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Photosensitization of TiO_2 by M_xO_y and M_xS_y nanoparticles for heterogeneous photocatalysis applications

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Abstract

Currently, TiO_2 is the most popular semi-conductor used in heterogeneous photocatalysis processes. Upon irradiation, conduction band electrons and valence band holes will be created in the relevant semi-conductor. These electrons and holes react with dissolved oxygen and/or adsorbed hydroxyl ions on the semi-conductor surface. That reaction will then initiate redox in the aqueous medium, resulting in the oxidization of organic pollutants. However, the rapid recombination that occurs in relation to photoproduced electrons and holes in TiO_2 significantly diminishes the efficiency of the photocatalytic reaction. In 1995, to enhance the photocatalytic efficiency of semi-conductors, Serpone et al. proposed an interparticle electron transfer process by coupling two semi-conductors with different redox energy levels to increase the charge separation for the corresponding conduction and valence bands. In the past decade, a certain number of studies related to the photocatalytic activity of TiO_2 coupled with other semi-conductors such as for example CdS, SnO_2, WO_3, Bi_2S_3, Cu_2O and CdSe. The main focus of this paper is to review the recent progress of the photocatalytic efficiency of coupled semi-conductors, comparing their efficiency with that of TiO_2 alone.

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Keywords: Photosensitization; TiO_2; Semi-conductor; Photocatalysis

1. Introduction

Photocatalytic oxidation using semi-conductors is one of the advanced oxidation processes (AOPs) for the rapid degradation of organic pollutants in water and air. TiO_2 is an excellent photocatalyst that can mineralise a large range of organic pollutants including some of the most refractory ones such as pesticides, herbicides and dyes [1–3].

The development of visible light photocatalysis has become one of the most important topics in photocatalysis research today. Most of the oxides used in photocatalytic applications (like TiO_2 or ZnO) are considered as semi-conductors with a wide band gap ($E_g = 3.2$ and 3.4 eV, respectively, for TiO_2 anatase and ZnO). The specific advantages of TiO_2 are its high chemical stability and appropriate flat band potential V_{bp}, which are required to induce the necessary redox reactions without external potential. Other advantage of TiO_2 is its low cost linked to the abundance of Ti (0.44% of the earth's crust). However, such oxides absorb only a small fraction of solar light (less than 5% in the case of TiO_2 anatase) and are of little practical use, unless means to extend their light response in the visible spectrum are found [4].

When, titanium dioxide is illuminated with light energy appropriate redox species (conduction band electrons e_{cb}^- and valence band holes h_{vb}^+) are eventually poised at the interface liquid/solid (in the case of TiO_2, as Ti^{III} for the electron and Ti^{IV}–OH for the holes). A limiting factor that controls the efficiency of photocatalysis is the rapid recombination of photogenerated electrons and holes in semi-conductor particles. The main challenge of the next decade is to postpone the e_{cb}^-/h_{vb}^+ recombination rate so as to improve the efficiency of TiO_2 photocatalyst and to extend its light absorption spectra to the visible region.

Most research work has centred on techniques for improving the process by the introduction into the TiO_2 of either anions (such as N^{3-}, S^{2-} or C^{4-}, these species substitute the oxygen lattice on TiO_2 and lead to a band gap narrowing, resulting in high visible absorption) [5–7]; or cations (like vanadium, iron, etc. [8]) and electron or hole scavengers adsorbed on the surface (H_2O_2, O_2, $S_2O_8^{2-}$, etc.) [9–11]. The process induces a change in the concentration of the hole or electron, thus increasing the charge carrier concentration and improving the conductivity of the materials.

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It is also possible to extend the light absorption spectra of non-porous titanium dioxide to the visible region by adsorption of organic dye mono-layer at the surface. Another method is to couple TiO_2 with a narrow band gap semi-conductor possessing a higher conduction band than that of TiO_2. In this application, the systems M_xO_y/TiO_2 or M_xS_y/TiO_2 can be used as photocatalysts for the decontamination of wastewater.

