

Synthesis and characterization of new modified photocatalysts for environmental and energy applications

Ana Laura Luna Barron

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Synthesis and characterization of new modified photocatalysts for environmental and energy applications

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Abbreviations — Glossary

- * MS mass spectrometry;
- ***** GC gas chromatography;
- * AQE apparent quantum efficiency;
- ***** TOC total organic carbon;
- * CB conduction band;
- ***** VB valance band;
- ***** E_g band gap;
- ***** DRS diffuse reflectance spectrometry;
- * NPs nanoparticles;
- ***** TRMC time-resolved microwave conductivity;
- * AOP advanced oxidation processes;
- ***** XPS X-ray photoelectron spectroscopy;
- ***** BE binding energy;
- ***** HPLC high performance liquid chromatography;
- * PL photoluminescence;
- ***** A acceptor;
- * D donor;
- ***** TRXRF X-ray fluorescence spectrometer;

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- $\pmb{\ast}$ e_s^- electron solvated also call hydrated electron;
- \bigstar h⁺ hole;
- **★** HO[●] hydroxyl radical;
- \bigstar M⁺ metal cation;
- * M^0 metal;
- * ROH alcohol;
- * I_{max} maximum value of the TRMC signal;
- * I_{40s}/I_{max} TRMC short-range decay, arbitrarily fixed up to 40 ns after the maximum of the pulse;
- **★** TiO₂ titanium dioxide;
- * O₂ oxygen;
- ***** $Ti^{(4+)}OH$ hydroxyl ions at the surface of TiO_2 ;
- * O^{2-} bridging oxygens ;
- * $O_2^{\bullet-}$ superoxide;
- $\pmb{\ast}$ H* atomic hydrogen ;
- ***** H_2 hydrogen;
- * $\operatorname{Ti}_{5C}^{4+}$ five-fold coordinated Ti^{4+} surface;
- ***** EB electron beams;

Synthèse

La photocatalyse est une technologie prometteuse pour l'environnement et l'énergie. L'intérêt actuel pour celle-ci découle des défis auxquels le monde doit faire face, liés aux changements climatiques et à l'approvisionnement en énergie. La photocatalyse a démontré qu'elle pouvait dégrader un grand nombre de contaminants dans l'eau et dans l'air ainsi que produire de l'énergie propre sous forme d'hydrogène en utilisant la lumière et un semi-conducteur en tant que composantes clés du processus. De plus, à côté de ses applications prometteuses, la photocatalyse se caractérise également par sa simplicité et son faible coût. Le processus photocatalytique global consiste en la génération de paires électron-trou, suite à l'excitation d'un semi-conducteur par une lumière ayant une énergie supérieure ou égale à l'énergie de la bande interdite de celui-ci. Les électrons et les trous sont à la base des réactions souhaitées de réduction et d'oxydation. Comme il l'a été mentionné précédemment, les deux éléments clés sont la lumière et le semi-conducteur. Le dioxyde de titane (TiO_2) est le semi-conducteur le plus utilisé en photocatalyse en raison de ses excellentes propriétés physiques et chimiques, de sa grande disponibilité et de son faible coût. Cependant, les deux principaux inconvénients de l'utilisation de TiO₂ photocatalytique sont la cinétique de réaction relativement lente et la nécessité d'utiliser un rayonnement UV. La modification de surface de TiO₂ avec des nanoparticules métalliques (NPs) est une stratégie classique pour surmonter ces inconvénients. Les photocatalyseurs modifiés (métal NPs/TiO_2) ont montré leur capacité à augmenter l'efficacité de la réaction photocatalytique sous lumière UV, en particulier pour la réaction de génération d'hydrogène, et dans certains cas pour la réaction de dégradation des polluants. En outre, certains métaux déposés ont montré un effet de sensibilisation de la surface de l'oxyde de titane, ce qui conduit à l'activation du photocatalyseur sous lumière visible. Récemment, il a été proposé de modifier la surface de TiO_2 avec des NPs bimétalliques. Les principaux points forts des systèmes bimétalliques sont: (1) dans la plupart des cas une activité photocatalytique supérieure comparée à

celle obtenue avec des modifications monométalliques et (2) la possibilité d'utiliser des métaux peu coûteux tels que Co, Ni et Cu. Malgré les grandes avancées réalisées dans l'étude de la modification de surface du TiO_2 par des NPs mono et bimétalliques sur l'activité photocatalytique, beaucoup d'aspects restent encore incompris. Notre travail présente la modification du TiO_2 commercial P25 par des NPs mono- et bimétalliques (Ni, Au, Ni-Au, Pd et Ni-Pd), leur caractérisation et leur évaluation photocatalytique. Cette étude complète relie les trois étapes principales du procédé photocatalytique: (1) l'absorption de la lumière (génération des paires électron-trou), (2) la dynamique des porteurs de charge et (3) l'efficacité photocatalytique. Les NPs métalliques ont été synthétisées directement sur la surface de TiO₂ par rayonnement gamma. La caractérisation exhaustive a été faite par Microscopie Electronique à Transmission Haute Résolution (MET-HR), Diffraction des Rayons X (DRX). Analyse Dispersive en Energie de RX (EDS). Spectrométrie Photoélectronique X (XPS), Spectroscopie UV-vis en Réflexion Diffuse (DRS) et Time Resolved Microwave Conductivity (TRMC). Les échantillons ont été testés, sous illumination UV-Visible poly et monochromatique (Action Spectra), par les réactions photocatalytiques suivantes: (1) dégradation du phénol et du 2-propanol, (2) production d'hydrogène et (3) oxydation et réduction du Pb2+. Les résultats montrent que les systèmes bimétalliques sont plus actifs que leurs homologues monométalliques respectifs. Nos résultats nous conduisent à affirmer que le rôle principal des NPs métalliques est, dans le cas de la production d'hydrogène photocatalytique, sur l'aspect catalytique. Cette étude ne rejette pas les arguments classiques des NPs métalliques agissant comme piégeurs d'électrons, mais montre que ce n'est pas leur rôle principal. Les échantillons Au/TiO_2 et Ni-Au/TiO₂ ont montré une activité photocatalytique dans la dégradation des composés organiques sous illumination visible. Ceci a été expliqué par l'effet plasmonique des NPs d'Au.

INTRODUCTION

The lifestyle of the modern society has provoked an increase of extraction and processing of resources to meet human consumption. This has been reflected in accelerated industrial growth, but also in negative environmental impact.

The energetic demand has increased considerably along with the industrial growth. From the past until nowadays, the fossil fuels such as coal, gas and petroleum have been considered as major energy resources. Approximately 85% of the world's energy is provided in the form of fossil fuels, which causes various serious environmental problems, namely atmospheric pollution (Figure 5.19), greenhouse effect, and depletion of natural resources.

Furthermore, the environmental impact by the industrial sector also affects unfortunately the waters. Due to poor environmental policies, industries have contaminated the waterways by release of toxic agents. The latter represent a serious and latent problem because freshwater is a limited and essential resource for life on Earth. From the total amount of water in the hydrosphere (1,386 million cubic kilometers) only 2.5 percent is freshwater, and only 0.26 percent of this freshwater is concentrated in lakes and river systems (accessible to humans). The rest is concentrated in Antarctic, Arctic and mountains in form of permanent ice or snow Holland *et al.* [2015]; Shiklomanov [2000]. Therefore misuse and pollution of water represent the lost of the ecosystem, which effects directly and indirectly the human being. The abnormal climatic changes that we are facing now are an irrefutable proof of the ecosystem alteration.

The direct effects of the water pollution on the humanity are already present. Around 4 billions of people have little or no access to clean water, and this has led to pollution-related diseases. The water scarcity has increased progressively in the last 60 years and the estimations reveal that, by 2025 the greater part of earth's population will likely live under conditions of low and catastrophically low water supply, see Figure 5.20. In view to suppress the worsening of clean water shortage, development of advanced with low-cost and high efficiency water



Figure 1: **Projections of global carbon emission and energy consumption rates.**(a) Carbon emissions in gigatons of carbon per year (GtC/yr) projected to year 2100. Black lines show total emission for different projection models. The colors indicate the fraction of the total due to coal, oil and natural gases sources. (b) Global energy consumption rates (primary power) projected to year 2100 and fractions from different energy sources Hoffert *et al.* [1998].

treatment technologies to treat the wastewater is desirable.

It should therefore be our goal to contribute to the development of technologies to treat wastewater and to provide energy— reliably, affordably and without endangering the natural environment. Both of these goals are the most urgent challenges scientists are facing today.

One thing everyone agrees on is that there are no obvious solutions. No single energy carrier or technology will be sufficient to safeguard our future energy supply. Similarly no single water treatment processes will be universal. Consequently, researchers must examine a broad range of options and develop many different kinds of technologies. This is the only way to create a sustainable energy and efficient wastewater systems that adequately takes local environmental, political,



Figure 2: Water availability of the world by natural-economic regions Shiklomanov [2000].

social, and economic conditions into account.

From broad spectrum of technologies currently explored by scientific community, photocatalysis represents an attractive technology to both energy supply and water treatment.

Photocatalysis is a promising technology to produce clean energy (hydrogen). The inexhaustibly abundant, clean, and safe energy of the sun can be used by photocatalysis for sustainable, nonhazardous, and economically viable technology capable to produce energy. Hydrogen is widely considered as the clean energy of the future. Using H_2 to supply the energy consumption leads to a markedly reduction of atmospheric pollution, because no greenhouse gases are produced

during the combustion process of H_2 .

Besides, photocatalysis is considered as an innovative water treatment technology, which is capable of degrading indistinctly organic compounds by highly reactive transitory species.

In either aforementioned applications (hydrogen generation or degradation of contaminants) the photocatalytic process is always present.

The two main components of the photocatalytic process is the light irradiation and the semiconductor. Titanium dioxide semiconductor has shown a great potential as photocatalyst for various significant reactions due to its chemical stability, non-toxicity, and high reactivity. The two main drawbacks of using TiO_2 as a photocatalyst are the relatively slow reaction kinetics and the necessity to use UV irradiation. To overcome the above drawbacks, many strategies have been investigated, for example doping, coupling it with a semiconductor, and surface modification with metal nanoparticles (NPs).

The deposition of metal NPs on titania surface has an important impact on the production of H_2 via photocatalysis. The addition of metals such as platinum or gold on a semiconductor surface leads to enhancement of its photoactivity for H_2 generation. This has been attributed to the ability of the metal to scavenge the photogenerated electrons. Surface modification of titania with metal nanoparticles can also improve its photocatalytic activity for degradation of organic pollutants.

Moreover some deposited metals have shown the ability to sensitize titania surface because they absorb visible light. This surface modification can lead to photocatalysts active under natural sunlight irradiation. However, the efficiency of metal nanoparticles to separate affectively the charge-carriers as well as the ability to absorb visible light depends on their nature, size, morphology, and loading.

Different recent publications report that surface modification of titanium dioxide with bimetallic NPs can lead to higher photocatalytic activity compared to titania modified with monometallic NPs. The bimetallic systems include not only noble metals, but also inexpensive transition metals such as Cu, Ni and Co, which represent an economic advantage.

Identifying the factors that govern the kinetics of the photocatalytic processes and understanding the role that metal NPs play is inherent to achieve the desired goal of developing more efficient systems.

Although great strides have been made in the study of the effect of surface modification of TiO_2 with mono- and bimetallic NPs on its photocatalytic activity, a lot still remains unknown. Most of the investigations have been based on the study of the kinetics or the mechanisms involved in photocatalysis. There are few reported studies, which integrate the absorption, dynamics of charge-carriers and photocatalytic activity.

The later has motivated the development of the present work, having the main objective to study systematically the effect of metal NPs on titania surface in the three principal steps of the photocatalytic processes: (1) absorption of light (generation of electron-hole pair), (2) dynamics of charge-carriers, and (3) efficiency of the photocatalytic activity.

The structure of this manuscript is the following:

Chapter 1 is devoted to provide a background about photocatalysis, its fundamentals as well as the still controversial issues. Photocatalytic applications such as hydrogen production and degradation of pollutants are also discussed. Moreover, a brief review recompilation of relevant reported results of TiO_2 surface modification with Au, Ni ad Pd is presented.

In Chapter 2, a detailed description of the synthesis conditions and depositions of metal NPs, technical aspects of characterization methods and set-up of photocatalytic tests are given. Both radiolysis (synthesis method) and TRMC (equipment to measure the kinetics of charge-carriers) are unconventional, then it was considered relevant to give an explanation of their fundamentals to help the readers to understand easily the results in the following chapters.

Chapters 3, 4, and 5 present the results of this work: Each chapter corresponds to one system. Chapter 3 refers to the TiO_2 surface modification with Nickel ions, the effect of the ions in the electronic and optical properties are studied, the photocatalytic activity is tested for the phenol degradation reaction. The results of surface modification of titania with mono- and bimetallic (Ni and/or Au) nanoparticles are presented in **Chapter 4**. First, the characterization of the photocatalysts is presented and discussed. Then, the photocatalytic efficiency is tested for different reactions such as phenol degradation, H₂ production, and reduction and oxidation of lead ions. Similarly, the effects of Ni and/or Pd nanoparticles deposited on the titania surface on its photocatalytic activity are presented in **Chapter 5**. Hydrogen generation from water/methanol solution was selected as a reaction to evaluate the photocatalytic activity for this system. For each photocatalytic system, we evaluated the absorption of the model pollutant, and we studied the charge-carriers kinetics and charge transfers. The photocatalytic activity was tested under both UV and visible light.

Chapter 1

THEORETICAL REVIEW

1.1 Heterogeneous photocatalysis

The field of heterogeneous photocatalysis has expanded rapidly during the last four decades and, has undergone various developments especially in relation to energy and environment. Heterogeneous photocatalysis is a natural phenomenon in which a material, called photocatalyst generates reactive species leading to chemical reactions with the compounds present at its surface, thanks to the action of light, without degrading itself. The only difference with conventional catalysis is the mode of activation of the catalyst in which the thermal activation is replaced by a photonic activation.

Heterogeneous photocatalysis can be carried out in a fluid phase either liquid or gaseous. As for classical heterogeneous catalysis, the overall process can be decomposed into five independent steps Chong *et al.* [2010]; Herrmann [1999]:

- 1. Transfer of the reactants in the fluid phase to the surface
- 2. Adsorption of a least one of the reactants
- 3. Reaction in the adsorbed phase
- 4. Desorption of the product(s)
- 5. Removal of the products from the interface region

The photocatalytic reaction occurs in the adsorbed phase (step 3). Such reaction is the consequence of an electron transfer from the photoexcited semiconductor to the adsorbed molecules (O_2 , H_2O , pollutants) Henderson [2011]. The electron transfer is the last step of the photocatalytic process. Then the step 3 occurs in the border between the photocatalytic process and the photoreaction mechanism (1,2,4,5 steps). Figure 1.1 shows the overall photocatalysis process.

In the following two sections a detailed explanation of photocatalytic process and mechanisms is given.



Figure 1.1: Scheme of heterogeneous photocatalysis. It involves two mainly subprocesses: 1) photocatalytic process inside of the semiconductor and 2) photoreaction mechanism.

1.2 Photocatalytic process

Since, first reports of Fujishima and Honda [1972] in the early 1970's, heterogeneous photocatalysis has been mostly based on TiO₂. It is estimated that from the total number of papers published in this field, approximately 80 % involved TiO₂-based materials Henderson [2011]. Compared to other semiconductor photocatalysts, titanium dioxide (TiO₂ or titania) has so far been shown to be the most promising material used for both fundamental research and practical applications, because it exhibits a higher photoreactivity and it is economically viable, nontoxic, chemically and biologically inert, and photostable Henderson [2011]; Schneider *et al.* [2014].

The absorption of light by semiconductors promotes redox reactions at their surface due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon, with an energy of $h\nu$ matches or exceeds the band gap energy (E_g) of the semiconductor, an electron (e⁻) is excited from the valence band (VB), into the conduction band(CB), leaving a hole (h^+) Hoffmann *et al.* [1995]. Such separation of charges is commonly called electron-hole pair.

These photogenerated electron-hole pairs may further be involved in the following three possible processes: (i) successfully migrate to the surface of the semiconductor and react with electron donors and electron acceptors adsorbed on the semiconductor; (ii) be captured by the defect sites in bulk and/or on the surface region of the semiconductor; and (iii) recombine and release energy in the form of heat or photon Hoffmann *et al.* [1995]. summarized a general mechanism of heterogeneous photocatalysis on TiO₂ by the following steps (Figure 1.2):

(1) Charge-carrier generation

$$TiO_2 + hv \longrightarrow h^+ + e^-$$
 (fs) (1.1)

(2) Charge-carrier trapping

$$e^{-} + Ti^{(4+)}OH \longrightarrow Ti^{(3+)}OH \quad deep \ trap \quad (< 200 \ ps) \quad (1.2)$$

$$e^- + Ti^{(4+)} \longrightarrow Ti^{(3+)} + e^-$$
 shallow trap (10 ns) (1.3)

$$h^+ + Ti^{(4+)}OH \longrightarrow Ti^{(4+)}OH^{\bullet}$$
 (10 ns) (1.4)

(3) Charge-carrier recombination

$$e^- + Ti^{(4+)}OH^{\bullet} \longrightarrow Ti^{(4+)}OH$$
 (100 ns) (1.5)

$$h^{+} + Ti^{(3+)}OH \longrightarrow Ti^{(4+)}OH \tag{10 ns} \tag{1.6}$$

(4) Interfacial charge transfer

$$Ti^{(3+)}OH + A \longrightarrow Ti^{(4+)}OH + A^{\bullet -}$$
 (ms) (1.7)

$$Ti^{(4+)}OH^{\bullet} + D \longrightarrow Ti^{(4+)}OH + D^{\bullet+}$$
 (100 ns) (1.8)

Therefore, it is possible to generalize the three key issues to TiO_2 photocatalysis. First, excitation or photon absorption. Second, the behavior of charge carriers after of their photo excitation, in particular recombination, charge transport to the surface and trapping. Third, the electron transfer starting the reaction mechanism.

Here, in the following section those three issues will be discussed in a compressive manner and based on published studies.



Figure 1.2: Schematic representation of the general photocatalytic process on TiO_2 nanoparticles.

1.2.1 Photon absorption: Charge-Carrier generation

The starting point in photocatalysis is the absorption of photons by the semiconductor. The bulk optical properties of TiO_2 anatase and rutile are well-documented in the literature. The minimal energy of the photons required to promote (excite) the electrons from the valance band (lower energy state) to the conduction band (higher energy state) is 3.2 and 3.0 eV for anatase and rutile respectively Kavan *et al.* [1996]; Murakami *et al.* [2001]. For rutile, such transition is direct while it is indirect for anatase Amtout and Leonelli [1995].

Although the photons with absorption threshold energy lead to electron excitation, the amount of those is not the optimum. Using Density Of State (DOS) calculations, it was estimated that maximum absorption occurs at $\sim 4 \text{ eV}$ for both anatase and rutile Amtout and Leonelli [1995].

The absorption thresholds can be altered by different factors such as photon energy, temperature and nanoparticle size Tang *et al.* [1994, 1995]. For example, it was observed that the anatase absorption coefficient increases exponentially with increasing photon energy while those of rutile increment more-or-less linearly. An increase of temperature induces a decrease of the optical absorption edge. For TiO_2 nanoparticles with size <10 nm the absorption edge is shifted it to the blue region Qu and Kroes [2006], as shown in Figure 1.3.



Figure 1.3: Effect of small size of TiO_2 nanoparticles in its optical absorption. The measurements were carried on for three size distribution of nanoparticles, peaked at ~2.8 nm (blue) to ~1.9 nm (red) and to ~1.5 nm (green) Qu and Kroes [2006].

The absorptivity of the TiO₂ can be altered from the bulk due to changes in transition energies and/or formation of surface states, which are induced by: 1) the incorporation or substitution of a foreigner atom into the TiO₂ lattice, commonly denominated doping, and 2) removal of some oxygen atoms from the titania lattice (oxygen vacancies). Both cases (doping or oxygen vacancies) provoke changes in the titania optical properties, which are usually a shift of the absorption toward longer wavelengths Hashimoto *et al.* [2006]; Henderson [2011].

