced by Borges et al. [27].

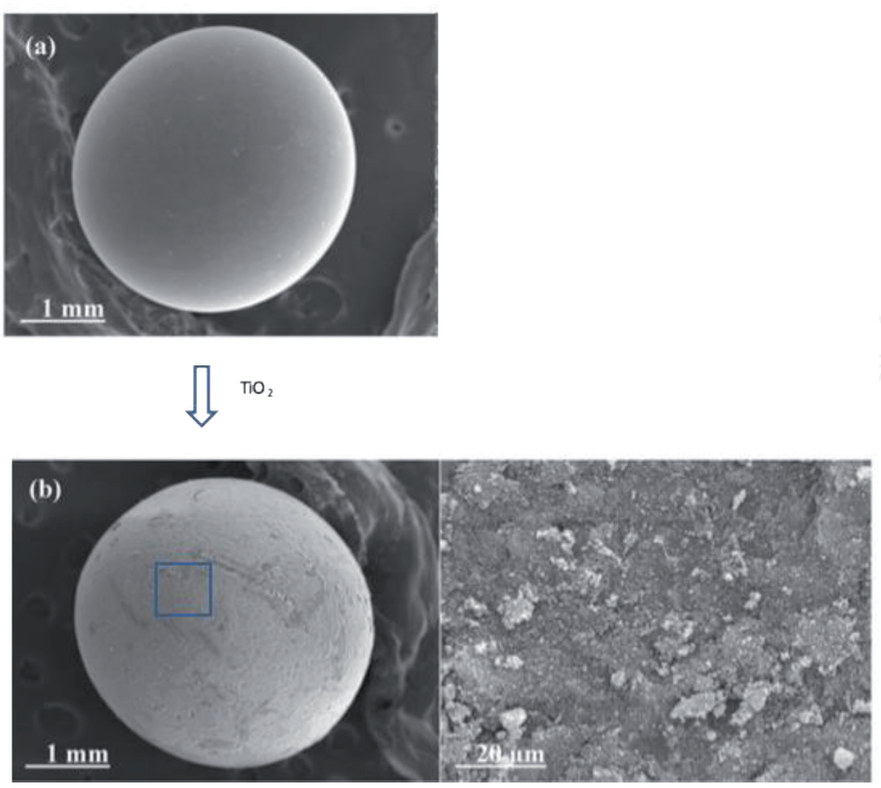

Figure 7.
SEM image of the glass sphere (a), SEM image of TiO_2 supported on the glass sphere (b). Reproduced by Borges et al. [27].