During the last past four decades the sensitization of wide-band gap semi-conductor by organic dyes has been intensively investigated (for example see Refs. [12,13]). This organic mono-layer was found to be a necessary requirement for an effective charge carrier separation. However, under these conditions, the amount of light absorption is negligible, and the resulting system offers only a limited efficiency in electron trapping [14]. Other drawbacks included poor overlapping of the sensitizer absorption with the solar emission spectrum, weak coupling of the electronically excited dye molecule with acceptor states of the semi-conductor substrate, and sensitizer stability.

At the beginning of the 1990s, O'Regan and Grätzel [15] developed a highly porous TiO_2 substrate electrode with a tris(bipyridil)ruthenium or a coumarine dye as sensitizer [15,16]. The crucial element in these cells called ''Grätzel cells'' is the organic sensitizer. Only a very limited number of dyes provide high photocurrent quantum yields and are also reasonably stable in relation to photodegradation [17]. Curently these electrochemical cells offer a possible, cheap alternative to amorphous silicon solar cells.

For obvious reasons these organo-mineral materials cannot be used in heterogeneous photocatalysis for the treatment of aqueous or gaseous effluents.

However, the organic dye can be substituted by a narrow band gap semi-conductor that might work as a sensitizer [18]. This system is then made of an heterojunction or a coupling of two semi-conductors.

In this configuration, several advantages can be obtained over organic dyes [12,19]:

(1) a lack of organic compounds in the photocatalyst (theoretically no risk of finding organic products resulting from the photocatalyst degradation in the treated water or air);
(2) an improvement of charge separation via interparticle electron transfer;
(3) the driving force for electron injection can be optimized through confinement effects;
(4) the ideal sensitizer having a 1.5 eV gap is appropriately replaced by a narrow band gap semi-conductor.

In 1984, Serpone et al. were the first to propose an interparticle electron transfer process (IPET), with subsequent enhancement of reductive processes on TiO_2 [20,21]. They demonstrated that the coupling of two semi-conductors (e.g., CdS and TiO_2), leads to an improvement in the dihydrogen production occurring in the photoreduction of water in the presence of hydrogen sulphide as sacrificial agent. Serpone has also demonstrated the photocatalytic worth of coupled semi-conductors in the dehydrogenation of alcohols and has investigated the IPET process by photoelectrochemical and photoconductivity experiments in solid system [22,23].

For an efficient interparticle electron transfer to occur between the semi-conductor used as a sensitizer and TiO_2, the conduction band of TiO_2 must be more anodic than the corresponding band of the sensitizer. Under visible irradiation, only the sensitizer is excited and the electrons generated from their conduction band are injected into the inactivated titanium dioxide conduction band. If the valence band of the sensitizer is more cathodic than that the TiO_2 one, the hole generated in the semi-conductor remains there and does not permit migration to TiO_2. These thermodynamic conditions favour the process of electron injections instead. Fig. 1 shows an illustration of interparticle electron transfer behaviour. CdS and ZnO fall within the category of photoexcited semi-conductors, which are typically coupled with non-photoexcited semi-conductors of TiO_2 and SnO_2 so as to promote a permanent charge separation (Table 1).

In the past decade, a certain number of studies have described the photocatalytic activity of TiO_2 and ZnO coupled with metal oxides such as for example CdS [24–26], SnO_2 [27–30], WO_3 [31], Bi_2S_3 [25], Cu_2O [32], Bi_2O_3 [32], Fe_2O_3 [33], CdSe [34a], ZrO_2 [34b] and In_2O_3 [34c]. The main focus of this paper is to review the recent progress of the photocatalytic efficiency of TiO_2 coupled semi-conductors, comparing their properties with that of TiO_2 alone especially under visible light irradiation.