The optical properties are usually inferred based in the bulk studies, however the surface of the material also has an important role in such properties. The surface atoms are different from those of the the bulk because of broken symmetry and bonds. Naturally surface states are formed due to the truncation of the bulk lattice influencing the absorptivity of the materials.

The surface can be reconstructed by the absorption of foreigner species, which lead to alteration of the optical properties of TiO_2 . For example the simple surface decoration with certain molecules as sensitizing dyes, stearic acid among other Hannappel *et al.* [1997]; Ramakrishna and Ghosh [2001]; Szarko *et al.* [2008]. Metal clusters such as Au, Ag exhibiting plasmonic band contribute to absorption of visible light Driessen and Grassian [1998]; Grabowska *et al.* [2013]; Hai *et al.* [2013]; Jovic *et al.* [2013]; Tian and Tatsuma [2005], see Figure 1.4.



Figure 1.4: Diffuse reflectance spectra of pure and modified P25 photocatalysts with bimetallic Au-Cu nanoparticles Hai *et al.* [2013].

In most cases of the latter examples, such modifications are the consequence of the incorporation of the optical transition proper to the modifier.

However, in other cases the modifier can affect the electronic states of TiO_2 . For example, a composite material formed by coupling a semiconductor such as, WO₃, SnO₂ or CuO to TiO₂ can be excited by UV/Vis light, through interfacial states created between them Luna *et al.* [2015]; Maeda and Hirota [2006]; Song

1.2. PHOTOCATALYTIC PROCESS

et al. [2006].

Although many groups have reported an extension of absorption TiO_2 to longer wavelengths using some of the strategies previously discussed, sometimes it does not correlated with its photoactivity.

1.2.2 HOLE TRAPPING

A possible fate of generated holes in TiO_2 is to be captured by trapping sites. Generally, bridging oxygens (O^{2-}) and hydroxyl groups (HO^{\bullet}), at the subsurface and surface of the TiO_2 , are considered as trapping sites Schneider *et al.* [2014]. From the interaction between holes and trapping sites, active centers are generated:

$$Ti^{(4+)}OH + h^+ \longrightarrow Ti^{(4+)}HO^{\bullet}$$
(1.9)

$$O^{2-} + h^+ \longrightarrow O^{-\bullet} \tag{1.10}$$

The nature of hydroxyl groups acting as trapping sites, has been a controversial issue in the photocatalysis field. First of all, the position of the valance band edge of TiO₂ is much more positive than standard redox potential of both hydroxyl groups and water, $E^0(OH^-/OH) = 1.9 V_{NHE}$ and $E^0(H_2O/OH) = 2.73 V_{NHE}$, then photogenerated holes are able to oxidize such species Wardman [1989]. Supporting the later, combined spin trapping and ESR techniques have provided evidence of photogeneration of OH radicals under UV illumination of TiO₂ aqueous suspensions Anpo *et al.* [1985]; Jaeger and Bard [1979]. However, recent theoretical studies using ab initio molecular dynamics (AIMD) simulations, has revealed that although OH radicals are formed on the surface of TiO₂, their potential barriers for the desorption are too high, consequently formation of free hydroxyl radicals is considered to be highly unlikely. Thus considering only the surface-bound hydroxyl radicals, the formation of both hydrogen peroxide and peroxide radicals is favored Bredow and Jug [1995]; Cheng *et al.* [2014].

Other severals experimental studies exclude both superficially bound and free •OH radicals, claiming that the primary products of the hole trapping are O^{•–} radicals ions in the TiO₂ lattice. For example, Imanishi *et al.* [2007]; Nakamura
and Nakato [2004] estimated the energy levels of the O 2p orbitals for H_2O and ^-OH , from the reported photoelectron emission spectra and Ti-OH under vacuum and at the TiO₂/ water interface from Ultraviolet Photo-electron Spectroscopy (UPS) spectra, as shown in Figure 1.5.



Figure 1.5: Energy levels of O 2p orbitals for oxygen species at the TiO_2 surface. It was estimated from UPS and photoelectron emission spectra, compared with the conduction and valence bands of n-TiO₂ at pH 0 Imanishi *et al.* [2007].

Their results show that the O 2p energy levels of Ti-OH are below to the valance band of TiO_2 , which means that those groups can not be oxidized by VB holes. Then, the only surface hole traps available seem to be those associated with O^{2-} .

More recently, Bahnemann *et al.* [1997] performed a laser flash photolysis study employing colloidal TiO₂ suspensions and found that at least two different types of holes have to be considered, deeply trapped holes, which are unreactive, and shallowly trapped holes, which exist in a thermally activated equilibrium with free holes and possess a very high oxidation potential. The deeply trapped holes were identified as surface-bound hydroxyl radicals.

Although the presence of bound and free •OH radicals remains a matter of

debate, the formation of •OH radicals during the photocatalytic process cannot be completely excluded, because •OH radical species can be formed either through the electroreduction of dissolved oxygen by photogenerated electrons via reactions or/and in acidic solution via the trapping of the holes by lattice bound O^{2-} Salvador [2007]:

$$O_{aq}^2 + e^- \longrightarrow O_2^{\bullet-} + H^+ \longrightarrow HO_2^{\bullet} + H^+, e^- \longrightarrow H_2O_2$$
(1.11)

$$Ti^{(3+)} + H_2O_2 \longrightarrow Ti^{(4+)} + HO^{\bullet} + OH^-$$
(1.12)

$$H_2O_2 + O_2^{\bullet-} \longrightarrow HO^{\bullet} + OH^- + O^2 \tag{1.13}$$

$$H_2O_2 \xrightarrow{\lambda} 2HO^{\bullet}$$
 (1.14)

$$O^{2-} + H^+ + h^+ \longrightarrow HO^{\bullet} \tag{1.15}$$

1.2.3 Electron trapping

As in the case of holes, photoexcited electrons can also be trapped. The electron trapping occurs on a timescale of sub-picoseconds and possible shorter than 100 fs, depending on the conditions Henderson [2011]. The trapping site has been a controversial topic. The discrepancies stemmed whether the electrons are rather trapped at the surface or in the bulk of TiO_2 .

Based on the band bending model, the photogenerated electrons are forced from TiO₂ surface into the bulk, due to the characteristic upward band bending of n-TiO₂. Once in the bulk, electrons can be delocalized over different Ti sites. Various reports support the latter idea Bredow and Jug [1995]; Shapovalov *et al.* [2002]. However, others studies propose that electrons can also be trapped by Ti ions bound to hydroxyls (Ti⁽⁴⁺⁾OH) located at the TiO₂ surface, resulting in the formation of Ti⁽³⁺⁾OH species:

$$Ti^{(4+)}OH + e^- \longrightarrow Ti^{(3+)}OH$$
 (1.16)

Therefore such species can attract holes, becoming a recombination center. Using hybrid functional electronic structure calculations Valentin and Selloni [2011] reported the possibility of electron migration to the surface by driving forces, which are the result of energy difference between the trapping energy levels at the surface and those in the bulk.

The size of the particles is also an important factor to be considered in the trapping electrons. In small particles no space charge layer or rather band bending exists, and thus both electrons and holes are available at the surface. It has been shown that, for small size of the TiO₂ nanoparticles the number of trapping sides increases. The presence of both electron and holes at the TiO₂ surface was observed, in the respective laser flash photolysis experiments, where the transient absorption bands of electrons and holes overlapped as shown in Figure 1.6 Bahnemann *et al.* [1997].



Figure 1.6: Transient absorption spectra from O_2 -saturated and N_2 saturated solutions. The measures were recovered 20 ns after laser excitation (λ_2 355 nm). The absorbed photon concentration per pulse by colloidal TiO₂ particles (pH 2.3; 1.0×10^{-4} mol L⁻¹) was 9 ×10⁻⁶ mol L⁻¹ Bahnemann *et al.* [1997].

In the presence of electron acceptors such as, O_2 , the maximum of these transient absorption spectra is shifted toward shorter wavelengths evidencing distinctive trapping of the holes at the surface. Saturation of the solution with

1.2. PHOTOCATALYTIC PROCESS

 N_2 , on the other hand, supports the electron trapping resulting in the formation of Ti^{3+} centers with their transient absorption maxima located around 650 nm.

Once the electrons are trapped, their trapping lifetime can be very long. Severals groups have determined the life-time of trapping electron in a wide range from hundreds of picoseconds to months. The lifetime of trapped electrons depends on measurement conditions. For example, Peiró *et al.* [2006] demonstrated, using transient absorption spectroscopy, that in the absence of ethanol or O₂ the lifetime of a trapped electron is around ~25 μ s. The corresponding decay has been attributed to the recombination at trap sites:

$$Ti^{3+} + O^{\bullet-} \longrightarrow Ti^{4+} + O^{2-} \tag{1.17}$$

While in the presence of ethanol (but still in absence of O_2), it was found that the lifetime of trapped electrons increases to 0.5 s. Ethanol is scavenging the holes, thus the recombination is avoided.

On the other hand, Kuznetsov *et al.* [2005] investigated the charge separation and storage of electrons in media-wet TiO_2 gels (anatase) and observed that under UV illumination more than 14% of the Ti^{4+} centers were converted into Ti^{3+} . The lifetime of trapped electron was found to be on time scales of months in the absence of oxygen.

1.2.4 CHARGE-CARRIER RECOMBINATION

In photocatalysis, recombination refers to annihilation of charge-carriers.

The word recombination has been used as a convenient term to explain photocatalytic activity. For example, when the activity of a given photocatalyst is lower than expected, the lower activity is attributed to fast recombination and vice versa. Then, recombination is considered an undesirable process in photocatalysis, however its study provides crucial information concerning the charge-carrier dynamics in TiO₂ Ohtani [2013].

Recombination generally proceeds with liberation of heat or light emission, called nonirradiative and irradiative routes respectively Henderson [2011]; Ohtani

[2013]; Schneider *et al.* [2014]. Generally, it is assumed that in TiO₂, due to its indirect band gap, the photogenerated electron-hole pairs predominantly recombine via non-radiative route. Non-radiative partway is quite difficult to observe in-situ directly, because detection of heat is not easy. Abe et al. [2008] could detect heat, during photocatalytic reaction on titanium oxide particles. However, the detected heat was attributed to the heat from exothermic chemical reactions, not the heat liberated by electron-hole recombination. The emission of light is quite simpler to detect than heat, thus measuring the emission is a way to study recombination. Although TiO_2 exhibits only a very weak emission of direct electron and hole pair recombination, the irradiative recombination involving trap states is optically allowed. Considering this and using the photoluminescence (PL) technique, the irradiative recombination in TiO_2 has been widely studied. Knorr et al. observed for anatase a broad visible PL band, which was interpreted as a combination of the recombination of mobile electrons with trapped holes (1 PL) and the recombination of trapped electrons with holes in the valence band (2 PL) (Figure 1.7).

A comparative study of charge-carrier dynamics between rutile and anatase TiO_2 was done by Yamate et al. They employed a combination of time-resolved PL, photoconductivity (PC), and transient absorption (TA), measurements and found longer lifetime for electrons in anatase (>few ms) in comparison with rutile (24 ns), while the decay for the holes in both crystal phases occurs on the nanosecond time scale.

Other techniques such as time resolved-absorption spectroscopy and microwave conductivity have been used to study recombination kinetics. According to the reported results, electron-hole recombination can be affected by many factors such as the sample preparation, the size, crystallinity and porosity of the sample, the reaction temperature, the charge trapping, the interfacial charge transfer, and the excitation light intensity. Consequently, the lifetime of the charge-carrier recombination in TiO₂ extends from the picosecond to the millisecond time scale.



Figure 1.7: Model for trap state photoluminescence in anatase. Wavy and straight lines indicate nonradiative and radiative transitions, respectively. The photoluminescence of anatase is considered to be a combination of both type 1 and type 2 PL, involving spatially separated hole and electron traps, respectively. The shaded regions represent the energetic distributions of traps estimated from the wavelengths spanned by the PL spectra

1.2.5 ELECTRON TRANSFER

In heterogeneous photocatalysis, electron transfer is an interfacial phenomena between the semiconductor surface and adsorbed species (chemi- or physisorbed). The transfer of electron is the last step of the photocatalytic process. The efficiency of such process is principally determined by the lifetime of charge-carriers and the electron transfers Henderson [2011].

Three possible electron transfer routes in TiO_2 are illustrated in the Figure 1.8.

The first one involves the electron transfer from a donor (e.g., dye molecules) to the conduction band of TiO_2 . In the second possible trajectory, the electron is transferred from the CB of TiO_2 to an acceptor, such process is called photoreduction dynamics. Finally the third possibility concerns the photooxidation dynamics, which is the electron transfer from a donor to the VB of TiO_2 , that process is commonly named hole transfer Henderson [2011].



Figure 1.8: Schematic illustration of three possible charge (electron or hole) transfer processes involving TiO₂. 'D' and 'A' correspond to a "donor" and an "acceptor", respectively.

The last two electron transfer routes (2 and 3) are related to excitation events in TiO_2 , while the first one deals with excitation events in an adsorbed molecules. The acceptor or the donor can be molecules, ions or solids with a band structure (metals or oxides).

Recently, two reviews exposing and discussing the factors affecting the efficiency of electron transfer have been published Henderson [2011]; Mohamed and Bahnemann [2012]. The size, surface composition, cristallinity or morphology of the photocatalyst are factors that influence the electron transfer. Moreover, one of the most important parameters that affect the electron transfer is the standard redox potential.

For the photoreduction dynamics, the redox potential position of the acceptor have to be more positive than, that of CB electron, producing a driving force favorable for the electron transfer. In case of photooxidation dynamics the redox potential position of the donnor have to be less positive compared to that of the VB hole. Increasing the driving force of the reduced couple leads to an efficient electron transfer as it is illustrated in Figure 1.9.



Figure 1.9: Dependency of interfacial electron transfer rates on the driving forces Mohamed and Bahnemann [2012].

In both photo- reduction or oxidation dynamics the coupling formed has to be strong in order to prevent back-electron transfer.

1.3 MECHANISM

The electron transfer is the final step of the photocatalytic process with TiO_2 material, and the next steps may be seen as a photoreaction mechanism. The mechanism or pathway reaction is different for each species and is sensitive to the reaction conditions and the photocatalyst. The adsorption and desorption form part of the mechanism and can promote, regulate, or inhibit the photocatalytic process on TiO_2 .

There are a large amount of studies, which try to elucidate the whole reaction mechanism of various organic and inorganic molecules. In this section O_2 and methanol have been selected to illustrated the mechanism of photo- oxidation and reduction reactions. Although, the mechanism will be explained from the point of view either oxidative or reductive, it is important to keep in mind that both reactions occur in a spatial region. This is the reason why there is a large thermodynamic and kinetically interdependence between oxidation and reduction reactions.

Methanol: Many alcohols, such as ethanol or methanol, are efficient electron donor, and they can be used in photocatalysis. Concerning the methanol mechanism it was found that it adsorbs predominantly via a dissociative pathway on the surface of TiO_2 nanoparticles, to produce surface methoxy and hydroxyl groups as follow:

$$Ti^{4+}OH + CH_3OH \longleftrightarrow Ti^{4+}OH \cdots O(H)CH_3$$
 (1.18)

$$Ti_{5C}^{4+} + CH_3OH + O^{2-} \longleftrightarrow Ti_{5C}^{4+} - O(H)CH_3 \cdots O^{2-}$$
(1.19)

$$Ti_{5C}^{4+} + CH_3OH + O^{2-} \longleftrightarrow Ti_{5C}^{4+} - O^-CH_3 \cdots HO^-$$
(1.20)

$$2Ti_{5C}^{4+} + CH_3OH + O^{2-} \longleftrightarrow 2(Ti_{5C}^{4+}) - O^-CH_3 \cdots HO^-$$
(1.21)

In the presence of surface methoxy species, holes can be trapped by the adsorbate:

$$Ti_{5C}^{4+} - O^- CH_3 + h^+ \longleftrightarrow Ti_{5C}^{4+} - OC^{\bullet}H_3$$
(1.22)

The scavenging of holes by methoxy groups inhibits, effectively, the recombination process between electrons and holes, increasing the population of free electrons in the CB.

The subsequent photochemistry induces a two-electron oxidative degradation process of the surface methoxy groups to formate as is shown in the following reactions:

$$Ti_{5C}^{4+} - OC^{\bullet}H_3 \longleftrightarrow Ti_{5C}^{4+} - OC^{\bullet-}H_2 + H^+$$
(1.23)

$$Ti_{5C}^{4+} - OC^{\bullet-}H_2 \longleftrightarrow Ti_{5C}^{4+} - OCH_2 + e^-$$
(1.24)

$$H^+ + O^{2-} \longleftrightarrow OH^- \tag{1.25}$$

In summary, the photooxidation of methanol leads to the relocation of the trapped holes and to the accumulation of the electrons on the TiO_2 surface Panayotov *et al.* [2012].

Oxygen: In photocatalysis, O_2 molecules play a key role, being the species mainly involved in the photoreduction processes accompanying the photooxidation ones. Furthermore, O_2 -derived oxidizing species are generally involved in the oxidation of organic compounds.

Based on density functional theory (DFT) method Mattioli *et al.* [2006] determined that the adsorption of oxygen occurs in five-fold coordinated Ti⁴⁺ surface ion. The value of the desorption enthalpy of oxygen was estimated, obtaining a value of -0.34 eV showing that O_2 molecule is weakly binded to the Ti ion. Although this is a weak bond, the O_2 molecule induces occupied and empty states in the anatase energy gap, corresponding to electronic eigenvalues located between 0.60 and 0.89 eV above the VB. The latter electronic state suggests an acceptor behavior of the adsorbed molecule. The formation of charged peroxo groups is a consequence of the scavenging of two photoexcited electrons by the adsorbed oxygen, see Figure 1.10.



Figure 1.10: Reaction pathway for the O_2 photoreduction as proposed by Mattioli *et al.* [2006].

1.4 Photocatalytic applications

Environmental pollution and increasing energy demand are some of the most serious problems the world faces. They both have become the most urgent scientific challenges. Photocatalysis have shown great potential as a low-cost, environmental friendly and sustainable solution to environmental and energetic issues.

1.4.1 WATER TREATMENT

Advanced oxidation processes (AOPs) are considered as highly competitive water treatment technology, such processes are based on the generation of highly reactive, transitory, and oxidizing species such as hydroxyl radical. Among these AOPs, heterogenous photocatalysis has attracted increasing attention because it has demonstrated to be efficient in the degradation of a wide range of refractory contaminants Antonopoulou *et al.* [2014]; Sillanpää and Matilainen [2015].

Photocatalysis exhibits several characteristics which are desired and useful for its application as water treatment technology: (1) low operating cost, (2) mild operating conditions (atmospheric temperature and pressure) and (3) complete degradation of the contaminant and intermediate compounds without secondary pollution.

As it was explained in the previous sections, heterogeneous photocatalysis involves the absorption of photons by a semiconductor creating a separation of charge-carriers inside of the semiconductor. In degradation of contaminants *via* photocatalysis, the recombination of those charge-carriers is avoided commonly by adding an oxygen flow in the system. Thus, the recombination between holes and electron are prevented and at the same time superoxides radical $(O_2^{\bullet-})$ are formed. Subsequently $O_2^{\bullet-}$ species lead to the formation of hydroxyl radicals (•OH) as it is shown in the equations 1.11-1.15. The degradation of the contaminant molecules until its completed mineralization is mainly carried on by (•OH), but a direct oxidation by the holes can not be dismissed. The overall degradation reaction is as follow:

Organic Contaminants
$$\xrightarrow{TiO_2/hv}$$
 Intermediate(s) $\longrightarrow CO_2 + H_2O$ (1.26)

The mechanism of degradation of many organic compounds, *via* photocatalysis, has been investigated, for example phenol, which is considered as one of the most representative contaminants discharger in wastewater. Phenol is a toxic and mutagenic substance at high concentration and can be absorbed through skin.