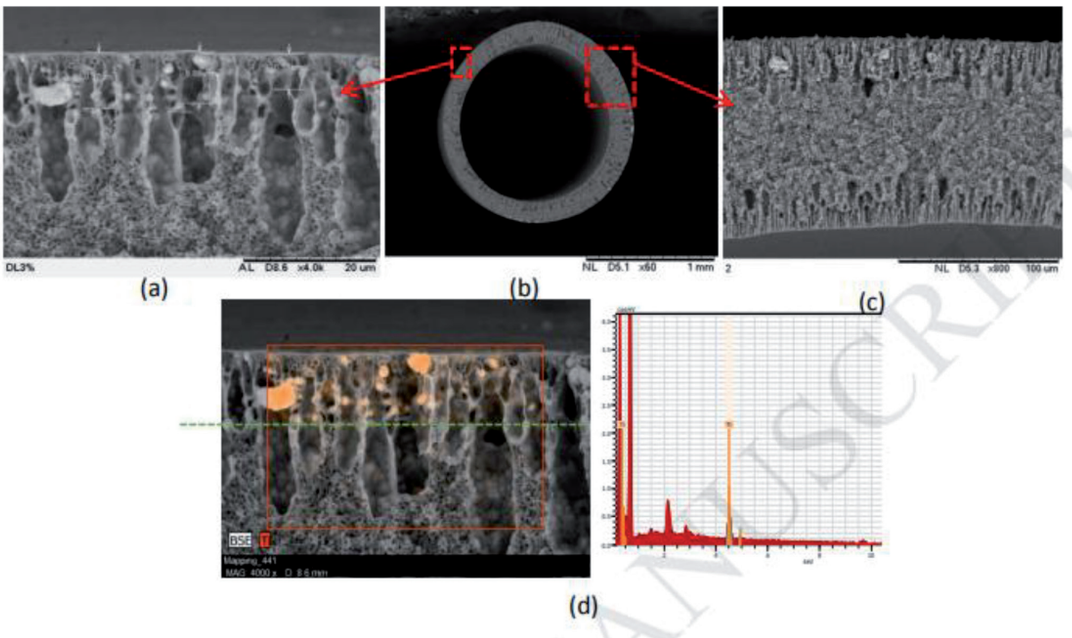

Figure 8.
Images of the PVDF membranes: (a) outer surface, (b) full cross section, (c) partial cross section, and (d) EDX images of TiO_2 nanoparticles at the outer layer. Reproduced by Paredes et al. [29].

The author demonstrated that the TiO_2 supported catalyst on PVDF membranes improved the photo-transformation rate of wastewater compounds during the photocatalytic treatment. The author also claimed that the supported catalyst could be easily recycled without any separation systems or catalysis recovery technologies.

It is already to know that TiO_2 is used as a photocatalyst in the ultraviolet light region due to its wide bandgap. To improve its photocatalytic efficiency in the visible light, efforts have been made such as, doping TiO_2 with anionic species (Fluorine, Sulfur, Nitrogen), or combining TiO_2 with other metal oxides. The combination of TiO_2 with other metal oxides can reduce the recombination effect of the electron-hole before they migrate to the surface of the material [30]. In addition, the composite of TiO_2 with other metal oxides can be generated in the surface hydroxyl groups, which can trap holes after the irradiation process, which improve the separation of the electron-holes. In some cases, the composite of TiO_2 with other metal oxides can enhance the crystallinity degree of TiO_2 and increases the specific surface area of the composite which are two important properties for a photocatalyst.

Recently, TiO_2 is widely combined with other metal oxides, such as ZrO_2, SnO_2, WO_3, CeO_2, ZnO, to improve the photocatalytic activity of TiO_2 in the ultraviolet light and improving its photocatalytic efficiency in the visible region.

For example, the composite of mixed oxide ZrO_2-TiO_2 material recently gains a great attention. By combining TiO_2 with ZrO_2, the surface acidity of the composite can be increased, hence improved the reactivity compared to the TiO_2 [31]. In addition, the hydroxyl groups are located on the surface of the catalyst, where the holes are trapped which could improve the efficiency of the degradation of organic pollutant [32]. Therefore, the mixed oxide ZrO_2-TiO_2 has been widely studied for the photodegradation of toxic organic compounds [31–35]. Many researchers also focused on the fabrication of ZrO_2-TiO_2 composite thin film and study its photo-catalytic efficiency under ultraviolet or visible irradiation [36–40].

Luo et al. has fabricated the ZrO_2-TiO_2 composite thin film on glass substrate using micro-arc oxidation process and used it for the degradation of rhodamine

B under ultraviolet irradiation [40]. The ZrO_2-TiO_2 composite thin film consists of three compounds: anatase, rutile, and ZrO_2 phases, results that the generated electron can transfer from rutile to anatase. This phenomenon inhibits the recombination of the generated electron-hole pairs, thus improved the photocatalytic efficiency of the composite. The photodegradation of MB under UV light irradiation shows that the photocatalytic activity of ZrO_2-TiO_2 composite thin film is three times higher than that of the pure TiO_2 thin film.