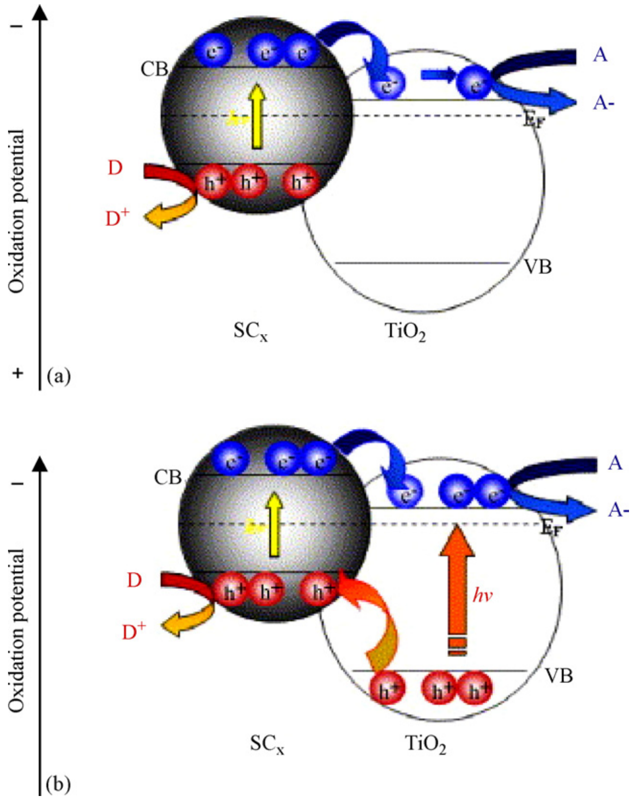

Fig. 1. (a) Energy diagram illustrating the coupling of two SC in which vectorial electron transfer occurs from the light-activated SC to the non-activated TiO_2. (b) Diagram depicting the coupling of SC in which vectorial movement of electron and holes is possible (from Ref. [32]).

Table 1
Band positions of some common semi-conductor photocatalysts in aqueous solution

Semi-conductor	Valence band (V vs. NHE)	Conductance band (V vs. NHE)	Band gap (eV)	Band gap wavelength (nm)
TiO_2	+3.1	−0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	−0.2	3.2	387
ZnS	+1.4	−2.3	3.7	335
WO_3	+3.0	+0.4	2.8	443
CdS	+2.1	−0.4	2.5	496
CdSe	+1.6	−0.1	2.5	729
GaAs	+1.0	−0.4	1.7	886
GaP	+1.3	−1.0	1.4	539

2. Photosensitization of TiO_2 by M_xS_y nanoparticles

2.1. Coupled system CdS/TiO_2

Cadmium sulphide is one of the very well-known semiconductors. It has a narrow band gap of 2.4 eV. It presents considerable interest, because of its applications in the solar cells or sensors technology, containing as it does mesoporous materials with nanoparticules of CdS [35,36]. Generally the nanoparticules of CdS supported on silica are prepared by adsorption or impregnation of metal precursors, followed by a reaction of sulphuration with hydrogen sulphide [37,38]. CdS is also an attractive material for a green light-emitting diode because of its direct band gap of 2.4 eV at room temperature [39]. CdS is tetravalent and is preferentially crystallized to Wurtzite in an hexagonal structure.

It has been shown that the CdS/TiO_2 system is effective in the case of the photodegradation of phenols and chlorophenols in water. These compounds exposed to irradiation with a wavelength $\lambda > 320$ nm in a Pyrex photoreactor at pH 12, are degraded in the presence of CdS alone, TiO_2 alone and of the junction CdS/TiO_2 [21]. By contrast, when only visible irradiation is used to illuminate the photocatalytic materials (wavelengths greater than 406 nm), there is no reaction with the TiO_2 dispersions (band gap, 3.2 eV; 380 nm). And for the CdS system, the rate is twice as fast as for the coupled CdS/TiO_2 system. The latter is activated in the visible region. The diffuse reflectance UV–vis absorption spectra of the different CdS/TiO_2 systems, pure TiO_2 and CdS show that the CdS sample exhibits strong absorption peaks in the visible region, while the absorption intensity for CdS/TiO_2 increases together with the CdS amount, in conjunction with the progressively intensive yellowing of the powders (Fig. 2) [32,40,41].