1.4. PHOTOCATALYTIC APPLICATIONS

Most of the studies, concerning the mechanism of phenol photocatalytic destruction, have reported that phenol destruction proceeds *via* •OH attacking the phenyl ring, yielding catechol, hydroquinone, resorcinol, and p-benzoqinone. Subsequently the phenyl rings in these compounds break up to give malonic acid, after short-chain organic acids such as maleic, oxalic, acetic, and formic are formed. CO_2 is the final product Grabowska *et al.* [2012]. One of the mechanism of phenol degradation proposed in the literature is showed in the Figure 1.11.



Figure 1.11: Phenol photodegradation route Guo et al. [2006].

The degradation of many other organic pollutants *via* photocatalysis has been well documented. Photocatalysis is not only limited to destruction of organic contaminants but it can be used also for removal (or treatment) of inorganic contaminants such as heavy metals Hoffmann *et al.* [1995]; Murruni *et al.* [2007].

1.4.2 Hydrogen production over titania photocatalyst

Hydrogen is considered as the clean energy of the future solving the global energy and environmental crises. Development of efficient and cheap materials for H_2 production is a main challenge towards a sustainable hydrogen economy. Nowadays, hydrogen is mostly produced from fossil resources, such as natural gas, oil, and coal, which are limited and expensive. Furthermore, hydrogen production from fossil resources has the disadvantage to emit high level of CO_2 as a byproduct Bahruji *et al.* [2010]; Chiarello *et al.* [2010]; Valdés *et al.* [2012]. The recent growing concerns about the global weather changes due to CO_2 emissions and the depletion of fossil fuel reserves have encouraged the development of new green and renewable technologies to produce hydrogen. In this context, photocatalysis is a promising method for H₂ production because it can use solar energy sustainably and efficiently, and is economically attractive compared to more conventional methods Bahruji *et al.* [2010]; Ismail and Bahnemann [2014].

The most widely used semiconductor in photocatalysis is TiO_2 because of its physical and chemical properties, excellent stability, high availability, and low cost Schneider *et al.* [2014]. TiO₂-based photocatalysts are still the most extensively studied materials for the photocatalytic production of hydrogen from water.

1.4.2.1 Basic principles of hydrogen generation via photocatalysis

Watter splitting has been considered "the holy grail" of heterogeneous photocatalysis. Many articles report on water splitting using TiO_2 as a photocatalyst, however the involved mechanism in both oxidative or reduction reactions are still unclear.

To understand the fundamentals of water splitting into H_2 and O_2 over photocatalysts, it is convenient to start showing the overall reaction (eq 1.27) and the schematic representation of the process (Figure 1.12):

$$H_2O \xrightarrow{hv/photocatalyst} H_2 + 1/2O_2 \qquad \Delta G = 237.2 \ kJmol^{-1}$$
(1.27)

First of all, the water splitting reaction is thermodynamically endothermic with a Gibbs free energy change of 237.2 kJ.mol⁻¹. Then the energy required for the reaction is indirectly obtained from the photons. The semiconductor converts the energy of the photons in chemical energy useful for the reaction.

As shown in the Figure 1.12, the photocatalytic process involves excitation in a semiconductor by photon of suitable energy (higher or equal to the band gap) leading to the formation of an electron-hole pair. The electrons and holes either recombine or migrate to the surface of the semiconductor particle and participate in reduction and oxidation reactions. When a photocatalyst is used for water splitting,



Figure 1.12: Basic principle of the overall water-splitting reaction on a semiconductor photocatalyst.

the energetic position of the bottom of the conduction band must be more negative than the reduction potential of water to produce H₂ ($E^{\circ}(H^+/H_2)=0.00 V_{NHE}$), while the top of the valence band must be more positive than the oxidation potential of water to produce O₂ ($E^{\circ}(O_2/H_2O)=1.23 V_{NHE}$).

Under that conditions, the theoretical minimal band gap for water splitting is 1.23 eV, which corresponds to a wavelength of about 1010 nm. However, in practice only the semiconductors with band gap larger than 2.0 eV are capable to split the water molecule. The disadvantages of this short band gap semiconductor are: 1) the fast recombination of charge-carrier and 2) little stability in aqueous solution under photo irradiation.

 TiO_2 (band gap 3.0-3.2 eV) is probably the most promising semiconductor for H_2 production from water or biofuels due to its excellent physical and chemical properties. The position of both CB and VB of the TiO_2 make it capable to carry on the water splitting reaction, see Figure 1.12.

 TiO_2 can be crystallized in three structures (rutile, anatase, and brookite). Rutile and anatase are the phases more frequently used as a photocatalyst for hydrogen production. Anatase has been found more active than rutile. The difference in activity has been explained in terms of CB position with respect to redox potential position of water. The band gap values for anatase and rutile are 3.2 and 3.0 eV respectively. The location of VBs of both phases is almost the same, however there is a slightly difference (0.2 eV) in their CB position. The anatase CB is considered 0.2 eV more negative than that of rutile. Consequently the driving force, for water reduction is smaller for rutile while the reduction takes place more effectively in anatase.

Nonetheless, recent studies using X-ray photoemission demonstrate that the CB of anatase is 0.2 eV below that of rutile, and consequently VB of rutile is above of anatase VB. These results invalidate the explanation based on CB position (previously described) about the difference in activity between anatase and rutile Scanlon *et al.* [2013].

Colbeau-Justin *et al.* [2003] show, using TRMC, that the recombination of charge-carriers in rutile is faster than in anatase, such difference was attributed to the fact that anatase has a higher amount of surficial OH groups, where the holes can be trapped leading to an enhanced charge separation. In the presence of water, a faster decay has been observed for the anatase sample, while the lifetime of the mobile electrons in rutile does not show any change after this surface treatment. These results reveals that factors as charge-carriers lifetime and/or surface composition also play an important role between anatase and rutile photoactivity.

The charge-carrier recombination is very important to be considered, and both surface and bulk recombination can be classified as deactivation processes. Therefore, charge recombination is ineffective for water splitting. Besides to avoid the recombination of electrons and holes, it is of key importance to elucidate the molecular mechanisms of the reactions, which should strongly depend on the morphology, and chemical and electronic structures of the materials at the surface as well as the reactivity (or energy) of photogenerated charge-carriers. In that context, some fundamentals studies of the chemistry of water (and hydroxyls) on TiO₂ surfaces have tried to explain the drawbacks of TiO₂ to generate hydrogen. Some of those studies, for both photooxidation and photoreduction reactions, will be discussed below.

1.4. PHOTOCATALYTIC APPLICATIONS

1.4.2.2 Oxidation of water

The overall objective in water photooxidation is to convert water to oxygen using VB holes, according to the reaction:

$$H_2O + 2h^+ \longrightarrow 1/2O_{2(q)} + 2H^+ \tag{1.28}$$

Although TiO_2 has demonstrated to be capable to produce oxygen under UV irradiation, the formation mechanism is still unclear. It has been assumed that the water oxidation at TiO_2 surface is initiated by oxidation of surface Ti-OH groups (or -OH ions in the aqueous solution) by photogenerated holes, h^+ , by an electron-transfer mechanism:

$$Ti - OH + h^+ \longrightarrow Ti^{\bullet}OH$$
 (1.29)

This mechanism has not been completely accepted by the photocatalysis community because a number of reports reveal that the water photooxidation reaction at TiO₂ does not produce neither absorbed nor free •OH radicals. Therefore, such reports propose that holes are trapped by bridging oxygen atoms at the surface O^{2-} (see hole trapping section).

Considering the latter, Nakato's group Imanishi *et al.* [2007]; Nakamura and Nakato [2004] has proposed that the key step in water photooxidation involves a nucleophilic attack of water in the aqueous/physisorbed phase with a trapped surface hole on a surface 3-coordinate O anion site and not due to a hole reaction with an adsorbed H_2O/OH^- species, scheme in Figure 1.13.

Although the mechanism of water oxidation is unclear, it has been proven that oxygen production occurs.

1.4.2.3 REDUCTION OF WATER

The limiting step in the hydrogen generation using TiO_2 is the reduction reaction. The amount of hydrogen produced using TiO_2 is negligible. Some basic studies have been performed using bare TiO_2 to explain the absence of H_2 when all the raw ingredients are present (two protons and two near CB edge electrons) in close



Figure 1.13: Water photooxidation propose by Nakato group. Here the reaction is initiated by a nucleophilic attack of a water molecule to a surface-trapped hole. It is assumed that the hole is trapped by triply coordinated O atoms and bridging O atoms at the surface Imanishi *et al.* [2007].

proximity. For instance, Li *et al.* [2008] observed the formation of atomic hydrogen in the surface of TiO₂ by STM, see Figure 1.14. They studied the hopping kinetics of H atoms along the O^{2-} bridging rows on rutile TiO₂ and they conclude that there are barriers in the approach of two H atoms to each other in order making impossible the formation of H₂.



Figure 1.14: STM images (a and b) on hydroxyl-covered R TiO₂(110) at 381 K acquired three minutes apart. (c) Difference image (b-a). The dark and bright spots represent the initial and final hydrogen positions, respectively. The black arrows show the hopping directions. Black lines mark positions of the bridging O rows. (Image conditions: 1.5 V bias, 0.1 nA current) Li *et al.* [2008].

1.5. METAL NANOPARTICLES DEPOSED ON TIO₂

The results of Yin *et al.* [2008] are in agreement with the latter. Their studies show conclusively that no thermal atomic hydrogen recombination to H_2 is possible on TiO₂ surface; it was speculated that the surface H atoms (H_{ads}) either penetrate into the bulk or diffuse across the surface instead of recombining.

Metal particles deposed on the surface of TiO_2 have been used as co-catalyst to assist in lowering the H₂ formation barrier but little is known about the molecularlevel details of mass and charge transport between TiO_2 and supported metal particles.

1.5 Metal nanoparticles deposed on TiO₂

Supported metal nanoparticles on TiO_2 surface usually have beneficial impact in photocatalytic reaction. Deposition of metal NPs often play a role of promoters, however in some cases they are considered as poisons. In heterogeneous photocatalysis, a promoter influences the interactions on ground (as in thermal catalysis) and excited (photoabsorption and electron transfer events) states Henderson [2011].

To understand the influence of supported noble metal NPs on TiO_2 , it is necessary to study deeply different factors such as: 1) the properties of the metal NPs, such as size, shape among other, 2) interaction between metal NPs and TiO_2 (e.g., creation of interfacial states), and 3) mass transport between the metal NPs and TiO_2 .

Many of these factors are characteristic for each metal NPs leading to unique properties of metal/TiO₂ photocatalysts. Here, is a brief discussion of the effect already reported for deposition of metal NPs used in this work (Au, Ni and Pd).

1.5.1 GOLD

Since the pioneering work of Haruta, Au clusters supported by oxides (Au/oxides) have perhaps become the most interesting systems in heterogeneous catalysis because of their unique catalytic properties at low temperatures for many reactions.

The properties of Au nanoparticles have also received considerable attention in heterogeneous photocatalysis. Severals groups have reported an enhancement of the photocatalytic activity under UV irradiation when gold is used as co-catalyst, such improvement has been related more to the size of the Au nanoparticles than the amount of metal loading. It has been demonstrated that the physical and/or electronic structures of small (≤ 3 nm) Au particles differ considerably from those of larger Au particles or extended Au surfaces.

In that context, the photocatalytic enhancement has been linked to the size of gold nanoparticles. For instance, Subramanian *et al.* [2004] (Kamat's group) found that smaller Au particles supported on TiO₂ were more effective as electron transfer centers in photoreduction of C₆₀ because the smaller particles shifted the Fermi level to more negative values, see Figure 1.15.



Figure 1.15: I-V characteristics of (a) TiO_2 , (b) TiO_2/Au (8 nm diameter), and (c) TiO_2/Au (5 nm diameter) composite film. Measurements were performed in a three-arm cell with Pt as counter electrode, a saturated calomel electrode as reference, and 3 mL 0.05 M NaOH as electrolyte. UV light from xenon lamp ($\lambda > 300 \text{ nm}$) was used as the excitation source Subramanian *et al.* [2004].

The influence of gold NPs size was also observed by Orlov and coworkers, who reported an improvement in 4-chlorophenol photooxidation when Au nanoparticles with size below of 3 nm were deposited on TiO_2 , while large particles suppressed reactivity. Murdoch *et al.* [2011] found that Au particle size, in a range of 3-12 nm, does not affect the photoreaction rate of hydrogen production.

Nowadays, there is a particular interest in use gold nanoparticles as co-catalyst to achieve visible-light photocatalytic response. The interest of gold come from its characteristic surface plasmon resonance (SPR), which is closely related with its magnetic, electronic, and optical properties. It has been observed that Au deposited on TiO₂ surface favors the generation of H₂ and degradation of contaminants under visible illumination, but in both cases the corresponding rates were found to be low as compared to the rates obtained upon UV irradiation. The properties related to SPR are strongly dependent on individual differences in size, shape, surface area, and crystalline form of the employed nanoparticles, as reported E. Kowalska and co-workers Kowalska *et al.* [2009, 2010, 2012]. For example by Tanaka *et al.* [2013] reported that large gold particles size (13 nm) on TiO₂ prepared by deposition method exhibits much stronger photoabsorption at 550 nm that small particles size (1.2 nm). However, the photocatalytic activity of Au/TiO₂ for H₂ evolution from methanol aqueous solution under visible irradiation at 550 nm, was found higher with small Au particles than with large ones.

Kowalska *et al.* [2009] showed that the oxidation of 2-propanol to acetone under visible ligth (>450 nm) is favored with big sizes of deposited Au NPs on titania, as is shown in Figure 1.16.

As for mechanism of SPR-induced photocatalytic reactions under visible light, it is considered that the charge separation occurs inside of the metal particles, consequently the electrons transfer is carried out from the metal NP to the CB of the semiconductor. Thus, the photooxidation takes place at the surface of gold nanoparticles while the reduction happens at the semiconductor surface. Tachikawa *et al.* [2012] studied the photocatalytic reduction sites of Au/TiO₂ using water-soluble fluorescent probe molecule and found that these sites were well distributed over the surface of bare TiO₂ while on the Au/TiO₂ surface these sites were concentrated around of Au nanoparticles. The latter shows that the injection of electrons from Au NPs to TiO₂ occurs but the electrons remain in the



Figure 1.16: Acetone generation under visible-light irradiation (>450 nm) on Au modified titania powders Kowalska *et al.* [2009].

vicinity of metal NPs.



Figure 1.17: Spatial distribution of fluorescence spots (red dots, >50 spots). They were collected from TiO₂ (a) and from 14 nm Au/TiO₂ particles (b). The SEM images of the particles analyzed are shown. Scale bars are 100 nm. The locations of the reactive sites and of the Au nanoparticles are surrounded with dashed lines in red and blue, respectively Tachikawa *et al.* [2012].

1.5.2 PALLADIUM

As co-catalyst on TiO₂, Pd contributes manly of the same benefits seen for other noble metal particles Behar and Rabani [2006]; Yang *et al.* [2006]. Sano and coworkers Belver *et al.* [2003] have shown that addition of Pd nanoparticles to TiO₂ resulted in more complete mineralization of vinyl chloride through surface reactions. Deactivation of TiO₂ as a result of strongly bound organic intermediates was also minimized with the presence of Pd. Shiraishi *et al.* [2003] examined the concentration of H₂O₂ formed from water and during the decomposition of formaldehyde (HCHO) using bare TiO₂ and Pd/TiO₂ as photocatalysts. They found that deposition of Pd on TiO₂ increases the rate formation of H₂O₂ decreases. A higher degradation rate of HCHO was observed using Pd/TiO₂ photocatalyst than bare TiO₂. The results suggested that Pd favors the H₂O₂ formation, which reacts with the CB electrons forming hydroxyl radicals responsible of HCHO oxidation.

Hydrogen production was enhanced for Pd/TiO_2 compared to TiO_2 alone. On the latter point, Al-Mazroai *et al.* [2007] examined the Pd loading (on P25) dependence on the anaerobic photochemical conversion of methanol and water to CO_2 and H_2 . As shown in Figure 1.18, they found that a sharp increase of the activity at low Pd loadings, with a maximum at 0.5% Pd, and a decrease of the activity to near zero at 5% Pd. Such behavior was explained by assuming that the active sites for the reaction are located at the periphery of the Pd particles adjacent to the titania. Oxidation of CO, which tend to cover the Pd particles, was considered as limiting step in the overall reaction.

1.5.3 NICKEL

Although Nickel does not form part of the groups of noble metals, the modification of TiO_2 with Ni can enhance its photoactivity. Recently Chen *et al.* [2015] considered nickel as the best candidate to replace expensive metals co-catalyst, since Ni is cheap, abundant, and has a high work function (Ni=5.3 eV). They



Figure 1.18: Effect of Pd loading on TiO_2 surface in H₂ yield. Comparison of the experimental data for the metal loading dependence of hydrogen yield (filled circles) with the theoretical dependence of the active sites on loading (open circles), in the theoretical model it is assumes that the active sites are located at the metal-oxide interface Al-Mazroai *et al.* [2007].

studied the H₂ evolution from an ethanol aqueous solution (20 % vol) under UV irradiation. A photocatalytic enhancement compared to bare TiO₂ was reported, and it was explained by the high work function of Ni, which allows scavenging of the CB electrons, thus the recombination of charge carrier is decreased. The optimal nominal Ni loading of ~0.5 wt% was found. On the contrary Ni was reported as an inefficient co-catalyst for the hydrogen production by Letters and The [1984]. In the last two mentioned works, Ni was presumably metallic (Ni⁰). However, it is quite susceptible to change of states depending on the conditions, for example nickel is quickly oxidized when it is exposed to air, and to ensure only the presence of Ni metal a careful management is required. The reoxidation of Ni does not have necessary a negative impact, in fact according to the work done by Domen *et al.* [1986], Ni/NiO co-deposition on a semiconductor improves its photoactivity for water splitting photoreaction compared to surface modification with only Ni or NiO. The issue then becomes the interplay between the various states of Ni on TiO_2 .

CHAPTER 2

EXPERIMENTAL SET-UP AND ITS FUNDAMENTALS

This chapter gives a description of the conditions of synthesis of the photocatalysts, the techniques used for their characterization, and the set-up for photocatalytic evaluation. The radiolysis method is a powerful technique but unconventional, therefore its fundamentals, the formation mechanism of metal NPs by this method, and the dose rate effect are also explained in this section. Similarly, the TRMC characterization technique is quite useful to study the charge-carrier dynamics in a semiconductor. This technique has demonstrated to be very convenient to understand the lifetimes of charge-carriers in the photocatalysis studies, then it is relevant to explain its principle, the main data obtained as well as the experimental device in order to facilitate the understanding of the subsequence chapters.

2.1 Fundamentals of metal nanoparticle synthesis by radiolysis

NPs are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. NPs are generally made out of metallic, semiconductors or insulating materials. Potential applications of nanosized materials in diverse fields have encouraged the interest in developing different methodologies to produce NPs of controlled size and shape. Among these, the soft-chemical techniques appear to be the most successful approach.

Specifically, the radiolysis method has been successfully applied to the synthesis of a wide range of monometallic, bi- or multimetallic NPs Belloni *et al.* [1998]; Hai *et al.* [2013]; Kowalska *et al.* [2008]. Outstanding advantages of this method in comparison with other ones are: (1) the mild conditions (atmospheric pressure and room temperature); (2) the homogeneous size distribution; (3) no additional reducing agent; and (4) most importantly control of composition and structure (core-shell or alloy) by fixing the dose rate Belloni [2006].

2.1.1 RADIATION CHEMISTRY OF WATER

The radiolysis method is based on ionization and electronic excitation of water (generally) by high-energy photons (1.17 and 1.33 MeV), which are emitted from a 60 Co γ -source (low LET irradiation) or by fast electrons from an accelerator with energy typically in the range 2-20 MeV (1 eV= 1.6×10^{-19} J). From such interaction, an ejection of a single electron from the water is obtained. The ejected electron is called secondary electron which itself may have sufficient energy to cause further ionization, but which rapidly (< 10^{-12} s) reaches thermal equilibrium with the water and becomes trapped as so-called solvated electron (e_s^-). Solvated electron may be visualized as an excess electron surrounded by oriented water molecules, see Figure 2.1.