Alotaibi et al. have reported the preparation of ZrO_2-TiO_2 composite thin film on glass substrate using aerosol-assisted chemical vapor deposition [32]. The photocatalytic activity of the fabricated composite thin film was evaluated through the photodegradation of resazurin redox dye under Ultraviolet light irradiation (**Figure 9**). The composite shows an enhancement of photocatalytic activity compared to a pure TiO_2 thin film fabricated by the same condition.

Tungsten oxide (WO_3) is a common dopant in heterogeneous photocatalysis. In the last decade, WO_3 was extensively combined with TiO_2 to improve the photocatalytic activity of TiO_2 in both UV and Visible light. Besides of using the catalyst in the powder form, the preparation of WO_3-TiO_2 film and its photocatalytic activity was extensively studied [41–44] due to its advantage of the recuperation way. The WO_3-TiO_2 film has been fabricated by several methodologies such as sol-gel and dip coating [45]; spin-coating [46]; solvothermal method combining magnetron sputtering [47]; or film on pyrex substrates by casting methodology [48].

For example, Fu et al. have fabricated the WO_3-TiO_2 film on quartz substrate by dip-coating synthesis [42]. The photocatalytic efficiency was evaluated by the degradation of 4-chlorophenol-4 CP, xenobiotic micropollutants, under the irradiation visible light. The result shows that by incorporation of WO_3 into TiO_2, the WO_3-TiO_2 film can shift the absorption band from near UV region to the visible region. Under visible light, for the degradation of 4-CP, the prepared composite film demonstrated a higher photocatalytic activity for than that of pure TiO_2 film.

Recently, Adel et al. have prepared the WO_3-TiO_2 thin film on glass substrate by reactive chemical spraying and tested its photocatalytic activity under visible light. The results show that the photocatalytic thin film can degrade completely dye in textile, wastewater leading to cleaner processes [49].

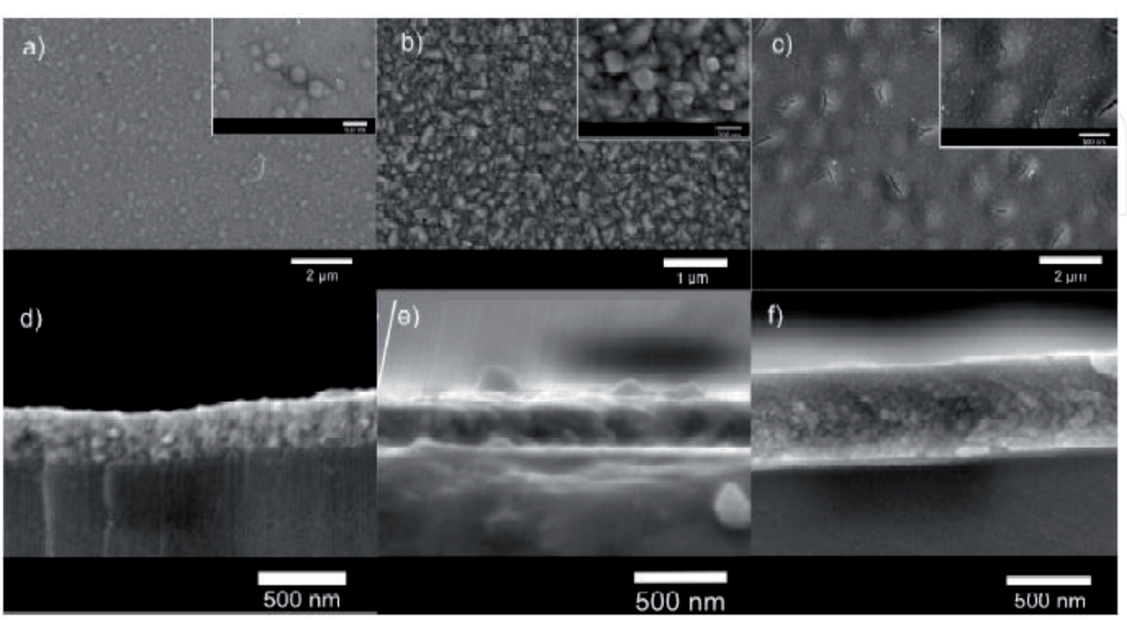

Figure 9.
SEM images of the (a) ZrO_2, (b) TiO_2 and (c) ZrO_2-TiO_2 composite films with the high magnification. The side on images—(d) ZrO_2, (e) TiO_2, and (f) ZrO_2-TiO_2 composite—shows the film thickness. Reproduced by Alotaibi et al. [32].

