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Photocatalytic Deposition of Metal Oxides on Semiconductor Particles: A Review

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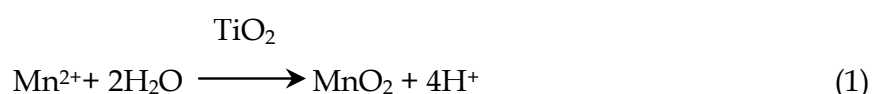Elim Albiter and Salvador Alfaro
Lab. Catálisis y Materiales, ESIQIE-Instituto Politécnico Nacional Zacatenco,
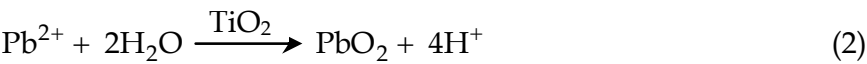*México D.F.,*
México

1. Introduction

As it has been well recognized in the last decade, heterogeneous photocatalysis employing UV-irradiated titanium dioxide suspensions or films in aqueous or gas media, is now a mature field [Chong et al. 2010, Ohtani B. 2010, Paz Y., 2010]. Semiconductor photocatalysis is considered as a green process that focuses basically on exploiting solar energy in many ways. Its investigations have been mainly targeted to the degradation/mineralization of organic pollutants and water splitting solar energy conversion, among others. However, there are other exciting applications such as metal photodeposition, organic synthesis, photoimaging, antibacterial materials, which have now an intense investigation [Wu et al. 2003, Chan S. & Barteau M. 2005, Litter M. 1999, Fagnoni et al. 2007, Choi W. 2006, Valenzuela et al. 2010, Zhang et al. 2010].

In particular, the photodeposition has been used since the decade of 70's by the pioneer work of Bard [Kraeutler and Bard, 1978] to prepare supported-metal catalysts and photocatalysts as well as to recover noble metals and to remove metal cations from aqueous effluents [Ohyama et al. 2011]. In this case, the reduction of each adsorbed individual metal ions occurs at the interface by acceptance of electrons from the conduction band forming a metallic cluster. A variant of metals deposition is the reductive deposition of metal oxides and a clear example of this route is the photocatalytic reduction of Cr (VI) which is transformed to Cr(III), so that in acidic environment, chromates are easily converted to Cr_2O_3 [Lin et al. 1993 and Flores et al. 2008].

The oxidative deposition of metal oxides is less frequently reported and it has been demonstrated that proceeds via the oxidative route [Tanaka et al. 1986]. For instance, checking the electrochemical potentials of Mn and Pb (Table 1), they are more easily oxidized by the valence band holes than reduced by the conduction band electrons in presence of TiO_2 as follows [Wu et al. 2003]:

$$Mn^{2+} + 2H_2O \xrightarrow{\quad TiO_2 \quad} MnO_2 + 4H^+ \tag{1}$$

$$Pb^{2+} + 2H_2O \xrightarrow{\text{TiO}_2} PbO_2 + 4H^+ \tag{2}$$

Half cell	E° (V)
MnO_2/Mn^{2+}	1.23
Mn^{2+}/Mn	-1.18
PbO_2/Pb^{2+}	1.46
Pb^{2+}/Pb	-0.12
Tl_2O_3/Tl^{1+}	0.02
Tl^{1+}/Tl	-0.336
Co^{2+}/Co	-0.28
Cr^{6+}/Cr^{3+}	1.232
Cr^{3+}/Cr	-0.744

Table 1. Half wave potentials of different couples.

These two reactions represent a good example of the photocatalytic deposition of metal oxides in aqueous solution onto titanium dioxide. This means that the complete photocatalytic cycle should consider the photoredox couple in which one metallic ion (single component) in solution is oxidized and the oxygen of the media is reduced. The deposition is driven by particle agglomeration after reaching their zero point charge and a critical concentration to be deposited on the surface of the semiconductor. It has been reported that single component metal oxides for example, PbO_2, RuO_2, U_3O_8, SiO_2, SnO_2, Fe_2O_3, MnO_2, IrO_2 and Cr_2O_3 can be deposited on semiconductor particles following a photo-oxidative or photo-reductive route [Maeda et al. 2008].

On the other hand, when a semiconductor is irradiated with UV light in presence of aqueous solutions containing dissolved Ag^+ or Pb^{2+} cations a redox process is undertaken giving rise to the reduction of silver ions or the oxidation of lead ions, according to the following reactions [Giocondi et al. 2003]:

$$Ag^+ + e^- \rightarrow Ag^° \tag{3}$$

$$Pb^{2+} + 2H_2O + 2h^+ \rightarrow PbO_2 + 4H^+ \tag{4}$$
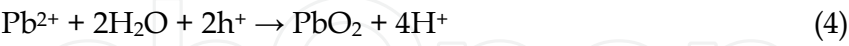
Lately, it has been reported the photocatalytic deposition of mixed-oxides such as $Rh_{2-y}Cr_yO_3$ dispersed on a semiconductor powder with applications in the water splitting reaction [Maeda et al. 2008]. Hence, we intend to offer the reader a condensed overview of the work done so far considering photocatalytic deposition of a single or mixed oxide on semiconductor materials by either oxidative or reductive processes.