At the same time, a chain reaction occurs from positive radical ion $(H_2O^{\bullet+})$ and the electronically excited stated (H_2O^*) (both also produced by the high energy absorbed). As a result of such reactions, transitory species are generated



Figure 2.1: Schematic representation of solvated electron in water.

(reducing and oxidizing species) ($\sim 10^{-7}$ s), which are homogeneously distributed Belloni [2008]; Le Caër [2011]. A general scheme of radiation chemistry of the water is shown in the Figure 2.2.



Figure 2.2: Radiation chemistry of the water.

The primary radicals are the hydrated electron (e_s^-) and the hydroxyl radical (•*OH*), which are powerful reducing and oxidizing species respectively. The reduction potential of hydrated electron is E° =-2.87 V, while the reduction potential of hydroxyl radical changes as a function of pH solution, $E^\circ(\bullet OH/OH^-)=1.90$ V and in neutral and acid solution respectively. The atomic hydrogen (H^\bullet) does not present an important participation in neutral or alkaline solution, but it becomes the major reductant $E^\circ(H^+/H^\bullet)=-2.31$ V in acid solution Belloni [2008]; Belloni and Mostafavi [2001].

2.1.2 RADIATION-INDUCED METAL NPS SYNTHESIS

Metallic clusters can be obtained successfully using the radiolysis method. The synthesis, by this method, starts with isolated atoms resulting from the reduction of metal ions by the radiolytic reducing species, mainly solvated electrons, which are homogeneously distributed in the solution. Consequently, the very first metal atoms produced are also uniformly dispersed in the liquid, and then undergo an aggregation process that leads to the production of size-homodisperse clusters. The particles size can be controlled by the preparation conditions.

A detailed explanation of reduced metal ions process by this method is described below: as previously mentioned, ionizing irradiation of water generates radiolytic radicals homogeneously distributed in the solution, see Figure 2.2. From those radicals, electron solvated (e_s^-) and atomic hydrogen (H^{\bullet}) , are strong reducing species $[E^{\circ}(H_2O/e_s^-)=-2.8 \ V_{NHE}$ and $E^{\circ}(H^+/H^{\bullet})=-2.31 \ V_{NHE}]$, their reduction potential values are so negative and capable to reduce the metal cations (M^+) Belloni [2006]; Belloni and Mostafavi [2001]. The metal reduction is carried out at each encounter with solvated electrons. The reduction of monovalent metal ions is represented by the equations:

$$M^+ + e_s^- \longrightarrow M^0 \tag{2.1}$$

$$M^+ + H^{\bullet} \longrightarrow M^0 + H^+ \tag{2.2}$$

However, the radicals HO^{\bullet} are also formed in radiolysis of water. The high reactivity of hydroxyl radicals leads to back reaction of metal ions already reduced. Then, to counter the participation of undesirable HO^{\bullet} ($E^{\circ}(^{\bullet}OH/OH^{-})=1.90$ V) a scavenging molecule of those such a secondary alcohol (isopropanol) or formate anion is generally added to the solution. The scavenging molecules react not only with the hydroxyl radical but also with atomic hydrogen; After such reactions secondary radicals with a strong reducing character are obtained:

$$(CH_3)_2 CHOH + HO^{\bullet} \longrightarrow (CH_3)_2 C^{\bullet}OH + H_2O$$

$$(2.3)$$

$$HCOO^{-} + HO^{\bullet} \longrightarrow COO^{\bullet -} + H_2O$$
 (2.4)

CHAPTER 2. EXPERIMENTAL PART

$$(CH_3)_2 CHOH + H^{\bullet} \longrightarrow (CH_3)_2 C^{\bullet}OH + H_2$$
(2.5)

$$HCOO^- + H^{\bullet} \longrightarrow COO^{\bullet -} + H_2$$
 (2.6)

The radicals $(CH_3)_2 C^{\bullet}OH$ and $COO^{\bullet-}$ are almost as powerful reducing agents as H^{\bullet} atoms: $E^{\circ}((CH_3)_2CO/(CH_3)_2\dot{C}OH) = -1.87 V_{NHE}$ Elliot and Simsons [1984] at pH 7 and $E^{\circ}(CO_2/COO^{\bullet-}) = -1.97 V_{NHE}$ Solutiono [1989] respectively. Thus, reducing conditions are obtained.

In the case of multivalent metal ions, they are reduced by multistep reactions, also including the disproportion of intermediate valences. An example of this kind of reduction is given by the equations from 2.7 to 2.9; considering a metal with two valences. During the first step M^{2+} is reduced to M^+ by reducing species; in the second step M^+ is reduced to M^0 but two different ways could take place: (a) direct reduction by reducing agent (eq. 2.8), and (b) the encounter between two ions (M^+) resulting in a metallic atom plus a cation as shown in the eq. 2.9. This kind of reaction is called disproportionation reactions.

$$M^{2+} + reducing \ species \longrightarrow M^+$$
 (2.7)

$$M^+ + reducing \ species \longrightarrow M^0$$
 (2.8)

$$M^+ + M^+ \longrightarrow M^0 + M^{2+} \tag{2.9}$$

The reduced atoms are homogeneously distributed throughout the solution. The dimerization of the atoms occurs on contact because the binding energy between metal atoms is stronger than the atom-solvent bond energy. The bonding between atoms or clusters (particles) with unreduced ions is also strong, therefore the ions are absorbed to metallic atoms or clusters and are subsequently reduced. Thereby, the dimers and oligomers progressively grow into clusters and eventually into precipitates Belloni [2006]; Belloni and Mostafavi [2001]; Belloni *et al.* [1998]. The precipitation step can be avoided using a stabilizing polymer, ligand or support. The general scheme of metal ions reduction in solution by radiolysis is shown in the Figure 2.3.



Figure 2.3: Scheme of metal ion reduction in solution by ionizing radiation. Alcohol ROH (or formate ion HCOO⁻) is added in order to scavenge oxidizing radicals. The isolated atoms formed M⁰ coalesce into clusters. They adsorb excess ions. They are stabilized by ligands, polymers or supports. The redox potential $E^0(M_n^+/M_n)$ increases with the nuclearity. The smallest oligomers may undergo reverse corrosion Belloni [2006].

2.1.3 Synthesis of bimetallic NPs by radiolysis

Metal NPs composed of two (or more) different metal elements have unique catalytic, electronic, and optical properties distinct from those of the corresponding monometallic particles. Such unique properties are currently the subject of intense investigation in various fields, such as catalysis, photocatalysis, magnetism and nanoelectronics Ferrando *et al.* [2008].

The reduction of two different metal ions, either by radiolysis or chemical method, leads to the arrangement of the metal atoms into different bimetallic structures: core-shell or alloys.

In radiolysis, the formation kinetics of such structures depends, on one hand,

on the electron transfer from the less noble metal atoms to the more noble metal ion, and, on the other hand, on the dose rate used to reduce both metal ions.

1) Electron transfer

The formation of the metal nanoparticles using a low dose irradiation (⁶⁰Co γ -source) is based on the potential reduction of the metal ions. Then, when two metals ions (M^+, Z^+) are irradiated in the same solution, they have the same possibility to be reduced simultaneously by solvated electrons.

$$M^+ + e_s^- \longrightarrow M^0 \tag{2.10}$$

$$Z^+ + e_s^- \longrightarrow Z^0 \tag{2.11}$$

However, when the reduced metals and ions coalesce, an electron transfer occurs from the less noble (Z^0) metal to the more noble one (M^+) . Then the reduction of the noble metal is favored leading (most of the cases) to a segregation of the two metals.

$$Z^0 + M^+ \longrightarrow (MZ)^+ \longrightarrow M^0 + Z^+$$
(2.12)

If the ionic precursors are multivalent, an electron transfer is possible as well between the low valences of both metals, thus increasing the probability of segregation. Once the reduction of the noble metal is concluded, the ions of the other metal (Z^+) are reduced at the surface of M_n . The final result is a core-shell nanoparticles where the more noble metal M is coated by the other metal Z.

2) Dose rate

To form alloys the intermetallic electron transfers have to be suppressed. Thus the M^0 or Z^0 coalesce between them forming metal nanoparticles. To suppress the electron transfer, a high dose rate is necessary, for example using electron beams.

To summarize, the core-shell structures are commonly obtained by low dose irradiation using ⁶⁰Co γ -source (Figure 2.4). The latter is principally due to the intermetallic electron transfer. While the alloyed structures are typically obtained using a high dose rate by electron beams (EB).



Figure 2.4: Scheme summarizing the influence of the dose rate during the radiolytic reduction of mixed metal ion solutions. It illustrates the competition between the inter-metal electron transfer and the coalescence processes. High dose rates favor alloying whereas low dose rates favor core-shell segregation of the metals in the clusters Belloni [2006].

In some cases (exceptions), alloying may occurs even at low dose rate (γ -irradiation) Morse *et al.* [1985], as for alloys Cu₃Pd, CuPd, NiPt, CuAu and AgPt clusters. In few cases, alloying is not obtained even at high dose rate. In spite of the very fast reduction (a few seconds for complete reduction with EB) in some systems the electron transfer was faster and metals are still segregated (Ag/Cu).

2.1.4 Supported Nanoclusters

One of the important applications of metal NPs is to be used as catalysts on solid supports. The radiolytic synthesis was successful in producing various supported NPs. The formation of the metal particles follows the reaction pathway previously mentioned. The metal NPs deposition on the support can be achieved by two possible methods: (a) preparing in solution the metal nanoparticles, and then putting in contact with the support (possibly by wet impregnation) or (b) in one put by irradiating directly the solution containing the metal precursors (adsorbed) on the support. The ionizing radiation penetrates throughout the support and forms the atoms in situ everywhere the ions have diffused. The fixation of the ions precursors on the support before the irradiation allows not only to control the size distribution, but also favors the formation of the nanoparticles, which is more difficult in the case of non-noble metals, like Ni, Cu, Co.

2.2 Metal nanoparticles synthesis

Materials

Commercial titanium dioxide P25, from Evonik (ca. 50 m².g⁻¹, anatase ca. 80 % with rutile) was used as a photocatalyst. Potassium gold choride (Sigma-Aldrich), nickel formate (Alfa Aesor), and tetraamminepalladium(II) dichloride (Sigma-Aldrich) were used as gold, palladium, and nickel precursors respectively. Methanol and 2-propanol were purchased from Sigma-Adlrich. Deionized water (Milli-Q with 18.6 M Ω) was used all through the experiments.

Photocatalysts preparation

Metal nanoparticles were synthesized by radiolysis on P25. Two different systems were prepared (Ni-Au and Ni-Pd) on TiO₂ and their respective single metal components. For each system, distinct total metal loadings and metal ratios were used, see Table 2.1 and 2.2. The number in the name code indicates the total metal loading. For the NiAu/TiO₂ samples the metal ratio used was 5:1, thus in the samples there is 5 times more Ni than Au. For the Ni-Pd system, the metal ratio used was 10:1, therefore the sample x-NiPd/TiO₂ contains 10 times more Ni than Pd. The concentration of Pd, in the sample x-PdNi/TiO₂, is 10 times higher then Ni. The suffix "real" in the samples x-Ni_{real}/TiO₂ or x-Pd_{real}/TiO₂ refers to that lowest metal loading deposed in the bimetallic samples

The metal precursors and others chemicals products used were of the highest purity commercially available. The solutions were prepared with deionized water.

For every photocatalyst, the needed amount of the precursors (indicated in Table 2.1 and 2.2) was dissolved in 35 mL of an aqueous solution of 0.2 M 2-propanol. Subsequently, the solutions containing nickel or palladium ions were alkalinized with ammonium hydroxide until reaching a pH 11. Afterward, 1.5 g of TiO₂ were added to each samples and stirred 24 h in order to adsorb the desired metal ions (Ni, Au,Pd or Ni-Au or NiPd) on TiO₂ surface by ionic exchange. After TiO₂ surface impregnation, a nitrogen flow was introduced during 20 min to the samples in order to remove oxygen. Then, the sample irradiation was carried out using a panoramic ⁶⁰Co γ -source with a dose rate 4.5 kGy.h⁻¹. The dosimetry of the source was done using the Fricke dosimeter. After irradiation, the samples were filtered under vacuum and dried at 30 °C for 16 h. Finally, colorful powders were obtained. A scheme of the procedure described before is shown in Figure 2.5.

Sample name	$\mathbf{m}_N i$ (mg)	$\mathbf{m}_A u$ (mg)	Dose (kGray)
0.1-Ni/TiO ₂	2.79	_	4.0
0.5-Ni/TiO ₂	14.03	_	20.2
$1-Ni/TiO_2$	28.21	_	40.6
0.1-Au/TiO ₂	_	7.10	5.4
0.5-Au/TiO ₂	_	35.66	27.1
$1-\mathrm{Au}/\mathrm{TiO}_2$	_	71.69	54.5
0.1-NiAu/TiO ₂ ratio(5:1)	2.33	1.18	4.3
0.5-NiAu/TiO ₂ ratio(5:1)	11.69	5.94	21.4
$1-NiAu/TiO_2 ratio(5:1)$	23.52	11.94	42.9

Table 2.1: Mass of the metal precursors and the doses used for each sample. The system x-NiAu/TiO₂, where x indicates the metal loading.
Table 2.2: Mass of the metal precursors and the doses used for each sample. The system x-NiPd/TiO₂, where x indicates the metal loading.

Sample name	$\mathbf{m}_P d$ (mg)	$\mathbf{m}_N i \ (\mathbf{mg})$	Dose (kGray)
$\overline{0.5-\mathrm{Ni}/\mathrm{TiO}_2}$	-	19	42.6
0.5-Pd/TiO $_{\rm 2}$	18.56	-	7.3
0.5-NiPd/TiO ₂ ratio(10:1)	3.36	19	32.7
0.5-PdNi/TiO ₂ ratio(10:1)	18.56	1.04	9.6
0.5-Ni _{real} /TiO ₂	0	1.04	2.3
0.5-Pd _{real} /TiO ₂	3.36	-	1.4
$1-Ni/TiO_2$	-	38	85.2
$1-\mathrm{Pd}/\mathrm{TiO}_2$	37.13	-	13.9
$1-\text{NiPd}/\text{TiO}_2 \text{ ratio}(10:1)$	6.73	38	86.1
$1-PdNi/TiO_2 ratio(10:1)$	37.13	2.09	18.1
$1-\mathrm{Ni}_{real}/\mathrm{TiO}_2$	0	2.09	4.7
$1\text{-}\mathrm{Pd}_{real}/\mathrm{TiO}_2$	6.73	-	2.8





2.3 MATERIAL CHARACTERIZATION

2.3.1 CHARACTERIZATION TECHNIQUES

Here, the condition and specification of the characterization equipment used are provided. Except for TRMC because most of the techniques employed are commonly used, no fundamentals are provided.

UV-Vis diffuse reflectance spectra of the photocatalysts were recorded in the region of 200 to 800 nm using an Agilent Technologies Cary 500 Spectrophotometer with PTFG as reference.

For High Resolution Transmission Electron Microscopy (HRTEM) observations, the suspensions containing modified TiO_2 were first sonicated for few minutes then a few drops of the suspension were deposited on copper coated carbon grids. HRTEM measurements were performed in a JEOL JEM 2010 transmission electron microscope equipped with a LaB6 filament and operated at 200 kV. The chemical analyses were obtained by selected Energy-Dispersive X-Ray Spectroscopy (EDS) Microanalyser (PGI-IMIX PC) mounted to the microscope. To realize X-Ray Photoelectron Spectroscopy (XPS) analysis, the powder samples were fixed on double-face adhesive carbon tape mounted on a steel holder. XPS measurements were performed on a K α X-Ray Photoelectron Spectrometer under ultrahigh vacuum (5x10⁻⁹ mbar) with an Al K α (h ν =1486.7 eV) monochromated X-Ray source operating at 3 mA and corresponding to a spot size of 400 μ m. Survey scans were acquired at a pass energy of 200 eV and 50 eV for the acquisition of high-resolution windows over the binding energy range of 1350-0 eV. The C 1s signal at 284.8 eV was used as reference to compensate any charging effects.

2.3.2 TIME RESOLVED MICROWAVE CONDUCTIVITY

2.3.2.1 Principle

The Time Resolved Microwave Conductivity (TRMC) technique is based on the measurement of the relative change of the microwave power reflected by a sample (semiconductor), $\Delta P(t)/P$, during its simultaneous irradiation by pulsed laser. Such relative variation can be correlated to small perturbation of the sample conductivity, $\Delta \sigma$, as shown in the following equation:

$$\frac{\Delta P(t)}{P} = A\Delta\sigma(t) \tag{2.13}$$

where A is a time independent proportionality factor. Because the electron mobility (μ_e) in TiO_2 is much larger than the hole mobility, $\Delta\sigma(t)$ can be attributed to excess electrons.

$$A\Delta\sigma(t) \approx \Delta n_e(t) \cdot \mu_e \tag{2.14}$$

The signal obtained by this technique displays the evolution of the sample conductivity, I(t), (denominated photoconductivity) as function of time (ns), see Figure 2.6. The main data provided by TRMC are given by the maximum value of the signal (I_{max}) , which reflects the number of the excess charge-carriers created by the pulse, and the decay due to the decrease of the excess electrons (free electrons) Colbeau-Justin *et al.* [2003]; Kunst and Beck [1986]. To analyze the TRMC signals, the decay is divided in two sections: (1) short-; and (2) long-range. The short-range decay, arbitrarily fixed up to 40 ns after the maximum of the pulse, is represented by the I_{40ns}/I_{max} ratio, which reflects the fast processes active during and just after the pulse. Most probably, electron-hole recombination and possibly electron scavenging by metal are responsible for this ratio. The long-range decay, here fixed after 200 ns until 1000 ns, is related to slow processes involving trapped species, i.e., interfacial charge transfer reactions and decay of excess electrons controlled by the relaxation time of trapped holes. In this range, the decay of TRMC signal can be fitted to a power decay according to:

$$I = I_D t^{k_D} \tag{2.15}$$

where I_D is the intensity of the signal due to charge-carriers that recombine after 200ns, and k_D is an adimentional parameter related to their lifetime value Meichtry *et al.* [2014].



Figure 2.6: A typical TRMC signal of TiO_2 P25 excited at 355 nm . It show two main parts: 1) maximum and 2) decay: short- and long range.

2.3.2.2 TECHNICALS ASPECTS OF TRMC

The TRMC device can be described as a sophisticated, ingenious and simple apparatus, with which valuable information about the charge-carrier kinetics can be obtained. The TRMC equipment is constituted by: (1) sample holder, (2) excitation source, (3) microwave circuit, (4) detection system, and (5) acquisition system (see Figure 2.7).

The sample holder consists of an aluminum cell connected to a microwave guide. In the cell cavity, a small PTFE support is laid, where the sample is deposited. The PTFE support allows the control of the amount of sample.

The pulsed light source was an OPO laser (EKSPLA, NT342B) tunable from 225 to 2000 nm. It delivers 8 ns FWMH pulses with a frequency of 10 Hz. The density of light energy received by the sample was around 747 μ J.cm⁻² at 355 nm. The light beam is directed to the sample by a mirror system. The mirrors-position reflects the beam vertically to reach the sample from above.

The incident microwaves were generated by a Gunn diode of K band at $30 \pm$ GHz, the frequency corresponding to the highest microwave power. The microwaves generated are directed toward the sample by a waveguide placed just below the sampler holder. The waveguide has a circulator system (Pamtech RYG2032), which directs both the generated microwave to the sample and reflecting microwaves to a detector (R422C, Agilent Technology). The detector used was a Schottky type diode. The function of the detector is to convert the power to voltage. The detector is directly connected to a voltage amplifier (DHPVA-200, Femto). In the system, the signal is amplified 10^6 times and the acquisition is realized by an oscilloscope.