Spanu et al. have prepared Pt deposited on WO_3-TiO_2 nanotube arrays on Ti foil by sputtering method in order to improve the photocatalytic activity of the WO_3-TiO_2 system. The photocatalyst was used for the fabrication of H_2 by photocatalysis. The Pt deposited on WO_3-TiO_2 nanotube arrays show highly enhanced photocatalytic H_2 evolution efficiency comparing to other single-photocatalyst system such as (Pt-TiO_2 and WO_3-TiO_2) and pristine TiO_2 nanotubes [50].

3. Supported ZnO photocatalysts

ZnO is a metal oxide with a broad energy band gap (3.37 eV), which is one of the best semiconductors in the last decade. Recently, ZnO is extensively used as a photocatalyst under UV or Visible light irradiation due to its outstanding electrical, mechanical, optical, and non-toxic properties. In addition, the production cost of ZnO is low cost comparing to the fabrication of other semiconductors [51].

The mechanism of photocatalysis process of ZnO to degrade organic compounds under irradiation light can be summarized as follows [52]:

$$ZnO \rightarrow ZnO\left(e^{-}_{CB}\right) + \left(h^{+}_{VB}\right) \quad (7)$$

$$ZnO\left(h^{+}_{VB}\right) + H_2O \rightarrow ZnO + H^{+} + OH^{\bullet} \quad (8)$$

$$ZnO\left(h^{+}_{VB}\right) + OH^{-} \rightarrow ZnO + OH^{\bullet} \quad (9)$$

$$ZnO\left(e^{-}_{CB}\right) + O_2 \rightarrow ZnO + O_2^{\bullet -} \quad (10)$$

$$O_2^{\bullet -} + H^{+} \rightarrow HO_2^{\bullet} \quad (11)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (12)$$

$$ZnO\left(e^{-}_{CB}\right) + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} \quad (13)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^{-} + O_2 \quad (14)$$

$$H_2O_2 + hv \rightarrow 2OH^{\bullet} \quad (15)$$

$$\text{Organic pollutants} + OH^{\bullet} \rightarrow \text{Intermediates} \quad (16)$$

$$\text{Intermediates} \rightarrow CO_2 + H_2O \quad (17)$$

ZnO shares many similar properties with TiO_2, including a similar band gap (see **Figure 1**). There have even been several examples of ZnO displaying a higher photocatalytic activity than TiO_2 [53]. In addition, ZnO exhibits a better quantum efficiency because it can absorb a larger fraction of the solar spectrum than TiO_2 [54] and its price is even lower than that of TiO_2 [55]. Compared to TiO_2, ZnO can be easily supported on different types of substrates by means of low-temperature synthesis methods [56].

We already know that the photocatalytic efficiency of a photocatalyst is evaluated through the photogeneration of electron-hole pairs and their time-life. However, the main limitation of ZnO as a photocatalyst is the rapid recombination rate of photogenerated electron-hole pairs, which decreases the photocatalytic efficiency of ZnO. In addition, the use of ZnO as a photocatalyst is limited by the photocorrosion phenomenon. This process occurs because of the action of UV

radiation. As a consequence, the catalyst is partially dissolved, which gives rise to a dramatic decrease in catalytic activity [57]. The mechanism of this process is represented by the following self-oxidation reactions [58–60]:

$$ZnO + 2h^+ + nH_2O \rightarrow Zn(OH)_n^{(2-n)+} + \tfrac{1}{2}O_2 + nH^+ \quad (18)$$

$$ZnO + 2h^+ \rightarrow Zn^{2+} + \tfrac{1}{2}O_2 \quad (19)$$

where h^+ is the positive holes created by the action of UV radiation. Photocorrosion is the main obstacle to the use of ZnO as an effective photocatalyst. Therefore, significant efforts have been made to reduce the degradation of ZnO.