## 2. Photocatalytic oxidation of a single component

2.1 Pb^{2+}

In regard with the very negative impact of lead on environment and population, many efforts are conducted to remove it from water of distinct origins. It is commonly removed by precipitation as carbonate or hydroxide; besides other physicochemical methods are available to lead elimination. The maximun contaminant level in drinking water established

by EPA is 15µg/l. However, it is desirable the total elimination of lead due to its extreme potential toxicity [Murruni et al., 2007]. In a first report concerning to the photodeposition of Pb^{2+} ions on TiO_2 and metallized TiO_2, it was found that the former only produces PbO, whereas the last converts efficiently Pb ions to PbO_2 [Tanaka et al., 1986]. In the same work, it was proposed a reaction mechanism in two steps involving the reduction of oxygen to form the superoxide ion and the subsequent oxidation of Pb ions:

$$2O_2 + 2e^- \rightarrow 2O_2^- \tag{5}$$

$$Pb^{2+} + 2O_2^- \rightarrow PbO_2 + O_2 \tag{6}$$

Their mechanism was supported by experiments carried out in different atmospheres: nitrogen, argon and oxygen at several partial pressures. In N_2 and Ar, irradiation of TiO_2 suspensions did not result in lead oxide formation. It is worth noting that a high pressure Hg lamp (500 W) was used for all their photocatalytic deposition reactions.

Litter et al. 1999, have proposed a different mechanism which involves two consecutive electron transfer reactions. Lead ions are oxidized by holes or by hydroxyl radicals passing through the divalent to the tetravalent state, equations 7 and 8:

$$h^+/HO^\bullet + Pb^{2+} \rightarrow Pb^{3+} + OH^- \tag{7}$$

$$h^+/HO^\bullet + Pb^{3+} \rightarrow Pb^{4+} + OH^- \tag{8}$$
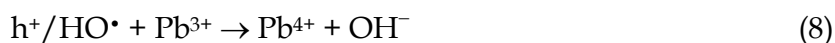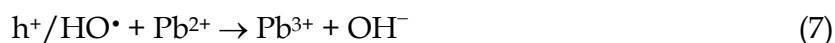
A further enhancement was achieved with platinized TiO_2 by decreasing the overpotential of oxygen. In fact, the role of oxygen is crucial to carry out the photocatalytic cycle and it has found a linear dependence of oxygen partial pressure based on a Langmuir-Hinshelwood mechanism [Torres & Cervera-March, 1992].

2.2 Co^{2+}

Recently, it has been highlighted many applications of cobalt compounds deposited on semiconductors such as: catalysts for solar oxygen production, gas sensors, batteries, electrochromic devices, among others [Steinmiller & Choi, 2009; Tak & Yong, 2008]. In particular, the photodeposition of Co_3O_4 spinel phase on ZnO has been prepared by two routes, one consisting in the direct photo-oxidation of Co^{2+} ions to Co^{3+} ions and the other by an indirect procedure involving the reduction of Co^{2+} to Co° and the oxidation of metallic cobalt to Co_3O_4 by means of the oxygen coming from the photo-oxidation of water.

By using the direct deposition route, a ZnO electrode was immersed in an aqueous solution of $CoCl_2$ mantaining the pH constant at 7 and illuminating with UV light (λ= 302 nm). Due to the oxidation potential of Co^{2+} to form Co_3O_4 is 0.7 V at pH= 7 at low concentrations of Co^{2+} (10^{-3} M) and the valence band edge of ZnO is located at around 2.6 V vs NHE, the photogenerated holes can easily oxidize Co^{2+} ions to Co^{3+} ions. The complete photocatalytic cycle must also include the reduction of water or dissolved oxygen in the solution to have an efficient Co^{2+} photo-oxidation [Steinmiller & Choi, 2009]:

$$2 Co^{2+} + 3H_2O \rightarrow Co_2O_3 + 6H^+ + 2e^- \tag{9}$$
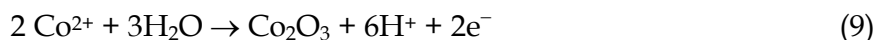
From a thermodynamic point of view, Co^{3+} ions can be deposited on any semiconductor that has a valence band edge located at a more positive potential than that of the Co^{2+} ions, as shown in Figure 1.
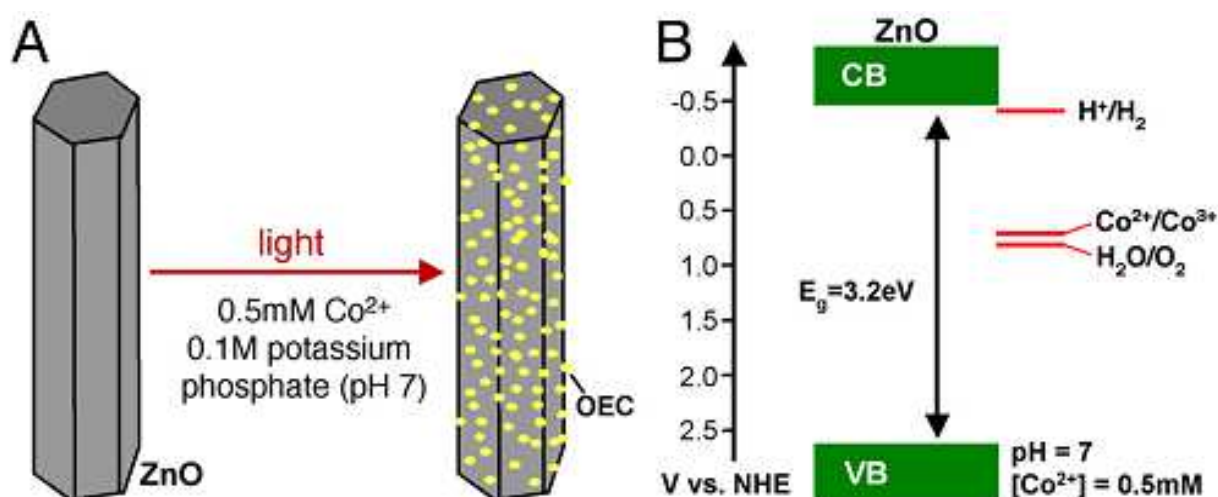

Fig. 1. Schematic representation. (A) Photochemical deposition of the Co-based catalyst on ZnO and (B) relevant energy levels. [Reproduced from Steinmiller and Choi, with permission from PNAS, copyright 2009 by National Academy of Sciences].