2.3.2.3 Energy of the excitation wavelength

The energy of the photons is expressed in joules (J). The excitation energy (E), known as fluence within the optic community, determines the amount of laser energy delivered in a single pulse and is expressed in joules/cm². Experimentally, the energy of the laser at a fixed wavelength is measured with a pyroelectric energy



Figure 2.7: Scheme of the TRMC set-up. The parts of this equipment are: (1) sample holder, (2) excitation source, (3) microwave circuit, (4) detection system, and (5) acquisition system

sensor (ES111C, Thorlabs) connected to a power meter (PM100D, Thorlabs). The energy pulse of the laser function of the wavelength is shown Figure 2.8.

Then, the numbers of incident photons $(n_{h\nu})$ in the samples can be calculated using the measurement of excitation energy by the following equation:

$$n_{h\nu} = \frac{E}{h.\upsilon} = \frac{E.\lambda}{h.c} \tag{2.16}$$

Because the number of photons is important, it is appropriated to express it as mole of photons also called Einstein (ein), therefore the Avogadro number have to be add to the equation:

$$n_{h\nu} = \frac{E.\lambda}{h.c.N_A} \tag{2.17}$$

where E is the excitation energy (J), λ is the wavelength (nm), h is the Planck constant (J.s), c speed of light $(m.s^{-1})$ and N_A Avogadro constant (mol⁻¹). The plot of I_{max}/n_{hν} values for each wavelength allows to obtain a spectrum called



Figure 2.8: Pulse energy as function of wavelength of the laser used as excitation source in TRMC setup.

TRMC action spectra. In this work, the range of the wavelengths examined was from 310 to 505 nm. The wavelengths and its corresponding excitation energy are shown in Annexes.

2.4 Photocatalytic evaluation

The activity of the modified titania was mainly tested for two reaction, organic compounds (phenol and 2-propanol) oxidation and hydrogen production. The response of the samples under UV and visible light were evaluated.

For the samples Ni-Au, the activity of modified samples for the reduction and oxidation of lead ions in solution was also studied. A detailed explanation of the testing protocols used for each reaction set is given below.

2.4.1 Hydrogen production evaluation

The photocatalytic activity of the modified samples for hydrogen generation was evaluated under UV light using a polychromatic light source. The effect of different irradiation wavelengths was investigated using monochromatic light source.

2.4.1.1 IRRADIATION SYSTEM USING A POLYCHROMATIC LIGHT SOURCE

The hydrogen production was evaluated using a mercury lamp, which emits a whole light spectrum with a maximum intensity of UV light. Two distinct set-ups were used: (1) a continuous reactor and (2) batch reactor. In the first one, the production of hydrogen was followed by Mass Spectrometry (MS), while in the second one, it was measured by gas chromatography.

For the continuous set-up, the reaction volume was 60 mL of a methanol solution 10vol% and the concentration of photocatalyst was 1 g.L⁻¹. The amount of H₂ was measured in real-time in the headspace thanks to an UGA mass spectrometer (SRS Instruments). The UGA is based on residual gas analyzer (RGA SRS Instrument - mass domain 1-300). The instrument is adapted for analysis at atmospheric pressure. The headspace gas of the reactor is pumped through a 1 m long capillary (peek tubing, 0.18 mm ID) thanks to a roughing pump. A pinhole (400 nm) allows a small portion of the gas to be transferred to the vacuum chamber. The pressure measured at the roughing pump is circa 1.1 mbar and the pressure in the vacuum chamber is 5.10^{-6} mbar. This pressure is kept constant during the analysis.

In case of the *batch* system, a glass reactor with a volume of 35 mL was employed. The photocatalyst (50 mg) was suspended in 5 mL of a methanol solution at 50vol%. A sample of 0.2 mL of the headspace gas was taken every 15 min during 1 h. The amount of hydrogen was determined using a Gas Chromatograph (GC). In both continuous and batch systems, prior to suspension irradiation, a flux of nitrogen was introduced in the system in order to evacuate the oxygen.

2.4.1.2 IRRADIATION SYSTEM EMPLOYING MONOCHROMATIC LIGHT: ACTION SPEC-TRA MEASUREMENTS

Experiments realized in Catalysis research center at Hokkaido university, Japan. The measurements of H_2 evolution were performed on bare and modified TiO₂. The amount of photocatalyst used was 30 mg. It was added to quartz cuvette of



Figure 2.9: Continuous and batch systems used for hydrogen production via photocatalysis.

10.5 mL volume containing 3 mL of 50vol% aqueous methanol. Before irradiation, the air was removed from the cell by nitrogen bubbling. The samples were irradiated under stirring with monochromatic light at 320, 350, 380, 410 and 440 nm (\pm 5 nm), using a diffraction grating-type illuminator (JASCO CRM-FD) equipped with a 300-W xenon lamp (Hamamatsu Photonics C2578-02). The total time of irradiation was 60 min, and each 20 min a gas sample of 0.2 mL was taken and monitored by gas chromatography (Shimadzu GC-8A). The Apparent Quantum Efficiency (AQE) as a function of monochromatic wavelength was calculated as a ratio of the number of electrons used in hydrogen production to the flux of incident photons on the system, according to the stoichiometry of the reaction where 2 electrons were required.

2.4.2 Phenol degradation

The photocatalyst activity was evaluated in a batch photoreactor using UV or Vis lamp as light source (Figure 2.11). 1 g.L⁻¹ of photocatalyst in 300 ml of 50 ppm aqueous solution of phenol was added to a 500 ml glass reactor. An oxygen flow of 20 mL.min⁻¹ was introduced, the system was magnetically stirred. After 20 min of stabilization the light was turned on. The above conditions were maintained for 90 min for UV test and 240 min for Visible test. The reaction run was tested

2.4. PHOTOCATALYTIC EVALUATION



Figure 2.10: Action spectra equipment.

every 5 min for the UV test, and every 30 min for the visible test by taking 5 ml of sample which was filtered.



Figure 2.11: Photoreactor used for phenol degradation.

The remaining phenol concentration was measured by UV-Vis spectrometry and High Performance Liquid Chromatography (HPLC) using a Varian Prostar 220/230/240. The mobile phase used in HPLC was water/acetronitrile (78/22 v/v) pH 3.5. The Total Organic Carbon was determined by Total Organic Carbon Analyser (TOC), from Shimadzu.

2.4.3 Photooxidation of lead ions (II)

Both photo- reduction and oxidation of lead ions experiments were realized at National Atomic Energy Commission in Argentina. The photocatalytic oxidation of Pb²⁺ was carried out in an open batch reactor, with magnetic stirring. A 150 W xenon lamp with an UV-Vis irradiation spectrum was used as light source. The reactor was irradiated with wavelength above 380 nm whereby a cut-filter was put between the reactor and the lamp. The irradiated volume was 25 mL. The Pb²⁺ was added from $[Pb (ClO_4)_2.3H_2O]$ and the photocatalyst concentration was 0.5 mM and 1 $g.L^{-1}$ respectively. Prior to irradiation, the pH of the suspension was adjusted to 3 using NaOH, and then it was sonificated during 2 min. The total irradiation time was 3 h with sampling time of 15 min during the first 30 min, and after, the sampling intervals were 30 min. The sample volume was 0.5 mL, which was subsequently filtered. The filtered solution was added to a flask of 10 mL, along with 1 mL of PAR (4-(2-pyridylazo)-resorcinol) solution (0.004%)). The volume was completed with water. The Pb(II) concentration changes were measured by colorimetry with 4-(2-pyridylazo)-resorcinol (PAR reagent) at 520 nm. In some cases, parallel determination were made by total reflection X-Ray fluorescence (TRXRF), using an X-ray fluorescence spectrometer composed of a Philips generator, a fine focus Mo X-ray tube and a TRXRF module; a CANBERRA Si(Li) detector with a Be window was employed.

2.4.4 Photoreduction of lead ions (II)

The experimental set-up is quite similar to the one described before. However, in this test a closed reactor was used. Also, before irradiation the oxygen was removed using a helium flow during 10 min. The volume of the samples was 0.5 mL, which was filtered and added to a 10 mL flask. Then the volume was completed with water. The reduction of Pb²⁺ was followed by conductivity. As a complementary study TXRF measurements were carried out for selected samples.

Only the initial and final point were evaluated with this technique.

2.4.5 Isopropanol photoxidation

The activity of the samples under Vis irradiation was also examined using a xenon lamp set-up. 5 μ g of photocatalyst were added to 5 mL of a solution of 2-propanol 50v/v %. The formed suspension was in a glass tube of 35 ml, which was kept in a water bath thermostated at 298 ± 5 K. The suspension was magnetically stirred and irradiated by a xenon lamp installed outside the water bath. To eliminate the UV radiation, a cut-off filter was used. A sample of 0.5 mL was taken every 30 min. The irradiation of 2-propanol solutions generated acetone, which was analyzed chromatographically by Shimadzu GC-14B equipped with an Flame Ionisation Detector (FID). Before injection of a portion of liquid phase to GC, the photocatalyst powder was separated from the suspension using a filter (Whatman Mini-UniPrep, PVDF).

CHAPTER 3

NICKEL IONS ON THE SURFACE OF TITANIA

It has been reported that some metal ions on the surface of TiO_2 are capable of working as sensitizers for visible light by formation of surface complexes. For this reason, the modification of titania surface with nickel ions, was the starting point of this study. This chapter presents the effect of nickel ions on the optical and electronics properties of TiO_2 as well as the photocatalytic activity of the surface modified TiO_2 for the degradation of phenol.

3.1 Sensitizing of TiO₂ surface with Nickel ions

The adsorption of nickel ions on titania surface was obtained using a simple procedure. Three grams of TiO₂ were added to 50 mL of an aqueous solution containing NiSO₄ at an adequate concentration to obtain the desired loading in Ni (0.5, 1, 2, 3, 4, and 5 wt%). The suspension was stirred for 12 h at room temperature. After that, it was filtrated, and the residue was washed with deionized water two times. The powders were dried at 50 °C for 12 h. Then metal-ion-modified TiO₂ (x-Ni²⁺/TiO₂) were obtained.

Strong electrostatic adsorption is indeed the simplest interaction that can occur between a complex and a surface. The only requirement is that the oxide surface and the metal complex have opposites chargers. Every oxide support has a point of zero charge (PZC), defined as the pH at which the surface is neutrally charged. The PZC value for TiO₂ is ≈ 6.5 . Since the support, TiO₂ in our case, has -OH functional groups on its surface, the hydroxyl groups will become protonated and positively charged when the pH of the solution is below the PZC, and then the surface can adsorb anionic metal complexes. The same groups become deprotonated and negatively charged when the pH of solution is above the PZC of the oxide support, and thus positively charged species can be adsorbed onto the support.

It must to mention that the pH of the NiSO₄ solution is 4.5, therefore a poor electrostatic adsorption of Ni²⁺ is expected. No adjustment of the pH of NiSO₄ solutions to above of PZC of TiO₂ was done (to values higher than PZC) because the modified samples were used in the test of phenol degradation, and the pH of phenol solutions is around 5.2. Then at this pH leaching phenomena should occur.

The addition of TiO_2 to the NiSO₄ solution leads to a decrement of the pH until 3.8, this suggests that bonds between Ni²⁺ and TiO₂ support are formed via surface oxygen atoms and proton release. It is proposed that the hydroxyl group of titanium dioxide is involved in the formation of surface complexes with metal ions:

$$2TiOH + Ni^{2+} \rightleftharpoons (TiO)_2Ni + 2H^+ \tag{3.1}$$

The adsorption below the pH_{zpc} (6.5) suggests an inner sphere type of complex formation between Ni(II) and the TiO₂ surface, see Figure 3.1. In the inner-sphere complexes a covalent bond between the metal and the electron-donating oxygen ions is formed. The surface hydroxyl groups act as σ -donor ligands, which increase the electron density of the coordinated nickel ions. Only a small amount of nickel ions were adsorbed because the number of adsorption sites was limited due to the pH suspension. The color of the filtrate indicates that a large amount of Ni ions were not adsorbed by titania.

The samples show a very light blue color and the intensity of the color does not change with the loading in nickel ions.



Figure 3.1: Adsorption of Ni ions on TiO_2 surface.

3.2 CHARACTERIZATION

The characterization of the modified samples was focused mainly in the study of the electronic and optical properties.

3.2. CHARACTERIZATION

3.2.1 DIFFUSE REFLECTANCE SPECTROMETRY

The surface modification of TiO₂ with nickel ions induced a change in absorption of the materials, see Figure 3.2. The modified samples absorb light in the visible region (contrary to bare TiO₂). This absorption can be due to the adsorbed nickel ions. A zoom of the DR spectra in the range 500-800 nm is presented in Figure 3.3, where it can be observed that the absorbance of the samples increase slightly with the ions loading. In the inset of Figure 3.2, the absorption spectrum of the $[Ni(H_2O)]^{2+}$ species in aqueous solution is presented. This absorption spectrum is quite similar to that of the modified samples in the visible region.



Figure 3.2: **DR spectra of bare and Ni ions modified titania.** The insert is the UV-vis spectrum of aqueous $NiSO_4$ solution.

It has been recently shown that diffuse reflectance spectroscopy may be used to investigate the mode of interfacial deposition of metal complex. The $[Ni(H_2O)]^{2+}$ in solution exhibits three bands at about 390, 720, and 655 nm which are characteristic of Ni²⁺ with octahedral symmetry. However, because of the strong absorption of titania below 400 nm, the band of $[Ni(H_2O)]^{2+}$ at 390 nm is not considered in the surface analysis. In Figure 3.3 the DR spectra of the modified samples and of $NiSO_2$ in aqueous solution (from 500 to 800 nm) are displayed.



Figure 3.3: **DR spectra of Ni ions modified titania and of NiSO**₄ aqueous solution from 500 and 800 nm. Modified samples (top) and NiSO₄ solution (down).

The modified samples show two bands at 673 and 745 nm, which are shifted to longer wavelengths compared with those of the $[Ni(H_2O)]^{2+}$. This shift can be explained by the presences of some weak ligand-filled donors in the coordination sphere of Ni²⁺ (inner-sphere complexes). The hydroxyl groups on the surface of TiO_2 are considered ligand-filled donors.

3.2.2 XPS

The selected samples (0.5, 3 and 5%w)were analyzed by XPS. The elements found in the survey spectra were Ti, C, O, S and Ni. The $2P_{2/3}$ nickel spectra (856.0 eV) were identified in the samples, see Figure 3.4. The binding energy (BE) of the absorbed nickel is close to the value of NiO (855.7 eV). The slight blue color of the samples is not the characteristic color of NiO. Then BE detected can be attributed to incorporation of hydroxyl ligands (from TiO₂ surface) in to the nickel coordination shell.



Figure 3.4: Nip $_{2/3}$ spectra of adsorbed Ni on titania .

A satellite signal at 862 eV was also detected, which has been assigned to ligand-metal charge transfer transitions. Oxygen atoms belonging to surface hydroxyl groups play the ligand role.

The satellite signals in the sample are symmetric. Such symmetry also suggests that the absorbed nickel is bound to surface hydroxide groups. An asymmetry satellite signal has been found in NiO and NiOH. The amount of Ni present in the samples is much lower than the nominal amount. This support the idea that TiO_2 surface, under the impregnation conditions used, can not adsorb a large amount of nickel ions. The atomic percentage of Ni in the three selected samples increases with the nominal loading of adsorbed nickel, suggesting that the adsorption increases with the concentration of nickel ions in the solution. However, even with a large concentration of nickel solution the total amount of nickel adsorbed is low, around 0.5% at.

Sulfur BE was also detected (167.9 eV). The powders were washed two times with water before drying. Clearly the washing step was not enough to remove the sulfates probably due to the adsorption of sulfates in surface hydroxyl.

3.2.3 TRMC

The dynamics of charge-carriers was studied for all the samples. Figure 3.5 shows the TRMC signals obtained with an excitation wavelength at 355 nm, which is the optimum one for titania. All the samples show a higher maximum intensity I_{max} compared to that of bare TiO₂. The maximum is related to the free electrons, therefore a higher signal suggests a larger number of electrons in the conduction band of TiO₂. A larger number of electron can be explained by excitation and injection of electrons from the metal complex (at the surface) to the conduction band of TiO₂.

Both the short and large range signals are not influenced (no change in the signal slope is observed) by the presence of adsorbed nickel ions. This reveals that the excess electrons injected does not influence the charge-carriers dynamics.

Under excitation wavelength larger than 355 nm, the modified samples with nickel ions exhibit signals. Figure 3.6 presents the maximum conductivity at different wavelengths. Under the same irradiation wavelengths, titania does not show a TRMC signal because the excitation does not generate electron-hole pairs. In the wavelength range of (450-550 nm), the samples exhibit the highest conductivity at 490 nm, and at larger wavelengths the conductivity progressively decreases. The DR spectra of the samples do not follow the profile of TRMC

spectra. The TRMC signals are obtained in the region were the absorption of photons is low (450 to 550 nm), while in the range (600 to 800 nm) where the light absorption is higher, no signals are detected. The decay profile of TRMC signals of the modified samples at $\lambda > 450nm$ is slow, indicating a long life time of CB free electron. The TRMC signals obtained at larger excitation wavelengths imply an electron injection from the nickel complexes to CB of titania. Since the holes, inside of TiO₂ are not present, the injected electrons have a long life time.

3.3 Phenol Degradation

The selected test to evaluate the photoactivity of the modified samples was the phenol degradation. The evaluation was done using different irradiation sources: UV or visible light. The phenol degradation profiles under UV light are presented in Figure 3.7.

Taking into account the standard deviation, we can say that under UV light the adsorbed ions on the TiO_2 surface have a little influence in the kinetics of phenol degradation. In table 3.1, the half life time of phenol degradation under UV light is presented. Almost all the samples show a higher photocatalytic activity for phenol degradation compared to bare TiO_2 , however the mineralization rate is quite similar than that obtained with bare titania.

Figure 3.8 shows the percentage of phenol degradation after 4 hours of reaction under visible light irradiation. Under such conditions all the modified sample are more efficient for phenol compared to bare titania. The activity increases with the Ni loading. The improvement in the percentage of phenol mineralization using the modified sample is not significant.

The degradation of phenol is around 10 times faster under UV light than under visible light.

Considering the TRMC results, the improvement of phenol degradation under both UV and visible light can be explained by the injected electrons from the metal ions to CB of the semiconductor. TRMC signals were observed using excitation wavelengths from 355 to 550 nm, such signals were always higher than



Figure 3.5: TRMC signals of bare titania and modified samples (nickel adsorbed on TiO_2). The signals were obtained using an excitation wavelength of 355 nm.

that obtained with bare TiO_2 suggesting an injection of electron from the adsorbed Ni ions to the CB of the semiconductor. Under excitation of the modified samples at 355 nm not change in the signal decay was observed. This indicates that Ni ions do not scavenge electrons from TiO_2 .



Figure 3.6: TRMC and DRS spectra of bare TiO_2 and selected modified samples.

The photocatalytic process under UV light involves the generation of the electron-hole pair and the injection of photoexcited electrons from Ni complexes into TiO_2 CB, then nickel complexes become oxidized into the Ni³⁺ state. Therefore the oxidation process occur by both hole (from the semiconductor) and Ni³⁺ species. The reduction of dissolved oxygen is carried out by the electrons from titania and those from absorbed nickel ions.

Under visible irradiation Ni complexes also are excited injecting an electron in the CB of TiO_2 , however in this case the participation of titania in the photocatalytic process is quite low. Then the improvement in the catalytic activity is markedly influenced by the absorbed Ni ions.

Sample name	t phenol degradation	t mineralization
	(\min)	(min)
TiO2	21.8	31.5
0.5	30.1	30
1	20.1	32
2	19.8	32.6
3	17	28.7
4	18.5	32
5	19	30.8

Table 3.1: Half life time of the phenol degradation and mineralization under UV light

3.4 CONCLUSION

The photocatalytic activity and electron migration in Ni²⁺/TiO₂ samples were investigated under UV and visible light irradiation. Ni²⁺/TiO₂ showed a higher photocatalytic activity than that of the bare sample. The adsorption of nickel ions on the surface occurs by the formation of inner-sphere complexes with the hydroxyl groups present in the surface of TiO₂. The adsorption of ions is low, and the maximum adsorbed amount of ions on the titania surface is around 0.5%at. The strong interaction between the adsorbed ions and the surface leads to electron injection from the nickel ions to the CB of the semiconductor. The injected electrons lead to formation of O₂^{•-}. These superoxide radicals and Ni³⁺ oxidize phenol leading to its degradation.