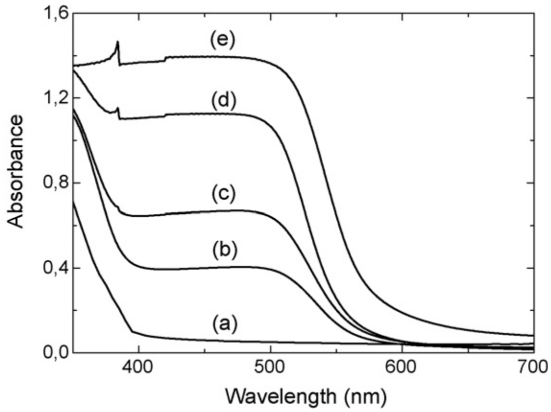

Fig. 2. UV–vis absorbance spectra of the pure and composite semi-conductors: (a) TiO_2, (b) $CdS(10\%)/TiO_2$, (c) $CdS(30\%)/TiO_2$, (d) $CdS(50\%)/TiO_2$ and (e) CdS (from Ref. [40]).

We have observed the same in relation to other compounds such as dyes, benzamide or hydroxybenzoic acid [32,40]. The photocatalytic efficiency of the CdS/TiO_2 coupling is highly dependent on the proportion of CdS. For example, in the case of Orange II photodegradation under UV–vis light, CdS/TiO_2 couplings containing a low proportion of CdS (5% and 10%) and pure TiO_2 show the best photocatalytic activity (Table 2). Under visible illumination, they exhibit a faster degradation rate than the individual components operating in isolation, evidencing an interparticle electron transfer (Fig. 1). The fact that the dye adsorbs much more on CdS than TiO_2 and the suitable level of its singlet excited state suggests that the electron transfer from the dye to CdS contributes to the degradation mechanism [40].

Kang et al. [42] compared the photodegradation of 4-chlorophenol with same catalysts. They found that the rate constants of adsorption are 1.5–2 higher for CdS/TiO_2 than for TiO_2 alone. The same observations were made by Doong et al. with 2-chlorophenol [43]. More recently Tristao et al. [44] studied the photocatalytic discoloration of organic dye Drimaren red in aqueous solution in the presence of TiO_2 and CdS/TiO_2 but only under UV–vis irradiation. Kinetic parameters obtained indicated that the most efficient photocatalyst is the CdS/TiO_2 system containing 5% of CdS.

In water, organic compounds such as phenols are adsorbed on the CdS particle surface. According to Serpone et al. [21]

Table 2
Initial degradation rates of Orange II in CdS/TiO_2 suspensions with amounts of CdS ranging from 0 to 100% (from Ref. [40])

	Degradation rate ($\times 10^{-3}$ min^{-1})	
	UV–vis	Visible
TiO_2	25	3
$CdS(5\%)/TiO_2$	25	16
$CdS(10\%)/TiO_2$	25	16
$CdS(30\%)/TiO_2$	17	7
$CdS(50\%)/TiO_2$	14	8
CdS	10	10

from the mechanistic point of view, the irradiation of aqueous CdS suspensions with visible light (wavelengths greater than 520 nm) generates conduction band electrons and valence band holes which migrate to the surface and subsequently become trapped as S^{2-} and Cd^{2+} (or Cd°) species [45] (Eq. (1)). In oxygen-equilibrated media, the trapped electrons are scavenged by molecular oxygen to yield superoxide radical anion and then peroxide ion (Eq. (2)):

$$\mathrm{CdS} + h\nu \rightarrow \mathrm{CdS}(\mathrm{e_{cb}}^{-} + \mathrm{h_{vb}}^{+}) \rightarrow \mathrm{CdS}(\mathrm{e_{tr}}^{-} + \mathrm{h_{tr}}^{+}) \tag{1}$$

$$\mathrm{e_{tr}}^{-}\mathrm{O_2} \rightarrow \mathrm{O_2^{-}} + \mathrm{e_{tr}}^{-}\mathrm{O_2^{2-\bullet}} \tag{2}$$