By the second route, the ZnO nanowires were grown by ammonia solution hydrothermal method and then coated with Co_3O_4 using a photocatalytic reaction. This last method was selected considering that the redox reactions of aqueous chemical species on irradiated semiconductor surfaces has characteristics of site-specific growth. Briefly, the ZnO nanowire array was immersed in an aqueous solution of $Co(NO_3)_2$ and was irradiated with UV-light of 325 nm from minutes to 24 h. According to the results of this work, the morphology of the heterostructures depended on the photocatalytic reaction parameters such as the concentration of Co^{2+} in solution, UV irradiation time and the geometrical alignment of the ZnO nanowires. The photocatalytic process was explained in terms of redox cycle which includes the reduction of Co^{2+} species into $Co°$ and the oxidation of water to produce O_2. In fact, after irradiation of ZnO with photon energy larger than the band gap of ZnO (3.4 eV) generates the charge carriers (electron-hole pairs). The photogenerated electrons in the conduction band reduce Co^{2+} to $Co°$ favoring the accumulation of holes in the valence band. In addition, the holes oxidizes water to molecular oxygen which carries out the partial oxidation of $Co°$ to $Co^{2+}Co_2^{3+}O_4$ spinel, as outlined in Figure 2. It seemed that this simple, room temperature and selective photodeposition process can be applicable to other semiconductors (e.g. TiO_2, CdS, SnO_2…) or to other shapes of nanomaterials.

2.3 Hg°

Mercury is a neurotoxic heavy metal frecuently found in industrial wastewaters at concentrations higher than 0.005 ppm and unfortunately it cannot be bio- or chemically degraded [Clarkson & Magos, 2006]. It is released to the environment by coal combustion and trash incineration, mainly as gaseous mercury producing methyl mercury in the aquatic ecosystem by the action of sulfate-reducing bacteria. Certainly, due to its multiple industrial applications (e.g. pesticides, paints, catalysts, electrical device etc.) it can also be found in
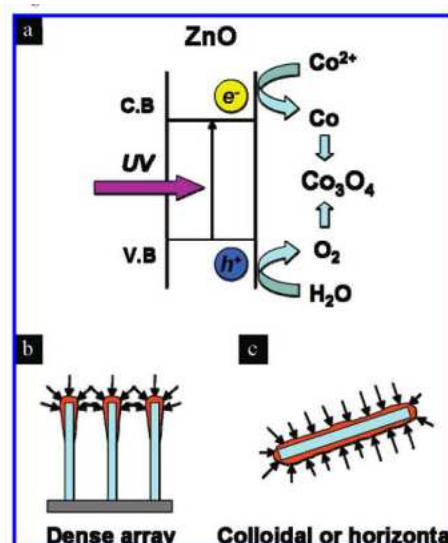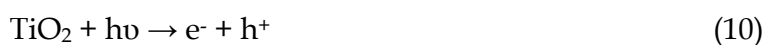
Fig. 2. (a) photocatalytic reaction scheme showing the reduction of Co ions to metallic Co and its oxidation to the spinel Co_3O_4, (b) Co_3O_4 deposited on the tip of ZnO, (c) Co_3O_4 deposited on the whole surface of ZnO. [Reproduced from Tak and Yong with permission from The Journal of Physical Chemistry; copyright 2008].

solution as Hg (II). Several methods have been investigated for its removal or control, such as, precipitation, ion exchange, adsorption, coagulation and reduction. However, the photocatalytic oxidation (PCO) of gaseous mercury by UVA-irradiated TiO_2 surfaces has been reported as a good option for its capture [Snider and Ariya, 2010].

For instance, an enhanced process including adsorption of gaseous mercury on silica-titania nanocomposites and then its photocatalytic oxidation has been published [Li and Wu, 2007]. However, some problems of reactivation of the nanocomposite as well as pore structure modification during Hg and HgO capture and deposition have to be solved. In the same work, it has been proposed the use of pellets of silica-titania composites and it was found that a decrease of contact angle was likely responsible for mercury capture for long periods. Usually, the experimental systems to evaluate the PCO of gaseous mercury include water vapor to supply the OH radicals required for the oxidation and a source of UVA irradiation (320-400 nm, 100 W Hg lamp). Figure 3 shows a typical schematic diagram for the PCO using titania-silica pellets.

According to the results obtained for the PCO of Hg in gas phase using a titania-silica nanocomposite [Li and Wu, 2007] , it has been proposed the following reaction mechanism:

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \tag{10}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{11}$$

$$h^+ + OH^- \rightarrow {}^\bullet OH \tag{12}$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{13}$$

$${}^\bullet OH + Hg^o \rightarrow HgO \tag{14}$$

which was successfully expressed by the Langmuir-Hinshelwood model. The rate of photo-oxidation of Hg was significantly inhibited by the presence of water vapor explained in terms of a competitive adsorption of water and mercury on the surface of TiO_2.