Figure 3.7: Phenol degradation(above) and mineralization(below) profile under UV light.



Figure 3.8: Conversion percentage of phenol degradation and mineralization under visible light. .

CHAPTER 4

SURFACE MODIFICATION OF TITANIA WITH GOLD AND/OR NICKEL NPS

This section is devoted to surface modification of TiO_2 with Ni and/or Au nanoparticles for application in photocatalysis. Synthesis, characterization and photocatalytic activity of the modified samples are presented. In the first part, characterization of the photocatalysts with different techniques and their electronic properties (charge carriers mobility) are studies. In the second part, the photocatalytic activity of the samples is tested for different reactions: phenol degradation, 2-propanol oxidation, hydrogen production, and oxidation and reduction of lead ions. Finally a general conclusion for titania modification with Ni and/or Au is given.

4.1 SAMPLES

After the impregnation step, Au^{3+} and/or Ni²⁺ ions were reduced using the ⁶⁰Co γ -source. The dose was chosen to ensure a complete reduction of the ions. The dose was deduced from the reduction yield in a free solution containing the metal ions in a concentration comparable to that of the impregnating solution.

As it was explained in the experimental chapter, the metal reduction is carried out mainly by reactive species such as solvated electrons (e_s^-) (which are strong reducing species) and H[•] radicals both generated by the excitation and ionization of water with high energy radiation.

Additionally, secondary reducing radicals $((CH_3)_2COH \text{ and } CO_2^-)$ also contribute to the reduction of metal ions. Those secondary species are generated from the interaction from the oxidizing radicals (HO[•]) and/or holes (h⁺, from titania) with 2-propanol and formate ions Chettibi *et al.* [2013]. During the irradiation electron-hole pairs (e⁻,h⁺), inside TiO₂, are formed.

After the deposition of metal particles on TiO_2 surface, different colors of sample were obtained: gray, purple and pink/violet respectively for nickel, gold, and nickel-gold deposition, and the tone increased with metal loading, see Figure 4.1.

4.2 CHARACTERIZATION

The influence of titania surface modification (with Ni and/or Au) on its light absorption property and on the mobility of charge-carriers was examined as well as the morphology and the chemical composition of the photocatalysts. The characterization of the surface modified titania is presented below.

4.2.1 UV-VIS DIFFUSE REFLECTANCE (DRS)

The absorption spectra of pure and modified TiO_2 are shown in Figure 4.2.

In addition to the characteristic ultraviolet absorption of TiO_2 , all the modified samples showed an absorption in the visible and near infrared regions, which



Figure 4.1: Images of the Ni and/or Au modidied titania.

varies with to the deposited metal. The samples containing only nickel show a flat absorption in the visible range. This absorption can be attributed to NiO, which is known to absorb in this region, due to the d-d transitions Guillou *et al.* [2006]; Hu and Teng [2010].

The samples containing gold show a maximum peak at 540-560 nm characteristic of the plasmon band of gold. This plasmon band is sensitive to the environment and the substrate. The coupling between metal NPs and TiO₂ support results in a shift of the plasmon band toward larger wavelengths compared to its position in water (for the same particle size). Au/TiO₂ samples show a localized surface plasmon resonance (LSPR) at slightly longer wavelength than those of NiAu/TiO₂, which indicates larger sizes of gold NPs. The difference in the size of gold NPs in Au/TiO₂ and NiAu/TiO₂ is also suggested by the colors of the samples. The pink/violet color exhibited by the bimetallic samples is attributed to smaller size particles, while purple color displayed by Au/TiO₂ samples reveals larger size. Similar observations between the color and gold LSPR shift on titania surface were reported by Kowalska *et al.* [2009].

The samples 0.5 and $1-Au/TiO_2$ show larger scattering compared to 0.1-



Figure 4.2: UV-Visible absorbance spectra of modified samples and bare TiO₂. (a) x-Ni/TiO₂; (b) x-Au/TiO₂; and (c) x-NiAu/TiO₂.

 Au/TiO_2 probably because of the larger Au nanoparticle size. For the NiAu/TiO₂ samples, the plasmon band increases with the metal loading. Similarly, a slight shift to shorter wavelength is observed as the metal loading increases.

On the other hand, the DRS of the modified samples show a slight shift in the

band gap toward longer wavelengths, this cab be partly due to oxygen vacancies generated in TiO_2 during the synthesis.

4.2.2 HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

Figure 4.3 shows a representative HRTEM image of the photocatalysts 0.1-Au/TiO₂ (a) and 0.5-NiAu/TiO₂ (b).



Figure 4.3: **HRTEM images of selected samples.** (a) x-Ni/TiO₂; (b) x-Au/TiO₂; and (c) x-NiAu/TiO₂.

Polycrystalline metal NPs are deposited on TiO_2 . EDAX analyses show that these nanoparticles are mainly composed of gold, however nickel signal is also observed in the 0.5–NiAu/TiO₂ sample (see Figure 4.4).

In 0.1-Au/TiO₂, the average diameter of gold nanoparticles is around 18 nm, while for 0.5-NiAu/TiO₂, the diameter of the metal particles is below 9 nm. This indicates that the addition of Ni has an influence on the growth of Au nanoparticles. Gold NPs in the 0.1-Au/TiO₂ sample are at the interface of two or more TiO₂ crystallites due to their large size, similar observation has been reported Murdoch *et al.* [2011]; Tsukamoto *et al.* [2012]. Thus, it is clear that the number of gold



Figure 4.4: **EDAX analyses.** a) 0.1-Au/TiO₂, b) 0.5-NiAu/TiO₂, and c) 0.5-Ni/TiO₂ samples

particles was limited and that only a small part of titania particles was contact with gold particles.

EDAX analyses show Ni signals for the samples $x-NiAu/TiO_2$ and $x-Ni/TiO_2$. In both mono- and bimetallic based photocatalysts, Ni nanoparticles on TiO₂ were quite difficult to be observed by HRTEM probably because of the close atomic numbers of Ni and Ti and the small size of Ni clusters.

4.2.3 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS was used to analyze the chemical composition of the modified TiO_2 and to probe the oxidation state(s) of nickel and/or gold on the surface of the photocatalysts. The elements identified in the survey spectra were Ti, O and C (Figure 4.5) for all the samples, and Ni and/or Au (Figure 4.6) for the modified photocatalysts.



Figure 4.5: **XPS spectra of peaks detected in both modified and bare titania.** a)O 1s; b)C 1s and c)Ti 2p.

The 1-Au/TiO₂ and 1-NiAu/TiO₂ samples exhibit peaks corresponding to Au 4f binding energy at 83.58 eV and 87.18 eV, which are respectively assigned to Au $4f_{7/2}$ and Au $4f_{5/2}$. The Au 4f signals obtained from the samples were compared with metallic gold foil (Au $4f_{7/2}=84.0$ eV and Au $4f_{7/2}=87.7$ eV) as shown in Figure 4.6a: We can consider that the position range of Au signals, is in agreement with Au(0) chemical state but with a specific low binding energy (BE) position

which has already been reported in the literature Chimentão *et al.* [2007]; Hai *et al.* [2013]; Tominaga *et al.* [2008].

This shift can reflect the strong interaction of gold-based NPs with TiO_2 changing their electronic environment Hai *et al.* [2013].



Figure 4.6: **XPS spectra of modified samples with metal loading of 1 at%.** (a) Ni 2p spectra of Ni⁰ and NiO references, and samples modified containing Ni; and (b) Au 4f XP core-level spectra for Au⁰ reference and samples modified containing Au.

The Ni 2p XPS spectra for the samples $1-Ni/TiO_2$ and $1-NiAu/TiO_2$ shown in Figure 4.6b are quite similar. In both samples, Ni $2p_{1/2}$ and Ni $2p_{3/2}$ peaks were identified at 873.4 eV and 855.7 eV, respectively. Such binding energies are attributed to the presence of Ni(II) and the satellite signal at 861.7 eV confirms the presence of NiO.

The fitting of the XPS spectra of the sample 1-NiAu/TiO₂ (Figure 4.7) reveals also the existence of a small amount of Ni⁰ (853.3 eV).

The exposition of Ni nanoclusters to air during the drying step may cause the partial oxidation of the samples and the formation of NiO clusters. Nevertheless,


Figure 4.7: XPS curve fitting for the sample $1-NiAu/TiO_2$.

the XPS results also indicate the presence of Ni⁰ proving that Ni clusters oxidation was not complete. The remaining amount of Ni⁰ is probably localized at the interface between NiO and TiO₂. It has to be noted that Ni 2p signals are also negatively shifted from those observed for pure metal or oxide references. Similar shift was reported by other groups Chen *et al.* [2015].

4.2.4 TIME RESOLVED MICROWAVE CONDUCTIVITY METHOD (TRMC)

The effect of the metal NPs on the charge-carriers kinetics of TiO_2 under excitation wavelength of 355 nm, which is the optimum one to photoexcite a larger number of electrons in bare TiO_2 , was studied. Both I_{max} and decay kinetics were analyzed for all the modified samples and compared with bare titania. The effect of different excitation wavelengths on the generation of charge-carriers and their dynamics were also examined.

4.2.4.1 INFLUENCE OF EXCITATION ENERGY AT 355 NM

The dynamic of excess electrons in the conduction band of the photocatalysts and their recombination kinetics were studied by time resolved microwave conductivity. TRMC measurements were carried on for all the samples (bare TiO₂, x-Au/TiO₂, x-Ni/TiO₂, and x-NiAu/TiO₂), see Figure 4.8. The transient photoconductivity data were displayed in double-logarithmic plots with a time scale from 0 to 1000 ns. The TRMC data (I_{max} , I_{40ns}/I_{max} , and k_D) for each sample are presented in Table 4.1.

The modified photocatalysts show a reduction of the I_{max} values compared to bare TiO₂. This decrease can be attributed to three phenomena linked to the metal deposition, and corresponding to the lost of charge-carriers during the pulse Emilio *et al.* [2006]: a) shield effect by metal NPs, b) surface recombination centers created by the synthesis method, and c) fast electron scavenging by the metal (<10 ns). A detailed analysis of the signal decays may help to understand the observed effect on I_{max} .

The analysis is not trivial, because different effects are observed, the signals can be slowed down or accelerated by the surface modification with metal nanoparticles. Anyway, a global tendency can by drawn.

As explained in the experimental section, the decay kinetics can be divided in two parts: the short-time range from 0 to 40 ns and the long-time range from 200 ns to 1000ns.

Figure 4.8 and I_{40ns}/I_{max} values of Table 4.1, characterizing the short time range, evidence that an opposite effect is observed for mono- and bimetallic modifications. All Ni/TiO₂ and Au/TiO₂ samples present a slightly slower or identical decay than bare TiO₂, when a faster decay is observed for the NiAu/TiO₂. A slower decay indicates that metal nanoparticles do not scavenge the electrons. This effect, already observed with Pt and Pd deposits Kowalska *et al.* [2008]; Tahiri Alaoui *et al.* [2012], indicates that the metal can help to avoid chargecarriers recombination. A faster decay can be explained by a) a higher rate of recombination of charge-carriers, may be due to surface defects generated by the



Figure 4.8: **TRMC signals of Ni and/or Au modified samples and bare TiO**₂ . The signals were induced by 355 nm light pulses at 747 μ J.cm⁻² excitation density. (a) x-Ni/TiO₂; (b) x-Au/TiO₂; and (c) x-NiAu/TiO₂.

deposition b) electron scavenging by the metal.

Figure 4.8 and k_D values of Table 4.1, characterizing the long time range, confirm mainly the tendency observed at short time range: an identical or slower decay for monometallic modification, and a faster decay for bimetallic one. This confirmation of an accelerated decay at long time range for NiAu/TiO₂ supports

	\mathbf{I}_{max} (mV)	$\mathbf{I}_{40}/\mathbf{I}_{max}$	\mathbf{k}_D
TiO_2	233	0.64	0.186
0.1-Au/TiO ₂	224	0.63	0.185
0.5-Au/TiO ₂	151	0.81	0.102
1-Au/TiO_2	155	0.77	0.143
0.1-Ni/TiO ₂	202	0.63	0.180
0.5-Ni/TiO ₂	135	0.74	0.128
$1-\mathrm{Ni}/\mathrm{TiO}_2$	158	0.45	0.197
0.1-NiAu/TiO ₂	187	0.49	0.208
0.5-NiAu/TiO ₂	190	0.58	0.186
$1-\mathrm{NiAu}/\mathrm{TiO}_2$	142	0.42	0.197

Table 4.1: TRMC parameters for bare and modified TiO_2 .

the hypothesis of electron scavenging by the metal. Indeed, the hypothesis of a higher rate of recombination of charge-carriers, due to surface defects, should not have been confirmed at long time range, because it corresponds to fast phenomena.

In the case of Ni/TiO_2 samples the hypothesis of electron scavenging is refused because, no fast decay at long time is observed, then the decrease of short-time decay can be explained by a higher rate of charge-carriers recombination, probably caused by surface defects generated by the metal deposition or during the synthesis.

In order to know if some defects were created on titania during the synthesis and if they have influences on the TRMC signals, 1 g of TiO₂ in 0.2 M 2-propanol solution was irradiated at different doses (200, 2000 and 4000 Gy). After irradiation, the powders present a gray-blue color indicating "trivalent titanium (Ti³⁺) formation" consequences of the semiconductor reduction by solvated electrons. After the drying step, that color decreases. The TRMC measures show that the I_{max} value of TiO₂ irradiated decreases but the signal decay profile, both short and long ranges, does not change for the samples subjected to 200 and 2000 Gy. However for the sample irradiated with 4000 Gy both I_{max} and short time decay 94

decrease Figure 4.9. The above results show that the change in I_{40ns}/I_{max} value of x-Ni/TiO₂ samples is cause by defects of titania generated during the deposition of the metal NPs. Probably, the dose used was higher than the required dose used for metal ions reduction.



Figure 4.9: TRMC signals of TiO_2 before and after irradiation at different doses..

The reduction of the support during irradiation is avoided thanks to ion metals, which are faster reduced by solvated electrons and alcohol radicals. Metal ions "protect" in such way the support from reduction. However, if the irradiation continues after reduction of all the metal ions (leading to NPs), then the solved electrons will reduce the support (titania). For the experiments, the necessary dose to reduce the metal ions was calculated, but the electrons produced by TiO_2 during its irradiation or secondary radicals from interaction of holes (from TiO_2) with water and 2-propanol were not taken into account. Such species, also contribute to the metal reduction, accelerating it.

TRMC measurements reveal also that gold nanoparticles in x-Au/TiO₂ are inefficient in electron scavenging. This is probably due to the large size of gold particles. Indeed, theoretical calculations have indicated that the transfer of excited electrons from the semiconductor to the metal is practically inefficient when the size of the metal nanoparticles is larger than 10 nm Ioannides and Verykios [1996]. The TRMC signals, of x-Au/TiO₂, show a slow decay revealing long lifetime of electrons. Long lifetime of electrons suggests that in somehow the interaction between the metal and support produce hole trapping.

4.2.4.2 Excitation at different wavelength: TRMC spectra

The influence of the different excitation wavelengths on charge-carriers generation was study for both bare and modified (0.5 at%) titania. The samples were excited at different excitation wavelengths from 310 to 505 nm, with intervals of 15 nm. The I_{max} values divided by the number of incident photons at each wavelength were plotted. The graphic obtained is called "TRMC action spectra". Figure 4.10 shows the comparison between the absorption spectra and the TRMC action spectra for each sample.

For bare TiO₂ both TRMC and absorption spectra the signals are zero for wavelength longer than 415 nm. Both the absorption and charge separation occurs in the UV region λ <415 nm. Based of DRS results the highest absorption come about λ < 320 nm, however TRMC results reveals that the large amount of photogenerated electrons is obtained with an irradiation wavelength of 355 nm, before and after of such wavelength the amount of electrons decrease. The above reveals that although the photon absorption is favored at shorter wavelengths it has a negative effect in the total number of photogenerated electrons.

For all the modified samples, the DRS spectra show an absorption in the visible region, but no charge separation at those wavelengths is observed by TRMC. Ni/TiO₂ samples were the exception, they show a small TRMC signal until 460 nm. In order to know if such TRMC signals were characteristic of NiO or if they were the consequence of the Ni-TiO₂ interaction, commercial NiO was studied by TRMC. It can be observed that NiO shows also a TRMC signal in part of the visible region (until 500 nm). The TRMC spectra of Ni/TiO₂ sample is similar to that obtained with commercial NiO in the visible region.

The samples containing Au (NiAu/TiO₂ and Au₂) do not show TRMC signal



since 410 nm, in which bare TiO_2 shows a separation of charge-carriers.

Figure 4.10: TRMC spectra and absorption spectra of modified samples, metal loading 0,5 at%.



Figure 4.11: TRMC spectra of commercial NiO.

4.3 Study of the photocatalytic activity

The activity of the modified samples was studied in both oxidation and reduction reactions, which involve: (i) phenol degradation, (ii) 2-propanol oxidation, (iii) oxidation and reduction of lead ions and, (iv) hydrogen production from a water/methanol mixture. The results, analysis and discussion for each photocatalytic reaction are presented.

4.3.1 Phenol degradation

One of the potential applications of photocatalysis is wastewater treatment. To evaluate the photocatalityc activity of the samples many compounds have been used as model pollutants, among which are methyl orange and some phenolic compounds such as phenolphthalein, gallic acid, and phenol. In this study phenol was used as a model pollutant because: (1) it is toxic and is a serious threat to many ecosystems, water supplies, and human health, (2) it is difficult to be degraded by conventional methods and, (3) it is highly stable under irradiation UV (it does not undergo photolysis).

4.3.1.1 Phenol photodegradation under UV light

Previous to photocatalytic test, an adsorption test during 5 h was carried out for all the modified samples and bare TiO₂. A small adsorption (<6%) was detected during this period. UV phenol photo-sensibility test was also done. Negligible phenol decomposition was observed under UV light irradiation even after 2 h. Therefore the phenol degradation was considered proper of the photocatalytic test.

The photocatalytic degradation of phenol with bare and modified TiO_2 is displayed in the Figure 4.12 which shows that almost all the modified samples (x-NiAu/TiO₂, x-Ni/TiO₂ and x-Au/TiO₂) did not exhibit better photocatalytic activity compared with bare TiO_2 . The sample 0.1-Au/TiO₂ was the exception, but the photocatalytic improvement was not substantial.



Figure 4.12: Phenol degradation kinetics for selected modified samples with 0.1 at % metal loading . Experimental conditions: (1) light source: UV xenon lamp; (2) initial concentration of phenol: 50 ppm; (3) mass of the photocatalyst: 1 g.L⁻¹; (3) oxygen flow: 20 mL.min⁻¹; and (4) volume photoreaction: 200 mL.

The kinetics of phenol degradation on a photocatalytic surface can be describe by the first order reaction:

$$ln\frac{C_0}{C_t} = kt \tag{4.1}$$

where k is the rate constant (min⁻¹), C_0 is the phenol initial concentration at irradiation time (t). The linear relation of $ln \frac{C_0}{C_t}$ versus time (t) was fitted to obtain the rate constants for phenol decomposition for all photocatalysts, which are summarized in the Table 4.2. It can be seen that rate constants of the modified photocatalysts are lower than that of bare TiO₂.