Under visible irradiation, TiO_2 in the CdS/TiO_2 coupling is not light activated. It can be sensitized by IPET from irradiated CdS particules to the conduction band (Fig. 1a) of TiO_2, thereby leaving an excess of surface trapped holes on CdS (Eq. (3)). This vectorial transfer of charge should therefore enhance the photo-oxidation of the adsorbed organic compounds (Eq. (4)):

$$\mathrm{CdS}_{(\mathrm{e^-}+\mathrm{h^+})} + \mathrm{TiO_2} \rightarrow \mathrm{CdS}_{(\mathrm{h^+})} + \mathrm{TiO_2} \tag{3}$$

$$\mathrm{CdS}_{(\mathrm{h^+}\ \mathrm{or}\ \mathrm{OH^\bullet})} + \text{organic compoundads}_{\mathrm{ads}} \\ \rightarrow \text{intermediates} \rightarrow \text{mineral products}$$

When both semi-conductors of the coupled system (CdS/TiO_2) are activated by the UV–vis irradiation and if the flat band potentials are suitably disposed (Fig. 1b), the electron transfer may occur from the conduction band of CdS towards the conduction band of TiO_2 and the hole transfer may occur from the valence band of TiO_2 towards the valence band of CdS. There is competition with the reaction of recombination hole-electrons in the respective semi-conductors. Finally, the excess of holes on CdS oxidizes the adsorbed organic compounds, and may also anodically autocorrode the CdS particules [46]. On the other hand the excess electrons on TiO_2 are trapped by chemisorbed molecular oxygen to produce the superoxide radical anion [21]. If the photogenerated holes do not react quickly with Cd–OH groups, or chemisorbed water and/or the adsorbed organic compounds, photoanodic corrosion occurs. It induces a release of ion cadmium in solution and the formation of an elemental sulphur layer on the surface of the CdS particles (this may affect significantly the photocatalysis reaction) according to

$$\mathrm{CdS} + 2\mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{Cd^{2+}} + \mathrm{S} + 2\mathrm{OH^-} \tag{5}$$

For example, Bessekhouad et al. [40] observed that the loss of Cd^{2+} in the solution upon illumination of the CdS/TiO_2 system prepared by sol–gel is comparable to that of a simple mixture of both components in the same proportion. In the other works, Spanhel et al. [26] have shown that after illumination of pure CdS no significant changes in the CdS concentration were found. However, in the presence of TiO_2, a rapid decrease in cadmium sulphide concentration was observed. Spanhel et al. explained that in the presence of TiO_2 the electrons rapidly leave the CdS particles and are picked up by oxygen on the TiO_2 particles. The lifetime of the remaining holes in the CdS surface is increased and enables them to react with O_2 molecules. That explains the significant increase in the rate of photoanodic corrosion of Cds in the presence of TiO_2.

For the previously mentioned reasons, the use of CdS as a photocatalyst has been limited due to its anodic decomposition, i.e., photocorrosion [21,24]. It is a well-known fact that from a practical point of view, the use of CdS in coupled systems is not to be recommended owing to the release of toxic cadmium [21,24]. However, from a fundamental point of view, there are still some attractive mechanistic aspects that are worth examination particularly if they deal with dye degradation.

Fuji et al. [24] have proposed a solution to solve this problem by embedding CdS fine particles into TiO_2 transparent gel matrix. In this case, it is necessary to pay attention during the heat treatment of the colloidal suspension of CdS, because cadmium sulphide is stable in air until 500 °C, after which it is partially oxidized in $CdSO_4$ sulphate and then in CdO starting from 800 °C. The conclusion of this line of enquiry is that TiO_2 gel was revealed to serve as a stable oxide matrix to protect the encapsulated CdS fine particles from photocorrosion, and thus catalytic evolution of H_2 was observed. Crystallization of the TiO_2 gel significantly improved the photocatalytic activity of CdS/TiO_2 system, implying that the improved semi-conducting properties of the matrix would facilitate transfer of electrons photogenerated in CdS. As a result, visible light sensitization of TiO_2 by the embedded CdS was successful, yielding an estimated net quantum efficiency of 13% [24].