Efforts to gas mercury oxidation in air are now focused by using immobilized semiconductors irradiated with visible light looking for a potentially safe, low-cost process [Snider and Ariya, 2010].
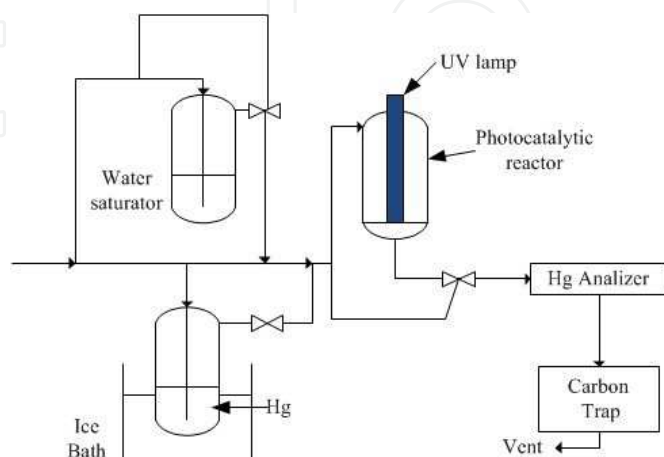

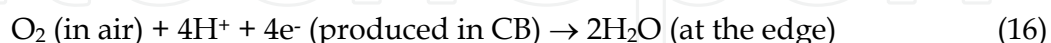Fig. 3. Schematic diagram for the photocatalytic oxidation of mercury gas. After [Li and Wu, 2007].
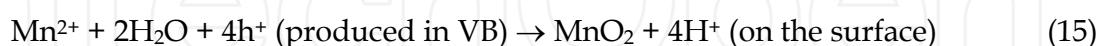
2.4 Mn^{2+}

Manganese (II) in aquatic systems is a problem of environment concern due to its slow oxidation to MnO_2 which is responsible for the formation of dark precipitates. The photocatalytic oxidation of Mn^{2+} to Mn^{4+} in the presence of irradiated titanium dioxide has been scarcely studied since the 80's [Tanaka et al. 1986, Lozano et al. 1992 and Tateoka et al. 2005, Matsumoto et al., 2008]. This process represents an alternative route for its removal and the resulting material could be used as supported metal oxides catalysts [Tateoka et al. 2005, Matsumoto et al., 2008]. In the first publication, it was used concentrations ranging from 10^{-4}-10^{-3} mol/L aqueous solutions of Mn^{2+} with irradiated TiO_2 and Pt/TiO_2 photocatalysts using a high pressure Hg lamp of 500 W. Mn^{2+} conversion to Mn^{4+} was 98 and 78% from low to high concentrations onto Pt-loaded TiO_2 in 1 h of irradiation time. In the second work published in 1992, the oxidation of Mn^{2+} was carried out in acidic conditions using TiO_2 Degussa P-25 and irradiating with a Hg vapor lamp of 125 W at initial concentration of Mn^{2+} of 10^{-4} mol/L. One of the visual evidence of the photocatalytic oxidation of Mn^{2+} to Mn^{4+} is the appearance of a slight dark coloration over the TiO_2. The overall reaction scheme for the photo-oxidation was presented as follows:

$$Mn^{2+} + \frac{1}{2} O_2 + H_2O \rightarrow MnO_2 + 2H^+ \tag{14}$$
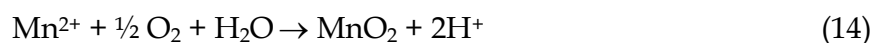
In a recent work, it was studied the photodeposition of metal and metal oxide at the TiO_x nanosheet to observe the photocatalytic active site (Matsumoto et al., 2008). It was investigated the photodeposition of Ag, Cu, Cu_2O and MnO_2 at a TiO_x nanosheet with a lepidocrocite-type structure prepared from K-Ti-Li mixed oxide. As expected, the photoreduction of Ag, Cu and Cu_2O, occurred mainly at edges where the photoproduced

electrons move in the network of Ti^{4+} ions in the nanosheet. On the other hand, the photo-oxidation of Mn^{2+} ions occurred on all over the surface of the nanosheet, which is indicative of the presence of holes at the O^{2-} ion. The photo-oxidation reaction was carried out in a diluted solution of $MnSO_4$ (10^{-6} M) in air at room temperature irradiating with UV light of 265 nm. It was found that pH played an important role in the photodeposition: the amount of formed MnO_2 increased at higher values of pH, and no metallic Mn was observed at lower values of pH (pH=2.1). The coupled reactions that takes place during the photodeposition of MnO_2 are described by eqs. (15,16):

$$Mn^{2+} + 2H_2O + 4h^+ \text{ (produced in VB)} \rightarrow MnO_2 + 4H^+ \text{ (on the surface)} \qquad (15)$$

$$O_2 \text{ (in air)} + 4H^+ + 4e^- \text{ (produced in CB)} \rightarrow 2H_2O \text{ (at the edge)} \qquad (16)$$

A complete model explaining the photodeposition process and charge mobility are illustrated in Figure 4. In other words, according to the results reported by (Matsumoto et al., 2008) the photoproduced electrons move at the 3d orbital conduction band of the Ti^{4+} network in the nanosheet, whereas the photoproduced holes are located at the 2p orbital as O^{2-} species at the surface. Finally, the charge carriers recombination is favored under low pH which was found as a key parameter to control the photoprocess on the oxide nanosheet.
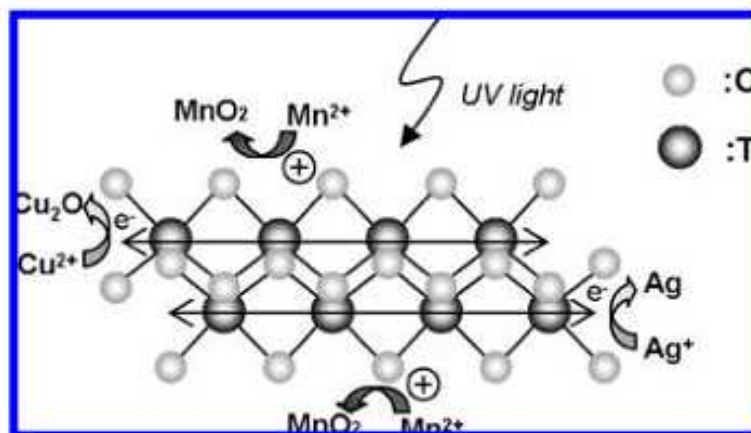