4.3.1.2 Phenol photodegradation under visible light

For phenol degradation a xenon lamp was used. To study the real effect of surface modification with metal NP_S on the photocatalytic activity under *visible light*, a NaNO₂ solution (10 g.L⁻¹) was used as a UV filter. Consequently, the

Photocatalyst	k (min)	\mathbf{R}^2
TiO_2	0.173	0.97
0.1-Au/TiO ₂	0.177	0.80
0.5-Au/TiO ₂	_	_
$1 - \mathrm{Au} / \mathrm{TiO}_2$	_	_
0.1-Ni/TiO ₂	0.1645	0.97
0.5-Ni/TiO ₂	0.1247	0.96
$1-Ni/TiO_2$	0.141^{*}	0.96
0.1-NiAu/TiO ₂	0.1552	0.95
0.5-NiAu/TiO ₂	0.1456	0.97
$1-\mathrm{NiAu}/\mathrm{TiO}_2$	_	-

Table 4.2: Kinetics data for bare and modified TiO_2 under UV light.

photocatalytic tests were conduced with wavelengths $\lambda > 420$ nm. However, a small photoactivity of P25 was observed even when a stable filter-solution was used to cut off the of UV-light. This can be explained by the coupling of anatase and rutile phases which leads to an activity under visible light. The effect of the surface modification of TiO₂ with different metal nanoparticles on the phenol photocatalytic degradation under visible light is present in Figure 4.13.

Clearly the modification of TiO_2 surface with metal NPs leads to an enhancement in the photocatalytic degradation of phenol under visible light. The efficiency is as follows: x -NiAu/TiO₂> x-Au/TiO₂ > x -Ni/TiO₂.

The activity of the co-modified TiO_2 with Ni-Au is found to be strongly dependent on the metal loading (Figure 4.14).

Surprisingly, low metal loading is benefitial for phenol degradation, see kinetic constants (Table 4.3). Also, under Vis light irradiation, the kinetics were fitted with a pseudo first order reaction like in the case of UV irradiation, see equation 4.1. The kinetic constants under visible light were two order of magnitudes slower than those of obtained under UV irradiation.



Figure 4.13: Kinetics of phenol degradation for selected modified samples with 0.1 at% metal loading. . Experimental conditions: (1) solar lamp light source; (2) initial concentration of phenol of 50 ppm; (3) 1 g.L⁻¹ of photocatalyst; (4) 20 mL.min⁻¹ oxygen flow; and (4) volume photoreaction: 250 mL.

Table 4.3: Kinetics data of bare and modified TiO_2 under visible light.

k (min)	\mathbf{R}^2
4.19x10-4	0.99
5.48x10-4	0.97
6.72x10-4	0.96
9x10-4	0.90
5.32x10-4	0.87
2x10-4	-
	k (min) 4.19x10-4 5.48x10-4 6.72x10-4 9x10-4 5.32x10-4 2x10-4

4.3.1.3 DISCUSSION

The purpose of deposition of metal NPs on the titania surface was to reduce the recombination of electron-hole pairs and consequently to improve the degradation of phenol molecules. The modification of TiO_2 with metal nanoparticles leads to



Figure 4.14: Kinetics of phenol degradation for selected modified samples of x-NiAu/TiO₂.

a slightly lower photocatalytic activity compared to bare TiO_2 under UV light. In fact, the kinetic constants do not show a noteworthy difference (<0.04 min⁻¹) compared to that of bare TiO₂. Based on the TRMC study and photocatalytic phenol degradation test, we can say that not favorable effect of metal NPs during photocatalytic process is observed. No scavenging of electron by the metal NPs occurs.

Clearly the photocatalytic activity under UV light is carried out at titania surface, where the metal NPs act like impurities, either as a recombination center of electron-hole pairs or as black points decreasing the interaction of the semiconductor with light. Therefore, the oxidation of phenol molecules follows the conventional phenol pathway degradation on titania: phenol degradation is carried out directly by holes (h⁺) as well as indirectly by photogenerated oxidizing radicals: $O_2^{\bullet-}$, $HO_2^{\bullet-}$, and $HO^{\bullet-}$, see Figure 4.15.

Moreover, phenol degradation was observed in both bare and modified TiO_2 under visible irradiation. However, contrary to UV irradiation, under visible light metal NPs exhibit a beneficial effect on the photocatality process. The



Figure 4.15: Schematic phenol degradation using surface modified titania with metal NPs under UV light. The photocatalytic process occurs only on TiO_2 surface and UV light irradiation. Metal NPs do not scavenge the photogerated electrons acting as impurities on TiO_2 and decreasing the light contact between light and titania.

activity under visible light of bare TiO_2 -P25 can be explained by the junction of anatase with rutile phase leading to a band alignment in which the electrons are injected from rutile to anatase Scanlon *et al.* [2013] .TRMC results support this explanation because a small but significant signal is observed under excitation at 450 nm.

The TRMC spectra of the samples Ni/TiO_2 show that nickel species lead to the formation of charge carriers under visible light, explaining the photoactivity improvement compared to bare titania. The samples containing gold NPs $(Au/TiO_2 \text{ and } NiAu/TiO_2)$ do not show any TRMC signal under visible excitation wavelengths, however, a good activity in the degradation phenol was observed. Gold NPs present a localized surface plasmon resonance (LSPR) with a maximum peak at 540-560 nm, which was observed by DRS characterization. Plasmon is the oscillation of free electrons, which is the consequence of the formation of a dipole in the material due to interaction with light, and such free electrons can contribute to phenol degradation. Injection of those free electrons into the CB of titania is not considered because no signal at larger wavelength (>450 nm) is detected by TRMC measurements. Therefore, we considered that the reaction with free electrons is performed directly on the metal NPs surface.

Based on the experimental results, a mechanism of phenol oxidation is proposed, where phenol is degraded directly either on the surface of the metals by free electrons or indirectly by $O_2^{\bullet-}$, $HO_2^{\bullet-}$, and $HO^{\bullet-}$ species.



Figure 4.16: Schematic phenol degradation using surface modified titania with metal NPs under visible light.

4.3.2 OXIDATION OF 2-PROPANOL

The photocatalytic activity under the visible light was also evaluated for 2-propanol oxidation in liquid phase. Such alcohol oxidation involves the formation of acetone before the CO_2 generation, see equation (4.2). Then, we follow indirectly the 2-propanol oxidation by acetone evolution.

$$2 - propanol \longrightarrow acetone \longrightarrow CO_2 \tag{4.2}$$

Figure 4.17 shows the acetone evolution with x-NiAu/TiO₂ and x-Au/TiO₂ samples using a xenon lamp equipped with a cut-filter ($\lambda > 450$ nm).



Figure 4.17: Acetone generation under visible-light irradiation. The evaluated samples were: a) NiAu and b)Au -modified titania powders. The irradiation wavelengths were $\lambda > 450$ nm.

The x-NiAu/TiO₂ show one-order of magnitude higher photoactivity than x-Au/TiO₂.

It should be noted that acetone was not detected in dark or under visible light irradiation neither for bare TiO_2 nor x-Ni/TiO₂ samples. Acetone evolution is

faster with increasing the Au loading. It is clear that the presence of gold NPs plays an important role in the oxidation of 2-propanol under visible light.

An action spectrum is a strong tool for determining whether an observed reaction with the modified samples occurs via a photo-induced or a thermocatalytic process. To obtain an action spectrum, acetone evolution from decomposition of 2-propanol with 1-NiAu/TiO₂ was measured at room temperature under monochromatic visible light irradiation (450, 480, 510, 540, 570 and 600 nm). The apparent quantum efficiency (AQE) was calculated. A good agreement between de action and absorbance spectra was observed, Figure 4.18, indicating that the photocatalytic activity of 1-NiAu/TiO₂ was induced by photoabsorption due to LSPR of gold.



Figure 4.18: Action spectrum of 2-propanol oxidation (red marker-line) and DR spectrum (purple solid line) of $1-NiAu/TiO_2$.



Figure 4.19: Schematic 2-propanol oxidation using surface modified titania with metal NPs under visible light..

4.3.3 Removal of lead (II) by photocatalytic reduction or oxidation process

Lead (II) is a toxic metal ion frequently found in wasterwater coming from industrial effluents. The usual treatments to remove lead from water, include precipitation, electrolysis or chemical oxidation. All these treatments are expensive, and other ways of lead elimination from wastewater have to be developed. In this sense, photocatalysis can be envisaged as a potential method for eliminating Pb(II) from aqueous solutions. The removal pathway can occur either by photooxidation or reduction of lead ions Murruni *et al.* [2008]. Oxidation and reduction of Pb(II) by bare titania, NiAu/TiO₂, Au/TiO₂ and Ni/TiO₂ powders were evaluated.

4.3.3.1 Photocatalytic reduction of Pb(II) ions

Because of the photoreduction was carried on at pH 3, no Pb^{2+} adsorption on the titania surface or modified samples was expected. The point zero charge value of titania is higher than at pH 3 (PZC, 6.5), consequently titania surface is positively

charged leading to a repulsion between it and Pb^{2+} ions.

Adsorption of lead ions on both bare titania and modified samples surface was studied, in dark conditions during one hour. Only a negligible adsorption (< 4%) was observed. The adsorption in the dark was then discounted and in all cases, the initial Pb^{2+} concentration was fixed at its value before illumination.

The results of the photocatalytic reduction of lead (II) using bare and modified TiO_2 are shown in Figure 4.20.



Figure 4.20: Photocatalytic reduction of Pb (II). The figure shows the time profile of normalized Pb (II) concentration follows by conductivity. Experimental conditions: (1) light source; (2) the initial concentration of Pb (II) was 0.5 mM ; (3) 1 g.L⁻¹ of photocatalyst; (4)volume photoreaction: 25 mL.; (5) deaerate atmosphere and; (6) 0.1 M of formic acid.

A better Pb^{2+} removal was reached with 0.5-NiAu/TiO₂ sample. The final reduction of Pb^{2+} to Pb^{0} by conductivity measurements was 53% at 120 min, the small standard error deviation plotted suggests good reproducibility. The final reduction using bare TiO₂ was 23%.

The modification of titania with monometallic metals seems to be harmful to lead (II) reduction. The sample 0.5-Ni/TiO₂ shows a small total removal (13%),

and a long time induction time of 60 min is observed. No removal of Pb(II) is measured using the 0.5-Au/TiO₂ sample.

After the photocatalytic reaction the samples turned to dark gray color because of deposited Pd on bare titania and on 0.5-NiAu/TiO₂ sample. In case of 0.5-Ni/TiO₂, no evident color change was observed because of: (i) similar gray color characteristic of that sample and (ii) low achieved conversion.

4.3.3.2 Photocatalytic oxidation of Pb(II) ions

Another alternative for lead ions removal is via photooxidation. Contrary to the photoreduction, in this pathway the presence of oxygen is required and no hole scavenger (formic acid) is added. Figure 4.21 shows the results of Pb^{2+} removal by photo oxidation.

Bare titanium dioxide exhibited no activity. Pb(II) oxidation was more efficient with the modified samples. The co-catalyst Ni-Au samples show the highest activity (55% at 180 min) while the monometallic modified titania present a lower activity around 22% less. Final conversion was determined either by colorimetry or by total reflection X-Ray fluorescence (TRXRF).

4.3.3.3 DISCUSSION

Under UV irradiation ($\lambda < 380$ nm), there is a formation of electron-hole pairs inside of titanium dioxide. Certain amount of those charge-carriers migrate to the surface of the semiconductor, where both reduction and oxidation reactions occurs (according the conditions of the system). Such charge separation in TiO₂ under UV light is confirmed by our TRMC characterization.

Using bare TiO₂, it should be highlighted that reduction of lead (II) ions is achieved while their oxidation do not occurs. This suggests that the removal of Pb²⁺ ion the electron transfer is influenced by other factors. In order to try to understand the factors involved in the transfer electron in both reduction or oxidation reactions, a detail analysis, based on our experimental results, observation, and literature is done.



Figure 4.21: Photocatalytic oxidation of Pb (II). The figure above shows the time profile of normalized Pb (II) concentration follows by colorimetry. The figure below displays the final reduction of Pb (II) follows by X-Ray fluorescence. Experimental conditions: (1) solar lamp light source; (2) the initial concentration of Pb (II) was 0.5 mM; (3) 1 g.L⁻¹ of photocatalyst; and (4) photoreaction volume: 25 mL.

(I) Removal of lead(II) by photo reduction

Based on: (a) previous works done by Martha Litter et. al (our experiments were carried out in her laboratory) who used the same reaction conditions, (b) gray color observed on the surface photocatalyst at the end of the reaction, and (c) ideal reducing conditions, we assume that the only possible reaction product is Pb^{0} .

During the photocatalytic process holes and electrons are generated, which are oxidizing and reducing species respectively. The addition of a scavenging of oxidizing species (formic acid in our case) prevents the re-oxidation of species already reduced. The COO^{•-} radical is produced by the reaction of h⁺ or HO^{\bullet} with formic acid. The COO^{•-} radical is a strong reducing species, with a redox potential of -1.97 V_{NHE} Soediono [1989]. Thus, the reaction system is in reducing conditions, in which only electrons and COO^{•-} are present. The reduction facility of lead ions depends on their redox potential position.

Lead (II) ions were negligible adsorbed (< 4%) on the photocalyst, then they can be considered as free ions in the solution. The reduction potential is $E^{\circ}[Pb^{2+}/Pb^{0}]=-0.126 V_{NHE}$ and it value corresponds to a global reduction process and stable solid metal formed. In the reduction of Pb²⁺ several intermediate reactions occur, consequently the reduction potential changes. Breitenkamp *et al.* [1976] tentatively estimated by pulse radiolysis study the potential for the systems $E^{\circ}[Pb^{2+}/Pb^{+}] = -1.0 V$ and $E^{\circ}[Pb^{+}/Pb^{0}_{solid}] = 0.75 V_{NHE}$. Belloni [2006] demonstrated that potential energies of the first metal atoms and small clusters formed are always more negative than for bulk metal. The $E^{\circ}[Pb^{+}/Pb^{0}_{atom}]=-0.82 V_{NHE}$ was calculated Breitenkamp *et al.* [1976]. The coalescence of the metal atoms leads to increase the redox potential until the $E^{\circ}[Pb^{+}/Pb^{0}_{solid}]$ value.

Considering the above explanation and the energy levels of conduction band edge of titania P-25, a scheme illustrating the reduction of lead (II) is proposed, see Figure 4.22:

It is evident that bivalent lead ions is reduced to Pb^+ only by $COO^{\bullet-}$ radical, see equation (4.3). The reduction by electrons in the conduction band are not thermodynamically possible. Similarly the reduction of Pb^+ to Pb^0 is carried out



Figure 4.22: Proposed scheme of the effect of $COO^{\bullet-}$ radicals and electron CB in the reduction of leads ions in aqueous solutions using TiO_2 .

(eq. (4.4)), however a disproportion reaction $\rm Pb^+$ and $\rm Pb^{2+}$ occurs as shown in equation (4.5) .

$$Pb^{2+} + COO^{\bullet-} \longrightarrow Pb^+ + CO_2 \tag{4.3}$$

$$Pb^{+} + COO^{\bullet -} \longrightarrow Pb^{0} + CO_2 \tag{4.4}$$

$$Pb^{+} + Pb^{+} \longrightarrow Pb^{0} + Pb^{2+} \tag{4.5}$$

The metal atoms will coalesce to form small cluster. The reduction potential of Pb^+/Pb_n^0 increases with the nuclearity n. For a certain number of lead atoms (n_c) the reduction of Pb^+ by the electrons in the conduction band will be possible.

$$Pb^+ + e^- \longrightarrow Pb^0 \tag{4.6}$$

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Thus, we can say that at the beginning of reduction the role of the semiconductor is the photocatalytic formation of $COO^{\bullet-}$, then the reduction by electrons in the conduction band will be possible when Pd clusters reach a critical size.

The modification of TiO₂ surface with metal NPs improves or harms the reduction of Pb²⁺ depending on the metal deposited. Baba et al. reports an improvement in Pb²⁺ reduction using titania platinizing suggesting that Pt island can increase the redox potential of electrons to more negative value. Such explanation is usually used when metals are deposed on TiO₂, then it is expected the same effect when Ni or Au NPs are deposed on TiO₂, however it does not happen. Then we consider that the position of the redox potential of the leads ions change in the present of the modified samples. In case of Au/TiO₂ or Ni/TiO₂ samples $E^{\circ}[Pb^+/Pb^{2+}]$ and $E^{\circ}[Pb^+/Pb^{2+}]$ has to be lower than COO^{•-} one, inhibiting completely the lead (II) reduction.

For NiAu/TiO₂ it is obvious that either $E^{\circ}[Pb^+/Pb^0_{atom}]$ or both $E^{\circ}[Pb^+/Pb^0_{atom}]$ and $E^{\circ}[Pb^{2+}/Pb^+]$ were displaced to more positive values than the value of the electron conduction band, improving the lead ions reduction. Figure 4.23 shows a proposed scheme of lead ions (II) reduction using the modified samples.



Figure 4.23: Proposed scheme of the effect of $COO^{\bullet-}$ radicals and electron CB in the reduction of leads ions in aqueous solutions using modified samples.

4.3.4 Hydrogen production

The photocatalytic production of hydrogen from water or alcoholic solutions have shown to be a promising alternative to produce hydrogen, in a cleaner and less inexpensive way than actual production route. The modification of titania surface with mono-metallic NPs has been widely studied. Recent studies have demonstrated that deposition of bimetallic NPs on semiconductor surfaces, can lead to enhancement the photocatalytic performance compared to the monometallic systems.

The motivation to evaluate the samples Ni-Au for this reaction lies in trying to understand the key factors that make the bimetallic samples more active than mono metallic ones.

4.3.4.1 PHOTOCATALYTIC HYDROGEN PRODUCTION UNDER XE LAMP IRRADIATION

The hydrogen production rates from methanol solution (50/50% v) with the photocatalysts as a function of metal loading are presented in Figure 4.24a. As expected, bare TiO₂ was largely inactive for the reaction because of fast recombination of charge carriers Ismail and Bahnemann [2014]; Schneider *et al.* [2014] and its short ability to act as a recombination center for atomic hydrogen Baba *et al.* [1985]; Islam *et al.* [2011]; Joo *et al.* [2014]. Clearly, the deposition of metal NPs (Au, Ni or Au-Ni) on TiO₂ surface improves the H₂ production rate. It must be highlighted that even if the conditions for reactions in continuous and batch systems are different, a clear tendency is observed: the photocatalysts x-NiAu/TiO₂ present the highest H₂ production followed by x-Ni/TiO₂ and x-Au/TiO₂ samples as shown in Figure 4.24 and in the Table 4.4.



Figure 4.24: Rates for H_2 photoproduction from methanol/water solutions under UV light. (a) R_{H_2} from 50vol% aqueous methanol for batch system; and (b) Continuous profile of H_2 generation using modified samples (0.5at%) in 10vol% aqueous methanol.

Concerning the metal loading of the modified samples (x-Au/TiO₂, x-NiAu/TiO₂ and x-Ni/TiO₂), three different effects were observed. The system Au/TiO₂ shows a slightly, but clear increase in H₂ evolution when the amount of metal increases, whereas for Ni/TiO₂ the amount of H₂ does not vary much with the metal loading.

Table 4.4: H_2 production rates with x-Au/TiO₂, x-Ni/TiO₂ and x-NiAu/TiO₂ samples and bare TiO₂ followed by gas chromatography and mass spectrometry. The reaction conditions for these two systems are described in the experimental part

	Gas chromatography	Mass spectrometry	
	\mathbf{H}_2 production rate (µmol.h ⁻¹)	\mathbf{H}_2 production rate (µmol.h ⁻¹)	
TiO_2	6.2	<1	
0.1-Au	29.0	25	
0.5-Au	31.6	46	
1-Au	39.2	78	
0.1-Ni	68.3	88	
0.5-Ni	58.2	135	
1-Ni	67.7	61	
0.1-NiAu	97.6	193	
0.5-NiAu	157.0	318	
1-NiAu	136.4	284	

The x-NiAu/TiO₂ photcatalysts show an optimal metal loading of 0.5 at% in metal.

4.3.4.2 ACTION SPECTRA MEASUREMENTS

To understand the H_2 production enhancement with the modified samples, a systematic study of the photocatalytic activity as a function of the irradiation wavelength was done. Action spectra of the different samples (x-Au/TiO₂,x-NiAu/TiO₂ and x-Ni/TiO₂ with a metal loading of 0.5 at%) were measured in the range 320-440 nm (with intervals of 30 nm).