Beside TiO_2 using as a photocatalyst, Jung et al. [61] studied the synthesis and photocatalytic activity of CuO-ZnO nanowires supported on stainless steel wire meshes (SSWM). They showed that CuO-ZnO structures supported on SSWM exhibit an enhanced photocatalytic activity with respect to catalysts using other supports, such as ITO. This result they attributed to the efficient charge separation of the electron-hole pair favored by the SSWM support [61]. Another advantage of SSWM is its flexibility, which allows the mesh to be easily shaped to the desired configuration.

In general, the procedures used to achieve this involves the deposition onto the ZnO surface of: (a) silver nanoparticles [62–66]; (b) polyaniline monolayers [67], (c) graphitic carbon [68]; (d) Nafion films [69]; (e) AlSi nanoclays [70]; and (f) C_{60} fullerenes which become hybridized with ZnO [59].

Although the above modifications improve the photocatalytic stability of ZnO, some problems persist. For instance, Bessekhouad et al. [71] have reported that the photocatalytic activity of the doped materials is impaired by thermal instability and by an increase in the number of hole/electron recombination centers. Therefore, the development of novel methods that provide effective protection of the ZnO photocatalyst against photocorrosion is required.

An attempt must be made to increase catalytic activity under visible irradiation, since the solar spectrum contains a large fraction of visible light compared to UV radiation. Recently, the photocatalytic activity of ZnO in the visible region has been improved by various techniques, such as: (a) modification of the ZnO surface by non-metal element doping [72]; (b) transition metal doping [73, 74]; (c) the combination of ZnO with another semiconductor [75], etc. Of these methods, the coupling of different semiconductor photocatalysts offers great promise as it increases the charge separation of the electron-hole pairs, resulting in an increase in photocatalytic decolorization efficiency [76].

Recently, ZnO has been combined successfully with TiO_2 [77], CdO [78], CdS [79], and WO_3 [80]. CdO is a good candidate for coupling with ZnO due to its band gap, ~2.2 eV [78], so that $Cd_xZn_{1-x}O$ nanostructures are active in the visible range. In addition, under visible light the excited electrons from the conduction band (CB) of ZnO can be easily transferred to the CB of CdO since the E_{CB} of CdO is lower than the E_{CB} of ZnO. These transferal processes increase the excess of electrons in the conduction band of CdO, which shifts in the Fermi level of CdO [81], increasing its photocatalytic efficiency. To the best of our knowledge, CdO-ZnO has been always synthesized in powder form. The use of CdO-ZnO supported on a target substrate (such as SSWM) as a photocatalyst for dye degradation processes in UV or visible has reported by Vu et al. [82]. They also attempt to demonstrate in parallel that coupling CdO and ZnO may be also an excellent method to avoid photocorrosion.

4. Supported WO_3 photocatalysts

Tungsten oxide (WO_3) is a high-ranking material in photocatalysis [83]. The WO_3 presents in several phases such as monoclinic, orthorhombic, triclinic, cubic, etc., but only the monoclinic phase exhibits the best photocatalytic efficiency. In addition, WO_3 is a material with many advantages, such as harmless, high stability in acidic and oxidative ambient, and its cost fabrication cost is very low compared with other photocatalysts [84].

It has been shown that the band gap energy of WO_3 is varied from 2.5 to 3.0 eV [85, 86], leading WO_3 can be used as a photocatalyst at the visible region. In recent times, there are many studies focused on the improvement strategies of the photocatalytic efficiency of WO_3 [84, 87].