Fig. 4. Model of the movements of the photoproduced electron and hole at the TiO_x nanosheet with a lepidocrocite-type structure. The electron moves in the 3d CB consisting of the Ti^{4+} network in the nanosheet and then reduces Ag^+ and Cu^{2+} at the edge, while the hole exists at the 2p VB consisting of the O^{2-} surface and oxidizes Mn^{2+} on the surface. Reproduced from Matsumoto et al., with permission from The Journal of Physical Chemistry C, copyright 2008.
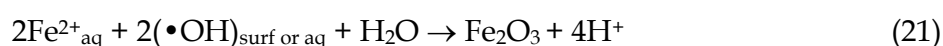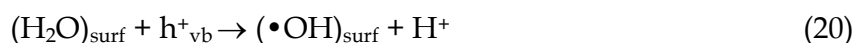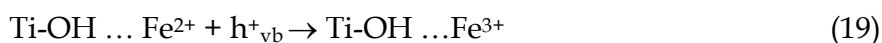
2.5 Fe^{2+}

One of the main drawbacks to commercialize the TiO_2 photocatalytic process at large scale is the use of UV light as irradiation source. Then, many efforts have been done during the past two decades to develop new photocatalysts active under visible light [Choi, 2006]. For instance, the presence of Fe^{3+} ions on TiO_2 favors the absorption of photons in the visible region as well as accelerates the photocatalytic oxidation of organic compounds. In this case, Fe^{3+} ions reduce to Fe^{2+} by the photoelectrons of the conduction band avoiding the charge

recombination and increasing the photonic efficiency. However, the reverse process, this means the photo-oxidation of Fe^{2+} has been scarcely studied. A photoelectrochemical oxidation of Fe^{2+} ions on porous nanocrystalline TiO_2 electrodes was studied by using in situ EQCM (electrochemical quartz crystal microbalance) technique [Si et al., 2002]. In this work, it was found that the pH of iron precursor solution plays an important role in terms of the amount of adsorbed Fe^{2+} ions. The maximum value was 1.1 mmol Fe^{2+} at pH 4. The stability and the adsorption process was studied by the EQCM technique and it was found that the adsorption amount of Fe^{2+} ions on TiO_2 support was not affected by bias potential drop. The above result was attributed to Fe^{2+} ions are coordinated with hydroxyl groups of TiO_2 surface by the following reaction:

$$\text{Ti-OH} + Fe^{2+} \rightarrow \text{Ti-OH} \dots Fe^{2+} \tag{17}$$
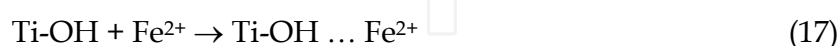
As is well known at low pH values, TiO_2 has negative surface charge favoring the electrostatic attraction of Fe^{2+} ions. Therefore, the adsorption-desorption behavior of Fe^{2+} ions on TiO_2 surface is strongly affected by pH changes. After irradiation of the adsorbed Fe^{2+} ions on TiO_2 the following photochemical reactions can be expected:

$$TiO_2 + h\nu \rightarrow h^+_{vb} + e^-_{cb} \tag{18}$$

$$\text{Ti-OH} \dots Fe^{2+} + h^+_{vb} \rightarrow \text{Ti-OH} \dots Fe^{3+} \tag{19}$$

$$(H_2O)_{surf} + h^+_{vb} \rightarrow (\bullet OH)_{surf} + H^+ \tag{20}$$

$$2Fe^{2+}_{aq} + 2(\bullet OH)_{surf\ or\ aq} + H_2O \rightarrow Fe_2O_3 + 4H^+ \tag{21}$$

2.6 Ce^{3+} and Sn^{2+}

Nowadays, the preparation of semiconductor nanoparticles with precise control of size and morphology has found new applications as ion-conducting, sun-screening, anti-corrosion and electro-catalytic properties [Kamada & Moriyasu 2011]. For instance, CeO_2 and SnO_2 have been synthesized as semiconducting oxide films by a photodeposition method [Kamada & Moriyasu 2011]. This method has the advantage of depositing homogeneously a thin film of the respective semiconductor by manipulating certain parameters such as concentration of the precursor, time and intensity of the irradiation, etc.

In the work reported by Kamada and Moriyasu, a photo-excited electroless deposition was carried out by the irradiation with UV light of an aqueous solution of cerium triacetate in a platinum substrate. It was observed an enhancement of the deposition of CeO_2, which was explained in terms of an electron transfer local cell mechanism. In this case, Ce^{3+} was oxidized by dissolved oxygen through an electron transfer in the Pt substrate and then transformed in a CeO_2 thin film, as shown in Figure 5. Surprisingly, the deposition rate was detrimentally affected by increasing the concentration of Ce^{3+} ions.