2.2. Other M_xS_y/TiO_2 systems

Other sulphide semi-conductors can be used for the photosensitization of nanocristalline TiO_2. Bi_2S_3 nanoparticle appears to be a good candidate material. It has a direct band gap of 1.3 eV. Its conduction band is less anodic than the corresponding band of TiO_2 and the valence band of this sensitizer is more cathodic than the valence band of TiO_2 [47] (Fig. 3). Bessekhouad et al. [25] have studied a Bi_2S_3/TiO_2 junction prepared by precipitation of Bi_2S_3 onto TiO_2 at different concentrations. The UV–vis diffuse reflectance spectra shows that Bi_2S_3 absorbs a large part of visible light and when the junction contains 10% by weight of Bi_2S_3 the absorbance starts at 800 nm. In this study, interparticle electron transfers occurring on the Bi_2S_3/TiO_2 junction were demonstrated by performing photocatalytic tests under visible light (with benzamide, 4-hydroxybenzoic acid and Orange II as pollutants).

In the other works, Vogel et al. [12], used quantum-sized (Q-size) PbS, Ag_2S and Bi_2S_3 particles as sensitizers for TiO_2. However, the aims of these studies are not the photodegradation of organic compounds in water but are rather certain applications in the fields of solar energy conversion and optoelectronics. Indeed for Vogel et al. [12] and other authors [48,49], one of the first uses of the quantum-size particles properties' for typical semi-conductor applications was to embed the particles into porous TiO_2 films and to use modified layers as light-converting electrodes. Visible light was absorbed by the quantum-size particles which, consequently, transferred electrons into the porous TiO_2 substrate. These authors

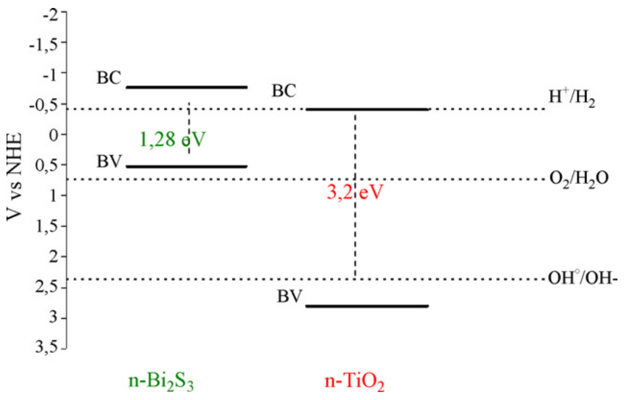

Fig. 3. Energetic diagrams of Bi_2S_3/TiO_2 heterojunctions.

mentioned that the photocurrent quantum yield reached values of more than 70% for Q-size CdS or Q-size PbS sensitized electrodes.

More recently in 2004, a new approach has been developed by Ho et al. [50] for the production of visible light photocatalysts from molybdenum and tungsten dichalcogenides. The interest in these semi-conductors stems from their band gaps (1.1–1.7 eV) that closely match the solar spectrum and from their stability against photocorrosion. Unfortunately, the conduction band energy levels of bulk MoS_2 and WS_2 are also less negative than that of TiO_2. These authors report that MoS_2 and WS_2 nanoclusters exhibited quantum confinement effects, thus the band gaps of these nanoclusters can be increased significantly, until the conduction band energy levels of MoS_2 and WS_2 are more negative than those of TiO_2 (Fig. 4). Ho et al. [50] have found a new and simple in situ photoinduced deposition method for the preparation of MoS_2/TiO_2 and WS_2/TiO_2 heterojunctions. The most attractive feature of this in situ reduction and deposition procedure is that the quantum-size MS_2 nanoclusters (M = Mo or W), which can act as a photosensitizer, are inherently bound to TiO_2. The photocatalytic activities of these materials have been evaluated by the degradation of methylene blue (MB) and 4-chlorophenol (4-CP). The results indicate that both MoS_2/TiO_2 and WS_2/TiO_2 heterojunctions are efficient in the photodegradation of MB and 4-CP under visible light irradiation ($\lambda > 400$ nm), while no photoactivity was observed in relation to the pure TiO_2 sample in the same conditions.