Recently, the researchers have proposed many strategies for the fabrication of WO_3 thin film [88], such as sputtering deposition [89–92], aerosol-assisted chemical vapor deposition [93, 94], sol-gel spin-coating [95, 96], hydrothermal-assisted growth [97, 98], and surfactant-assisted spray pyrolysis [99, 100]. Many works focused on the photocatalytic efficiency of WO_3, especially the studying of WO_3 thin film as a photocatalyst in the visible region [84, 101].

For example, the author fabricated a WO_3 thin film with a thickness 500–600 nm deposited on a quartz substrate by DC reactive magnetron sputtering [102]. The fabricated film WO_3 used for the degradation of CH_3CHO (acetaldehyde) under ultraviolet, standard fluorescence, and visible light. The result shows that WO_3 film fabricated by sputtering can be a good photocatalyst under visible light region.

To improve the separation of photogenerated charged and to increase the photocatalytic activity, many researchers combined other elements with the WO_3 thin film. For example, Higashino et al. have fabricated a layer of WO_3 on the Al-W allow coatings by selective solution and heat treatment (**Figure 10**). The formed thin film WO_3 exhibits photocatalytic self-cleaning properties under the visible light irradiation [103].

Takashima et al. have taken advantage of the multielectron reduction of Pt to improve the photocatalytic activity of WO_3 thin film on W foil. The author fabricated Pt loaded WO_3 thin film using a reactive DC magnetron sputtering technique or low damage reactive gas flow sputtering [104]. The formed Pt-WO_3 thin film was used to photodegrade CH_3CHO under visible light. The result shows that the fabricated thin film demonstrates excellent photodecomposition rates under visible light.

Another approach to improve the separation of photogenerated charged, C_3N_4 is combined with WO_3 film to form a heterojunction composite WO_3/C_3N_4. The

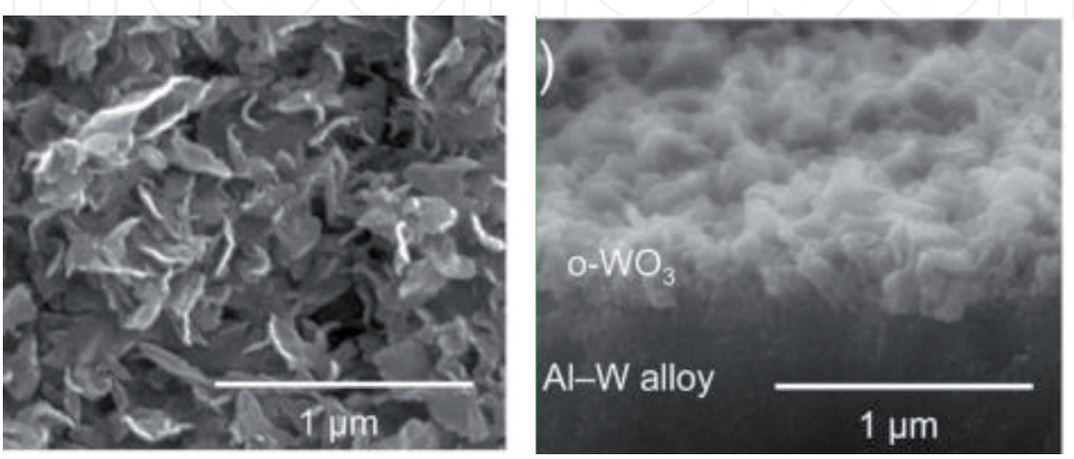

Figure 10.
SEM images of the surface and cross-sectional of WO_3. Reproduced by Higashino et al. [103].

fabricated composite was deposited don fluorine-doped tin oxide (FTO) substrate [105]. The photocatalytic activity of the composite was tested by photocatalytic degradation of MB and Cr^{6+} in wastewater under UV illumination.

The supported WO_3/C_3N_4 composite present higher photocatalytic activity on the decoloration of MB and the reduction of Cr^{6+} to Cr^{3+}, compared to the photocatalytic activity of WO_3 thin film.