In a similar way, Sn^{2+} ions were anodically oxidized to Sn^{4+} and deposited on a Pt electrode with UV light irradiation. This process was followed through a different reaction mechanism than that of cerium. Tin oxide deposition proceeded by a photochemical reaction started with the disproportionation of Sn^{2+} and the further production of Sn^o and

Sn^{4+}. Then Sn^{4+} was hydrolized to the insoluble H_2SnO_3, which finally is decomposed to SnO_2.
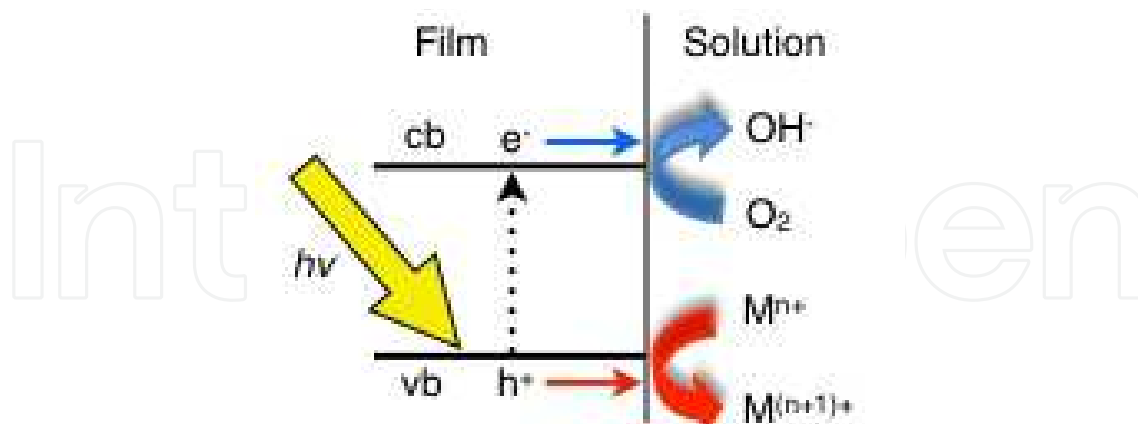

Fig. 5. A schematic representation of the photocatalytic oxidation of metal oxides in presence of a conductive substrate (Pt film) and dissolved oxygen. After [Kamada and Moriyasu 2011].

3. Photocatalytic reduction of single component

3.1 MnO$_4^-$/MnO$_2$

This particular route for depositing metal oxides on semiconductors, also called reductive deposition, has been studied intensively for its potential in environmental remediation: for instance in the partial reduction of chromates (Cr^{6+} are extremely toxic) to the much less toxic Cr^{3+} or for UO_2^{2+} to UO_2 or but also in the preparation of special catalysts containing Cu_2O obtained by the partial reduction of Cu^{2+} to Cu^{1+} [Wu et al., 2003].

Lately, it has been reported works devoted to the reductive deposition of Mn_3O_4 or RuO_2 on titanium dioxide by using $KMnO_4$ contained in waste water or pure aqueous solutions of $KRuO_4$. The reaction mechanism involves a cathodic process where anions (e.g. CrO_4^{2-}, MnO_4^-, etc.) having strong oxidation power effectively accept the photogenerated electrons of the conduction band of TiO_2 after irradiation with UV light and the deposition of the corresponding oxide. On the other hand, in the anodic process the holes found in the valence band oxidize the sacrificial oxidant agent to produce the proton required for the photoreduction of the anion.

In this sense, Nishimura et al., 2008, have prepared coupled catalysts nanoparticles of MnO_2/TiO_2 by the photoreduction of harmful MnO_4 anions in water, see Fig. 6, and applied to the decomposition of hydrogen peroxide in the dark or irradiated with UV light. This coupled semiconductors can improve the charge separation efficiency through interfacial electron transfer. In addition, it is well known the catalytic properties of MnO_2 for the oxidation of organic pollutants which coupled with TiO_2 could have a special synergism in conventional catalytic or photocatalytic reactions. It was used a 10^{-3} M aqueous solution of $KMnO_4$ at pH 7, UV light ($\lambda > 300$ nm) and inert atmosphere to carry out the photoreduction reaction of manganate ions. In a blank experiment during the irradiation of the solution of $KMnO_4$ (without TiO_2) it was only found a partial decomposition of MnO_4^- ions to MnO_4^{2-} and O_2. The photodeposition of Mn_3O_4 on TiO_2 was confirmed by XPS and these stick-

shaped nanoparticles were converted to cubic β-MnO$_2$ by heating a 600°C.The overall photodeposition reaction of Mn$_3$O$_4$ was as follows:

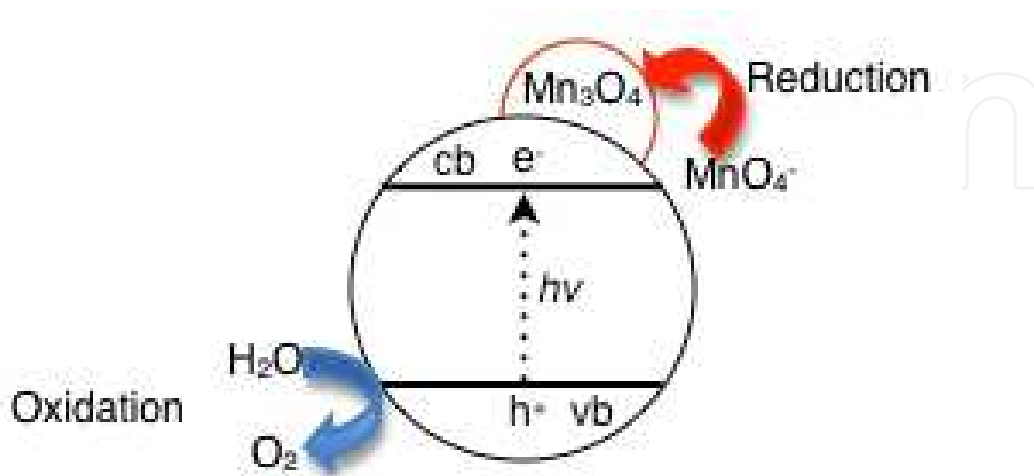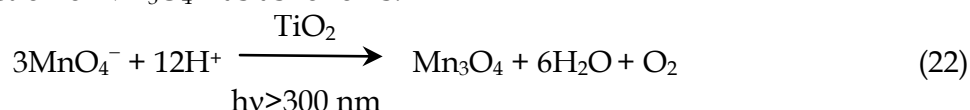$$3MnO_4^- + 12H^+ \xrightarrow[h\nu>300\ nm]{TiO_2} Mn_3O_4 + 6H_2O + O_2 \tag{22}$$