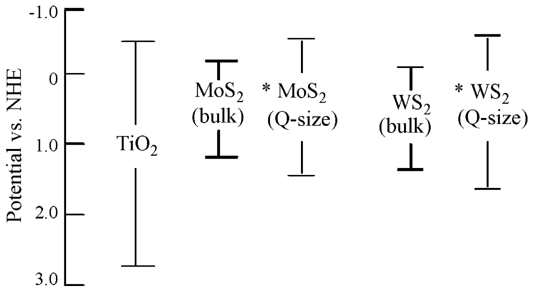

Fig. 4. Energy levels of the conduction and valence band edges vs. normal hydrogen electrode (NHE) for pure TiO_2, WS_2, and MoS_2 with various sizes at pH 7 (asterisk indicates band gap increase due to the quantum-sized effect; from Ho et al. [50]).

2.3. *$CdSe/TiO_2$ system*

The coupling of CdS/TiO_2 has been frequently studied by the researchers working on heterojunctions. This is not the case for the $CdSe/TiO_2$ system. CdSe has a lower band gap (1.7 eV compared to CdS of 2.4 eV), and consequently this is another potential material to form a composite semi-conductor with TiO_2. To our knowledge, the photocatalytic properties of the $CdSe/TiO_2$ coupling have been studied only by Lo et al. in 2004 [34]. These authors prepared a $CdSe/TiO_2$ photocatalyst system by liquid phase deposition with TiO_2 particles as a platform to chemically couple CdSe precipitate in three steps. The photocatalytic efficiency of the $CdSe/TiO_2$ was carried out under 420 nm irradiation conditions in a 4-chlorophenol aqueous solution. The results show a lower photoactivity of the coupling under visible irradiation (only 10% of 4-CP photodegradation was obtained, pure TiO_2 is not activated). For the authors these results indicate the effectiveness of interparticle electron transfer process of activated CdSe to TiO_2. The efficiency of these junctions is very much lower compared to that of CdS/TiO_2 and for Lo et al. this is due to the insufficient amounts of CdSe on the TiO_2. However, the elemental composition of the composite $CdSe/TiO_2$ by ESCA shows that the atomic percentages of Cd(3d) and Ti(2p) are 27.6% and 72.4%, respectively.

3. Coupling of TiO_2 by M_xO_y nanoparticles

3.1. *WO_3/TiO_2 systems*

Catalysts containing the WO_3/TiO_2 system have been used for a long time for the selective catalytic reduction of nitrogen oxides of NO_x by NH_3 (for example see Ref. [51]).

Recently, many studies related to the characterization and the photocatalytic activity of WO_3/TiO_2 for the purpose of improving TiO_2 photocatalytic efficiency have been carried out [31,52–55]. The band gap of WO_3 is 2.8 eV and both the upper edge of the valence band and the lower edge of the conduction band of WO_3 are lower than those of TiO_2. Thus WO_3 can be excited by illumination with visible light and the photogenerated holes can be transferred from WO_3 to TiO_2 [53] (Fig. 5). Li et al. [31] have prepared WO_x–TiO_2 samples by sol–gel process. They concluded that tungsten oxides added into TiO_2 could shift the light absorption band from near UV range to the visible range and could hinder the recombination of excited electrons/holes. Moreover, under visible light, the photocatalytic oxidation of methylene blue in aqueous solution is more effective with WO_3–TiO_2 than pure TiO_2. The authors assume that the complex comprised of $W_xTi_{1-x}O_2$ would form the TiO_2 doped with tungsten oxides, which had a lower energy level than that of TiO_2. However, this assumption needs to be confirmed by defining the position of the tungsten impurity ($W_xTi_{1-x}O_2$) energy level.

For similar applications (self cleaning surface preparation), the photoinduced hydrophilicity of TiO_2 with WO_3 layers has been investigated by some groups (for example Miyauchi et al. [53] and Irie et al. [56]).

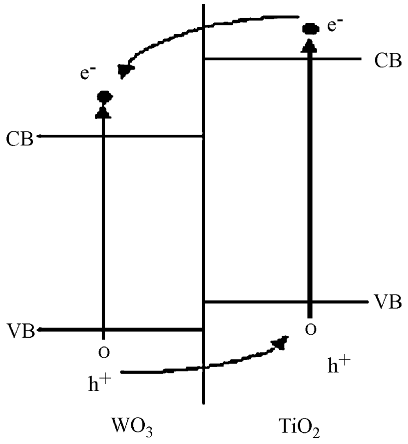

Fig. 5. Energy diagram for the WO_3/TiO_2 composite system.