5. Supported SnO_2 photocatalysts

SnO_2 is an inorganic compound that is exhibiting high optical transparency, excellent thermal and chemical stability, and strong oxidizing properties [106]. The band gap of SnO_2 is quite large, around 3.6 eV, which leads that SnO_2 can be used as a photocatalyst at the UV region. This property makes SnO_2 becoming an excellent photocatalyst for the degradation of many organic compounds.

Recently, SnO_2 played an important role in the photo-oxidation of pollutants and received a lot of attention despite the outstanding properties of this material. However, the vast number of researches used SnO_2 in the powder form as a photocatalyst for the degradation of the toxic organic compound, and the experiments are usually performed using SnO_2 in the powder form. There are only a few works describing the use of supported SnO_2 thin film as a photocatalyst.

In recent times, many methodologies have been applied for the fabrication of SnO_2 thin films such as, sol-gel [107], pulsed plasma deposition [108], pulsed laser deposition [109], reactive evaporation [110], and chemical bath deposition [111] methods.

For example, Jana et al. used the galvanic technique to fabricate SnO_2 thin film on transparent conducting oxide (TCO) [112].

Figure 11 shows the nanoporous flake-like structure, which allows more efficient transport of reactant molecules to the active interfaces and results in a higher photocatalytic activity for degrading methyl orange (MO) dye than that of P25 under UV light [112].

However, the SnO_2 in the powder form presents low photocatalytic activity comparing with other semiconductors due to its wide-band gap, 3.6 eV, and the rapid recombination of the photo generated electron-hole pairs. Thus, the SnO_2 thin film could present lower photocatalytic efficiency comparing with SnO_2 in the bulk form. Therefore, the SnO_2 thin film is widely combined with other metal ions such as Ni, Co, Fe [113], Cr [114], Zn [115], Sb [116], W [117], or other semiconductors, such as ZnO [118], TiO_2 [119], etc.

For example, the W-doped SnO_2 thin films are fabricated on glass (ITO) substrate by simple chemical deposition techniques [120]. The result showed that the energy band gap is varied by the doping concentration of W, which is in the range of 3.46–3.35 eV. In addition, the UV-Visible absorption and Photoluminescence characterization results demonstrated that W-dopant SnO_2 could narrow the band gap, thus enhancing the photocatalytic efficiency of the W-doped SnO_2 in the visible light (**Figure 12**). The author used the fabricated W-doped SnO_2 for the degradation of Methylene Blue and Rhodamine (RHB) under the visible region. The W-doped SnO_2 thin film presents higher photocatalytic efficiency comparing to the pure SnO_2 thin film in the visible light irradiation.

In recent time, Sr-doped metal oxides have great attention in electronic and optoelectronic applications. Besides, when Sr is combined with SnO_2, the crystal growth rate of SnO_2 is reduced, making the Sr-doped SnO_2 to have a higher specific surface area. Thus, the combination of Sr with SnO_2 can improve the photocatalytic activity of SnO_2. For example, Haya et al. have prepared Sr-doped SnO_2 thin film

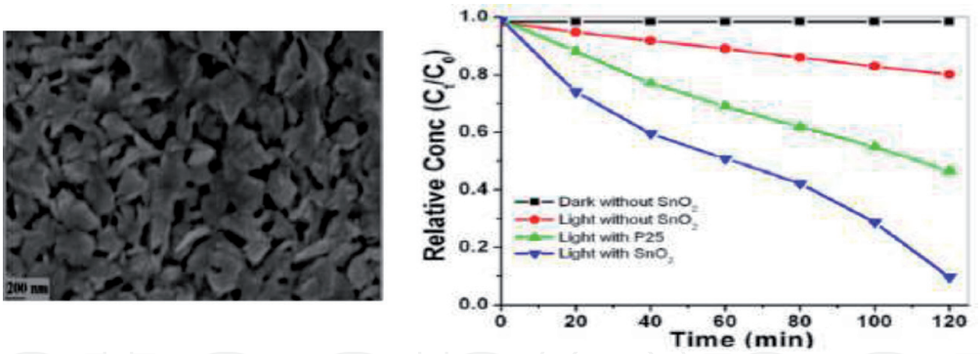

Figure 11.
The SnO_2 thin film and the photocatalytic activity of SnO_2 thin film. Reproduced by Jana et al. [112].