Fig. 6. Scheme showing the simultaneous photocatalytic reduction of permanganate anions in aqueous solution forming Mn$_3$O$_4$ and the photooxidation of water forming oxygen during UV illumination of TiO$_2$. After Nishimura et al., 2008.

3.2 RuO$_4^-$/RuO$_2$

The photocatalytic decomposition of water strongly requires the presence of effective catalysts for hydrogen and oxygen evolution. Usually, most published works are focused to the overall water splitting and a few have independently tested the water photo-oxidation reaction. In particular, the water photo-oxidation has been successfully studied with partially dehydrated RuO$_2$. However, its loading onto substrate surfaces by the conventional thermal methods lead to deep dehydration and sintering, reducing dramatically its activity and stability. An early work of Mills et al., 2010, has achieved the photodeposition of RuO$_2$ on titanium dioxide by a simple reaction of an aqueous solution of KRuO$_4$ mixed with TiO$_2$ and irradiation with a Xe or Hg lamp and Ce^{4+} ions as sacrificial electron donor. The following reaction scheme was proposed:

$$4RuO_4^- + 4H^+ + 4TiO_2 \rightarrow 4TiO_2/RuO_2 + 3O_2 + 2H_2O \tag{23}$$
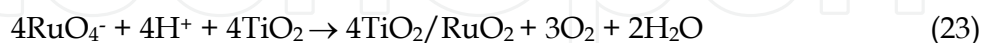
The photoreduction of ruthenate ion (RuO$_4^-$) in the absence of the titania photocatalyst remain unchanged.

4. Photocatalytic oxidation to obtain mixed oxides

4.1 Rh$_{2-y}$Cr$_y$O$_3$

The direct photodeposition of nanoparticulate mixed oxides on semiconductors was firstly reported by Maeda et al. [Maeda et al. 2008] supported in the pioneer work of Kobayashi et al. 1983, who studied the simultaneous photodeposition of Pd/PbO$_2$ and

Pt/RuO$_2$ on single crystals of TiO$_2$. Searching a good photocatalyst for overall water splitting, Maeda et al., 2006, developed a complex semiconductor $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ as a promising stable material active under visible light irradiation. However, this semiconductor only presented activity for water oxidation and its activity for water reduction was very low. Therefore, an effective modification of the GaN:ZnO semiconductor to promote the water reduction photoactivity was required. As is well known, noble metals or transition-metal oxides are often employed as cocatalysts to facilitate the water reduction reaction. Then, it was proposed the preparation of a noble-metal/mixed oxide (core/shell) supported on the GaN:ZnO solid solution by in situ photodeposition method [Maeda et al., 2006]. A two steps procedure was employed, Rh nanoparticles were firstly deposited on the mixed support with an aqueous precursor of Na$_3$RhCl$_6$.H$_2$O and then Cr$_2$O$_3$ was deposited from a K$_2$CrO$_4$ solution, in both steps visible light irradiation was employed (λ>400 nm), as shown in Fig. 7. The authors confirmed the formation of a Rh/Cr$_2$O$_3$ core/shell nanoparticle with an average size of the ensemble of 12 nm and found a dramatical change in photocatalytic activity for overall water splitting in comparison with Rh or Cr$_2$O$_3$/GaN:ZnO supported systems.

In a second similar work of Maeda et al., 2008, it was reported a method to prepare mixed oxides of rhodium and chromium on five different semiconductors. They used aqueous solutions of (NH$_4$)RhCl$_6$ and K$_2$CrO$_4$ containing dispersed semiconductor powders and irradiated them during 4 hours with wavelengths whose energy exceeded those of each semiconductor band gap, as shown in Table 2.

Semiconductor	Rhodium (%wt)	Chromium (%wt)	Irradiation wavelength (nm)
$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ (x=0.12)	1	1.5	>400
$(Zn_{1+x}Ge)(N_2O_x)$ (x=0.44)	1	1.5	>400
SrTiO$_3$	0.5	0.75	>200
Ca$_2$Nb$_2$O$_7$	0.5	0.75	>200
ß-Ga$_2$O$_3$	0.5	0.75	>200

Table 2. Semiconductor powders and Rh-Cr content for mixed oxide photodeposition.

Based on XPS characterization, authors concluded that photodeposited mixed oxides have the composition Rh$_{2-y}$Cr$_y$O$_3$ and explained that the photoreduction of both, Rh^{3+} and Cr^{6+} proceeds via a band-gap transition of the semiconductor powder.

Furthermore, it was found that this mixed oxide is only formed when Rh and Cr are simultaneously present in the precursor solution. The photocatalytic performance of the materials was investigated for the evolution of H$_2$/O$_2$ in water splitting displaying different photocatalytic activity values depending of the support employed. In particular, photocatalyst containing the mixed oxide Rh$_{2-y}$Cr$_y$O$_3$ exhibited a two fold activity compared to that of semiconductor alone.