3.2. SnO_2/TiO_2 systems

Conversely TiO_2 can be used as photosensitizer for certain semi-conductors having weak photocatalytic properties. Shi et al. [30] obtained coupled particles of SnO_2/TiO_2 by homogeneous precipitation. Thus ultrafine TiO_2 particles were coated with SnO_2. The basic method is to disperse TiO_2 particles in the alkaline solution of $SnCl_4$, and to complete the process by a thermal treatment. The authors observed that pure SnO_2 shows little catalytic activity compared to a TiO_2-based photocatalyst, because the band gap of SnO_2 (3.8 eV) is not sufficient to initiate photocatalytic reaction after UV illumination. In this case titanium dioxide plays the role (function) of photosensitizer for SnO_2. The conduction band of SnO_2 is approximately 0.5 V more positive than that of TiO_2. The photocatalytic activity of the coupled particles is higher than that of pure ultrafine TiO_2 for the solution of active red X3-B azodye and also, in other study, than that of acid Orange 7 and naphthol blue black [28]. For Gopidas et al. [57] that seems to be accompanied by an improvement of charge separation in the coupled systems. More recently, a new approach towards the improvement of the photocatalytic activity of TiO_2 is the substitution of Sn for Ti in the TiO_2 lattice. The incorporation of Sn leads to a better charge separation [29,58]. Moreover, the UV–vis absorption spectrum of the nano-sized coupled photocatalyst $(Sn_{0.25}Ti_{0.75})O_2$ shows an enhanced absorption to the visible light [59].

Akurati et al. [60] reported the one step flame synthesis of SnO_2/TiO_2 composite nanoparticles. These authors evaluated the photocatalytic activity of this materiel by the decomposition of methylene blue in water under UVA irradiation ($\lambda = 355$–360 nm). They observe that the photocatalytic efficiency of SnO_2/TiO_2 composite particles is higher than that of pure TiO_2 synthesized under similar conditions. Akurati et al. ascribed this higher activity to the lower recombination rate of photoexited electrons and holes facilitate by coupling of TiO_2 with SnO_2.

3.3. Other MO_x/TiO_2 systems

Some other semi-conductors were used for enhancing the photoactivity of titanium dioxide, but only to a limited extent in the photocatalytic treatment of water or air. Recently cuprous oxide was reported to act as a stable catalyst for water splitting under conditions of visible light irradiation (<600 nm) although its exact role is unclear [61,62]. Cu_2O/TiO_2 heterojunction as a potential thin-film photocathode for hydrogen production has been studied by Siripala et al. [63]. It was observed that at -1 V bias, high photoactivity was obtained with additionally limitation of Cu_2O corrosion. Li et al. [64] created a nano-size TiO_2–Cu_2O particle composite by an electrochemical method. The Cu incorporation in TiO_2 is beneficial to the degradation of dye brilliant red. These authors suppose that the Cu_2O component can accelerate the step of electron transfer to oxygen during the photocatalytic reaction. In other works, Bessekhouad et al. [32] mixed Cu_2O and TiO_2. The photocatalytic efficiency of the composite obtained under visible light depends on the structure and physico-chemical properties of the organic compounds.

Many other oxides were used in coupling with titanium dioxide like Bi_2O_3 [32], $ZnMn_2O_4$ [32], ZrO_2 [65,66], ZnO [67,68]; however, they were not studied very much for applications in heterogeneous photocatalysis for the destruction of organic pollutants in water or air.

4. Conclusion

This report which is a non-exhaustive one, gathers the main studies concerning the composite material formation and the coupling between titanium dioxide with other semi-conductors (MO_x and MS_x). All these studies mainly aim to

- the limitation of the charge recombination phenomena;
- extend photocatalyst light response in the visible region;
- prepare stable, effective materials easy to implement.

They are the main challenges to be raised in this beginning of XXI century in the field of heterogeneous photocatalysis.

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