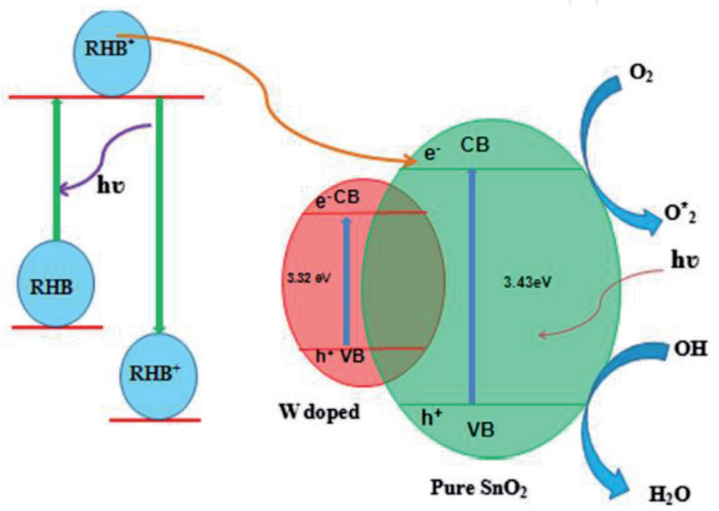

Figure 12.
Schematic representation for photocatalytic mechanism of RHB in W-SnO_2 thin films. Reproduced by Vadivel et al. [120].

on glass substrate by simple sol-gel technique and study its photocatalytic activity under UV-irradiation [121]. The doping of Sr makes the SnO_2 thin film to decrease its degree of crystallinity, reducing the particle size and increasing the specific surface area of the thin film. The results show that the Sr-doped (8%) SnO_2 film has higher photocatalytic activity compared to undoped SnO_2 thin film.

In addition, many researchers also combined with other metal elements to improve the photocatalytic activity of SnO_2 thin film such as Cu-doped SnO_2 [122], Fe-doped SnO_2 [123], F- or Sr-doped [124], and Cl-doped SnO_2 [125] on glass substrate.

Recently, to improve the photocatalytic efficiency of SnO_2 thin film, B/Ag/F was doped with the SnO_2-ZnO composite film on glass by the sol-gel route. The fabricated composite thin film was used for the degradation of methyl green and formaldehyde under UV irradiation. The result showed that the synergy of ZnO and tri-doping B/Ag/F had improved the photocatalytic activity of SnO_2 thin film [126]. In addition, Kong et al. also prepared B/Fe co-doped SnO_2-ZnO thin film on glass substrates using the sol-gel technique. The prepared composite thin film improved the lifetime of the photogenerated charge carriers and optical absorption properties. The photocatalytic efficiency of the composite thin film was evaluated through the degradation of organic pollutants such as acid naphthol red and formaldehyde. The B/Fe co-doped SnO_2-ZnO film exhibits the highest photocatalytic activity compared with an undoped or only singly doped SnO_2 thin film [127].

6. Conclusion

In this chapter, an overview of the development of supported catalysts and their prospects from a scientific point of view is presented. We can see that the field has experienced major advances in the last 5 years, especially in the area of supported TiO_2, ZnO, WO_3, SnO_2, and mixed oxides on several types of substrates (SSWM, quartz, glass (ITO)). Based on the literature presented here, we believe that there is still quite a lot that can be achieved in improving the performance of supported catalysts for photocatalytic applications.

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