4.2 NiCoOₓ

In 2006, Buono-Core et al. 2006 reported the photodeposition of NiCoOₓ on Si (100). Interest in this mixed oxide system regards on its antiferromagnetic characteristics. Authors synthesized NiCo(DBA)₂ as a single source precursor for the preparation of NiCo mixed oxide thin films, Figure 8. A solution of precursor in chloroform was prepared and then spin coated onto Si (100) chips. The films were irradiated under a 200 W Hg-Xe lamp (λ ~254 nm) until no ligand absorptions were observed in FT-IR. Characterization by AFM and XRD lead the authors to conclude about the amorphous nature of the mixed oxide films. After annealing at 600 °C of those films, XRD evidenced individual NiO and CoO oxides confirming the metastable nature of NiCoₓ films. Furthermore, EDAX analyses demonstrated homogeneity of Ni and Co dispersion throughout Si (100) surface. Finally, authors suggest the extendibility of this technique for rendering a wide range of binary metal oxide phases.
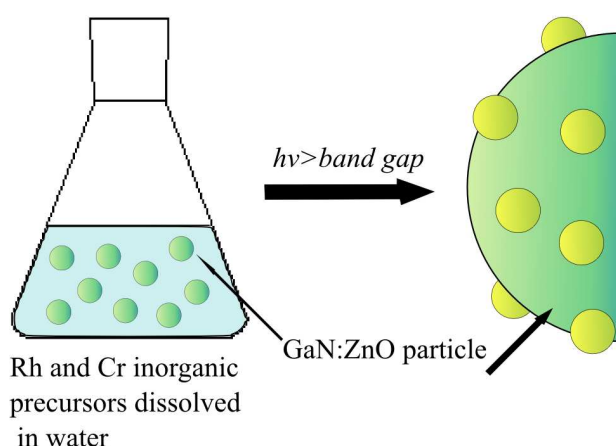

Fig. 7. Scheme showing the photoconversion of inorganic precursors of Rh and Cr and their deposition of particles of GaN:ZnO. After from Maeda et al., 2008
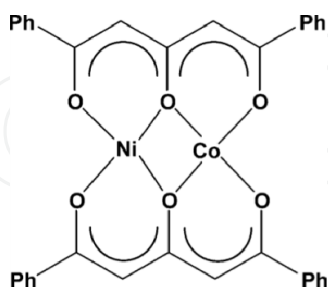

Fig. 8. NiCo(DBA)₂, DBA stands for Dibenzoylacetone.

5. Conclusions

Photocatalytic deposition methods have been shown to be of high potentiality for loading small-size dispersed metal oxides on powder or film semiconductors. This

method also is a promising technique to obtain composite nanomaterials with the possibility to control the structural properties. Size, morphology and structure of the deposited oxides depend of the concentration of precursor and semiconductor, pH of the solution, light intensity and wavelength, illumination time and the type of sacrificial electron acceptor employed.

Although most work has been focused to the use of titanium dioxide as supporting material, other semiconductors have now been investigated (e.g. ZnO, WO_3, SnO_2, ZnS, GaO). So that, it is possible to design new advanced compositing materials by selecting the appropriate semiconductor and depositing pure or mixed oxides with specific applications in solar energy conversion, purification of water and air streams, metal corrosion and prevention, chemical synthesis and manufacturing, nanoelectronics, medicine, among others.

In addition, this method has the main advantage of not using high pressures and temperatures and in most cases the synthesis is carried out in aqueous solution. In spite of the photodeposition methods seem to be ideal for the synthesis of catalytic materials, to date, research reports have mainly focused in the photoreduction of noble metals. Therefore, the range of metal oxides deposited by a photoxidative or photoreductive routes has been limited. Finally, the oxidative deposition of metal oxides in semiconductors requires a deep investigation from fundamental to practical application. This is of crucial importance for understanding the mechanism of simple or mixed oxides formation (core-shell or alloys) during the irradiation step and the interfacial reactions of the process.

6. Acknowledgements

7. References

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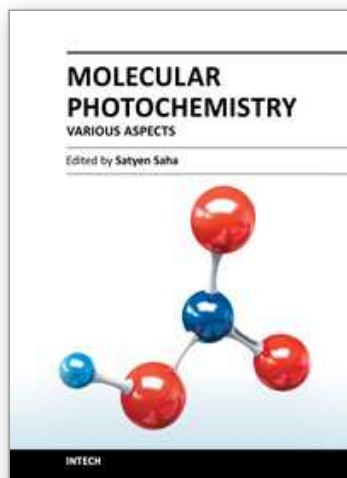
Molecular Photochemistry - Various Aspects

Edited by Dr. Satyen Saha

There have been various comprehensive and stand-alone text books on the introduction to Molecular Photochemistry which provide crystal clear concepts on fundamental issues. This book entitled "Molecular Photochemistry - Various Aspects" presents various advanced topics that inherently utilizes those core concepts/techniques to various advanced fields of photochemistry and are generally not available. The purpose of publication of this book is actually an effort to bring many such important topics clubbed together. The goal of this book is to familiarize both research scholars and post graduate students with recent advancement in various fields related to Photochemistry. The book is broadly divided in five parts: the photochemistry I) in solution, II) of metal oxides, III) in biology, IV) the computational aspects and V) applications. Each part provides unique aspect of photochemistry. These exciting chapters clearly indicate that the future of photochemistry like in any other burgeoning field is more exciting than the past.

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