Figure 4.25 displays the AQE determined by the action spectra for each sample. The absorbance obtained by DRS, and the Imax/photons obtained by TRMC have also been plotted to follow the evolution with the wavelength of the three steps of the photocatalytic mechanism: photon absorption, charge-carrier formation, and

chemical surface reaction.



Figure 4.25: Absorption spectra (photon absorption), TRMC spectra (charge-carrier formation) and action spectra (apparent quantum efficiency). The selected samples were those of metal loading of 0.5 at% and bare TiO_2 .

It can be observed that the AQE of bare TiO_2 is very weak. The action spectrum shows that the maximum amount of hydrogen is obtained at a wavelength of 350 ± 5 nm. This suggests that the highest density of electrons in the conduction band is obtained at this energy. This is in agreement with the TRMC results, where the highest photoconductivity was obtained under irradiation at 355 ± 5 nm.

Detailed analysis of AQE spectra of the three modified compounds suggests appreciable differences among them; the action spectrum of 0.5-Au/TiO₂ shows a low level and a maximum at 380 nm, while the action spectra of compounds containing Ni present higher levels and follow the absorption spectra. 0.5-Ni/TiO₂ and 0.5-NiAu/TiO₂ samples show similar profiles, but an enhancement of the AQE is clearly shown for 0.5-NiAu/TiO₂. Considering the small amount of gold, the enhancement in H₂ production cannot be explained only by an additional effect of gold, but by a synergistic effect of gold with nickel. P25 is a mixture of anatase (the main phase) and rutile with absorption edge at 380 and 410 nm, respectively, it contains also a very small amount of amorphous TiO₂. Thereby a shoulder of its absorption spectrum at ca. 400 nm is assigned to rutile phase. The observed action spectra of modified compounds suggest that gold and nickel particles were loaded predominantly on rutile, and anatase particle, respectively. It has been observed that platinum particles were photodeposited preferentially on rutile in P25 if the number of platinum particles was small and the corresponding action spectrum showed a dip in the wavelength region at around 350 nm Ohtani *et al.* [2010, 2015]. This was explained by the disturbance of rutile photoabsorption by inactive anatase crystallites in the relatively short wavelength region. Thus, anatase and rutile crystallites mainly work in 0.5-Ni/TiO₂ and 0.5-Au/TiO₂, respectively, even though both crystallites absorb light, and 0.5-NiAu/TiO₂ might show activity higher than the sum of activities of singly modified samples due to both crystallites work effectively.

For the bare TiO_2 , the low AQE values are associated to high TRMC signal. In comparison, modified compounds present higher AQE values corresponding to slightly lower TRMC signal. This point confirms the assumption that the positive effect of the NPs is more effective on the H₂ overpotential, i.e. its ability to act as a recombination center of atomic hydrogen, than on the separation of charge-carriers.

4.3.4.3 DISCUSSION

According to TRMC results, the metal loading on the surface of TiO₂ does not have a strong influence on the photocatalytic activity of TiO₂. For nickel and nickel-gold/TiO₂ samples a very small transfer of photoelectron to metal was observed, while for gold/TiO₂ samples no transfer of electron from the metal to TiO₂ was observed. Surprisingly, however all the modified samples show enhanced hydrogen production, in increasing order from x-Au/TiO₂, x-Ni/TiO₂ and x-NiAu/TiO₂. The results evidence that the role of the metal is not only to avoid the recombination of charge-carriers by trapping electrons Ismail and Bahnemann [2014]; Schneider *et al.* [2014], but also to act as recombination center of atomic hydrogen (H•) coming from TiO₂ surface to form hydrogen, as it has been recently proposed Joo *et al.* [2014].

Both theoretical and experimental results demonstrate that TiO_2 can reduce the protons (H⁺) to atomic hydrogen, however TiO_2 surface is not capable to act an efficient recombination center of H[•] Islam *et al.* [2011]; Joo *et al.* [2014]. In this context and considering the results obtained in this work, we propose a photocatalytic mechanism for each system.

It is well known that a Schottky contact is formed between Au and TiO₂, where the electron transfer depends on the size of metal NPs: For example small metal particles improve the electron transfer and vice versa Ioannides and Verykios [1996]; Subramanian *et al.* [2004]. The HRTEM study for Au/TiO₂ photocatalysts reveals a large average particle size (mean size 18 nm), such a size is too large to scavenge photoexcited electrons Ioannides and Verykios [1996]; Murdoch *et al.* [2011]; Subramanian *et al.* [2004]. TRMC results support the idea of negligible electron scavenging by Au NPs in x-Au/TiO₂ samples. H₂ production by Au/TiO₂ photocatalysts can be explained by the facts that Au NPs decrease the electronhole recombination and act as recombination centers of atomic hydrogen (H[•]) coming from TiO₂ surface as is shown in the Figure 4.26.

For Ni/TiO₂ samples, most of the nickel is dispersed as small NiO clausters on the semiconductor surface. In order to find out the photocatalytic role of nickel species deposed on TiO₂, a series of hypotheses are discussed. Firstly, the NiO/TiO₂ junction hypothesis is disregarded, because of the position conduction band energy level of NiO is higher than of that of TiO₂ Yip and Jen [2012], then an electrons transfer from TiO₂ to NiO is not probable. Another, possibility is that NiO act as active site for H[•] recombination. However, it is worth mentioning that in our samples a small amount of Ni⁰ is also present. Because of the high reactivity of metallic nickel with the air, it is expected that the remaining Ni⁰ (detected by XPS) is between the interphase of TiO₂ and NiO clusters. It has been reported that a mix of NiO-Ni deposited on a semiconductor has a higher photocatalytic activity than the single components Domen *et al.* [1986]. The latter evidence shows the Ni⁰ importance in the sample. It is well known that Ni forms an ohmic



Figure 4.26: Gold NPs acting as recombination site during the photocatalytic H_2 formation.

junction with TiO_2 , through which the photo-excited electrons migrate to the metal. In our samples the Ni⁰ amount is small, therefore the electrons transfer should be small.

In addition, TRMC signals and action spectra suggest that both NiO and TiO_2 are photoexcited simultaneously under UV-light irradiation. Based on our observations, we propose a scheme for Ni/TiO₂ that explain the photocatalytic activity, see Figure 4.27.

The photons absorption induces excitation of both TiO_2 and NiO. The oxidative part (protons formation, H⁺) is carried out only in the valence band of TiO_2 , while the reduction of protons is carried out in both conduction bands of NiO and TiO₂ semiconductors. H₂ production (hydrogen atomic recombination) takes place only on NiO surface. The TiO₂ electrons transferred by Ohmic contact to NiO recombine with the holes of NiO. Thus, the amount of photoexcited electrons is identical to that of bare TiO₂, this idea is supported by TRMC results, which show an identical decays for x-Ni/TiO₂ and bare TiO₂. The advantage of an ohmic contact in the photocatalyst is a larger number of holes available in the



Figure 4.27: Proposed mechanism of H_2 production on x-Ni/TiO₂ samples.

valence band of TiO_2 .

Finally for the NiAu/TiO₂ samples, an alloy is not expected because of the immiscibility between nickel and gold Ferrando *et al.* [2008]; Zhou *et al.* [2009]. The characterization of the samples confirms the metal segregation. In TRMC signals, the NiAu/TiO₂ samples exhibit a change in the charge-carrier kinetics attributed to electrons scavenging by the metals. However, that change is not evident suggesting that only a small amount of electrons are trapped. The decrease of gold particle size, as evidenced by HRTEM results, is probably the cause of electron scavenging improvement. The Au loading in NiAu/TiO₂ samples is five times smaller than the Ni loading. The hydrogen generation improvement cannot be attributed only to small amount of gold.

The x-NiAu/TiO₂ samples are much more efficient in photocatalytic hydrogen generation than the monometallic samples. For example, in the batch system the rate of generated hydrogen using x-Ni/TiO₂ and x-Au/TiO₂ were 31 and 58 μ mol.h⁻¹ respectively, while the sample x-NiAu/TiO₂, under the same conditions, reaches an H₂ rate of 157 μ mol.h⁻¹. Clearly, the improvement of the photocatalytic

performance was due to a synergetic effect between Au and Ni(O) since it was not a simple additive effect.

The synergetic effect has been observed using bimetallic NPs in catalysis and photocatalysis Doherty *et al.* [2012]; Zielinska-Jurek [2014]. In photocatalysis, the synergy has been commonly related to electronic and geometry effects. However, further experiments are needed to deeply understand the origin of this synergetic effect.

Based on our experimental results, we propose a reaction scheme for hydrogen photoproduction on x-NiAu/TiO₂ samples (Figure 4.28).



Figure 4.28: A propose mechanism of H_2 production onx-NiAu/TiO₂ samples.

The mechanism is similar to that proposed for x-Ni/TiO₂. The generation of the electron-hole pair takes place on the TiO₂ and NiO surfaces. The holes, coming from TiO₂, oxidize water and/or the methanol mixture generating protons, which are then reduced at the surface of both TiO₂ and NiO forming atomic hydrogen. Finally, H[•] recombination occurs on the surface of metal NPs forming H₂. The improvement of hydrogen generation compared with that of the monometallic samples is attributed to a synergetic effect between both Ni(O) and Au acting as a better atomic hydrogen recombination site than the monometallic samples.

According to a recent review on supported model catalysts, the catalytic activity depends mainly on the size and shape of the metal nanoparticles, but in some cases also on the distance between them. Therefore, despite the segregation between Ni(O) and Au in our co-modified samples, the proximity between Au and Ni-based nanoparticles seems to be enough to act as a better active site for atomic hydrogen recombination, consequently a synergetic effect can be considered Henry [2015].

4.3.5 CONCLUSION

Ni and/or Au NPs were synthesized on P25 TiO_2 by radiolysis. According to the characterization results, a segregation of the two metals was observed. Large Au NPs and Ni nanoclusters (partially oxidized) were obtained on TiO₂. The kinetic study of charge-carrier of modified samples reveals no scavenging of electrons by the metallic NPs deposed, except for bimetallic modification (NiAu).

 TiO_2 surface modification with metal nanoparticles (mono or bimetallic) does not improve the photooxidation of phenol under UV showing that the metal NPs do not help to decrease the charge-carrier recombination in TiO_2 . This is confirmed by the TRMC analysis.

Hydrogen generation, using a methanol-water solution under UV light, increase with the metal NPs on the surface of TiO_2 . The highest production of hydrogen was obtained with the NiAu/TiO₂ samples, which was explained in terms of a synergetic effect by the presence on Au NPs and Ni⁰-NiO clusters on TiO₂, acting as recombination sites for atomic hydrogen conversion to molecular hydrogen.

We have found that a very small amount of gold associated to nickel (atomic ratio Ni:Au 5:1 and total metal 0.1 to 1 at%) can induce a significant increase in H_2 formation, thus the costs of photocatalyst preparation are relatively low.

The photocatalysts containing gold (NiAu/TiO₂ or Au/TiO₂) showed a photocatalytic activity under visible light ($\lambda > 450nm$). Both phenol and 2-propanol oxidation reveal a dependence between the activity and metal loading. Phenol oxidation is favored with low loading metal (0.1 at%), increasing metal loading reduces the phenol adsorption ($\approx 5\%$) then the oxidation begins to be difficult. In case of 2-propanol oxidation, acetone formation is favored with the increasing of metal loading. SPR leads to separation of electrons and holes inside of gold NPs. Then the holes are easily trapped by 2-propanol (hole scavenger) which is oxidized by them on the surface of gold NPs. The electrons from gold SPR are captured by oxygen, see Figure 4.18. Electron injection from gold NPs to TiO₂ is not considered in TRMC results because signals at longer wavelengths of 410 nm were not observed, then we propose that both oxidation and reduction reactions take place on the surface of the gold NPs. $NiAu/TiO_2$ photocatalyst show the best response under visible irradiation.

 $\rm NiAu/TiO_2$ photocatalyst was more efficient in the lead ions (II) removal, under UV irradiation via phooxidation or photoreduction, than monometallic and bare titania. Such activity is explained in terms of a synergetic effect by the presence on Au NPs and Ni⁰-NiO clusters on TiO₂.

CHAPTER 5

NICKEL AND/OR PALLADIUM NPS Synthesized on Titania

In the present chapter, the study of titania surface modification with metal Ni and/or Pd nanoparticles synthesized by radiolysis is presented. The modified photocatalysts were characterized by High Resolution Transmission Microscopy (HRTEM), Energy-Dispersive X-ray Spectroscopy (EDS), UV-Vis Diffuse Reflectance Spectroscopy (DRS) and X-Ray Photoelectron Spectroscopy (XPS). The charge-carrier mobility was studied by Time Resolved Microwave Conductivity (TRMC). The photocatalytic activities were tested under UV/vis irradiation using polychromatic and monochromatic light (action spectrum analysis of apparent quantum efficiency). Surface modified TiO₂ with Pd and Ni NPs show high photocatalytic activity for hydrogen evolution from aqueous methanol solution. An enhanced hydrogen evolution rate is obtained for TiO₂ co-modified with Pd and Ni, where synergetic effect of the two metals was observed.
5.1 SAMPLES

Recently, Marignier [2014] demonstrated by pulse radiolysis that the reduction of Ni²⁺ to Ni⁰ is favored in the presence of a stabilizing agent (polyacrylated anion, PA⁻). The complexation of Ni²⁺ by PA⁻ leads to a shift of the reduction potential such that $E^0[Ni^{2+},PA^-]/[Ni^+,PA^-] < E^0[Ni^+,PA^-]/[Ni^0,PA^-]$, see Figure 5.1. Then, the formation of Ni oligomer (Ni⁰_{at}) is carried out by solvated electron and disproportionation reactions, driving to nucleation and formation of Ni NPs (Ni_n).



Figure 5.1: Scheme illustrating the effect of complexation on the reduction potentials of nickel ions in aqueous solutions with or without PA⁻. The value of $E^{\circ}[Ni^{+},PA^{-}/Ni^{0},PA^{-}]$ is an upper limit, and that of $E^{\circ}[Ni^{2+}/Ni^{+}]$ is a lower limit. The potentials should fulfill the condition $E^{\circ}[H_2O/e_{sol}^{-}] < E^{\circ}[Ni^{2+},PA^{-}/Ni^{+},PA^{-}] < E^{\circ}[Ni^{+}, PA^{-}/Ni^{0},PA^{-}] < E^{\circ}[Ni^{+}/Ni^{0}] < -2.55 V_{NHE}$ Marignier [2014].

The reduction potential of $[Ni^{2+}/Ni^+]$ and $[Ni^+/Ni^0]$ is not modified in absence of PA⁻, see Figure 5.1. Consequently, both the disproportion reaction of free Ni⁺ into Ni²⁺ and Ni⁰ atom and the fast consumption of solvated electrons prevent the formation of Ni⁰_{at} and Ni_n. These results highlight the importance of the stabilization of small oligomers to form the metal NPs.

The production of colloidal solutions of Pd and Ni clusters stabilized by polyvinil alcohol (PVA) by radiation-induced reduction of the corresponding metal ions in aqueous solution, has been reported Redjala *et al.* [2008]. Nickel NPs have been also synthesized by radiolysis in solutions or on oxide supports for catalytic applications Chettibi *et al.* [2013]. The oxide support plays an analogous role of stabilizing agent, leading to a change in reduction potentials of the metals ions favoring the formation of metal NPs. Hence, it is important to fix the ions metal prior to irradiation in order to: 1) achieve an effective reduction of metal ion, specially non-noble metal ions and 2) avoid the highly dispersed aggregates on the oxide.

To assure the adsorption or the fixation of the metal precursor on the support, a compromise has to be done between the three following factors: (1)the charge of the precursor in relation with the Point of Zero Charge (PZC) of the oxide, (2)the hydrolysis of the metals, and (3)the radiolytic conditions. The precursor fixation kinetic follows an ionic exchange process with surface groups of the support. The PZC of TiO₂ is 6.5. The fixation of metal the ions (Ni²⁺ and Pd²⁺) is assured at pHs higher than the PZC of titania because its surface is negatively charged. The pH=11 allows the optimum fixation by ionic exchange of both Ni and Pd ions to TiO₂ surface Chettibi *et al.* [2013].

Ni and Pd ions are divalents, the reduction involves firstly the reduction into M^{2+} to M^+ and then the reduction of M^+ into zero valence. At the beginning, the reduction of the metal precursor into an unusual valence state (Ni⁺ and Pd⁺) is carried out by the radiolytic reducing species, mainly solvated electron, which are strong reducing agents homogeneously distributed in the solution. Based on a recent work reported by Marignier [2014], it can be proposed that the Ni²⁺ reduction into Ni⁺ and after into Ni⁰ is carried out at the beginning of the reducing process, only by solvated electrons because the redox potential of secondary radicals can not reduce nickel ions. The Pd²⁺ is reduced by both solvated electrons and organic radicals. Palladium is a noble metal, then it is easier to reduce than nickel ions. The irradiations were carried out with a ⁶⁰Co

 γ -source with a dose rate of 4.5 kGy/h (low rate dose). The reduction of two metal precursors with very different redox potentials and the use of low dose rate favores the formation of core-shell structure. However the formation of alloys can not be ruled out because even using low dose rate some alloy formation has been reported, for example PdCu Morse *et al.* [1985].

The surface modification of TiO₂ with Pd and/or Ni NPs induces a change in the color of the powder from white to grey, as shown Figure 5.2. Different tones of gray can be observed: Ni/TiO₂ samples are light gray(whitesmoke) compared to Pd/TiO₂ samples. The NiPd/TiO₂ samples show a silver color and the PdNi/TiO₂ samples exhibit a dark/gray color. The difference between the two last catalysts is the metal ratio. The metal ratio for PdNi/TiO₂ samples is Pd/Ni=10 while for the NiPd/TiO₂ sample is Pd/Ni=0.1. The suffix "real" in the samples x-Ni_{real}/TiO₂ or x-Pd_{real}/TiO₂ refers to that lowest metal loading deposed in the bimetallic samples.



Figure 5.2: Images of modified samples of with Ni and/or Pd.

5.2 CHARACTERIZATION OF THE SAMPLES

Undoubtedly, deposition of metal NPs on TiO_2 causes changes in the electronic and optical properties of the semiconductor. Such changes were studied by DRS and TRMC techniques. Size, morphology and structure of metal NPs, and chemical states were examined by HRTEM and XPS. The results are presented below.

5.2.1 UV-VIS DIFFUSE REFLECTANCE

The diffuse reflectance spectra (DRS) of bare and modified TiO_2 are shown in Figure 5.3. For all the samples, the highest absorbance was obtained below 400 nm, which is mainly attributed to the intrinsic band gap absorption (3.15 eV) of the TiO_2 support. A zero absorbance at wavelength greater than 400 nm, characterizes the TiO_2 spectrum. However, surface modification of TiO_2 with metal NPs leads to an additional absorption in the visible region, and this absorption depends on the deposited metal and on the loading.

The visible light absorption of Pd NPs on TiO₂ surface is probably caused by their surface plasmon absorbance. The absorption properties of Pd particles highly depend upon their size and shape. Pd clusters with size smaller than 10 nm show a maximum plasmon absorbance in the UV region (maximum at 250 nm in water and at lower wavelength in air), but larger NPs and 2D-nanostructures (such as sheets) have shown an absorption in visible region Leong *et al.* [2015]; Mohapatra *et al.* [2008]; Siril *et al.* [2009]. Therefore, the plasmon absorption of x-Pd/TiO₂ samples in the visible region suggests a size of Pd NPs larger than 10 nm.

A similar absorbance spectrum was observed in the x-PdNi/TiO₂ samples, however remarkable visible-red absorbance was obtained (Figure 5.4), indicating an increase in size and/or irregular shape of Pd NPs in the x-PdNi/TiO₂ photocatalysts compared with the monometallic materials.



Figure 5.3: UV-Visible absorbance spectra of modified samples and bare TiO₂. (a) x-Pd/TiO₂; (b) x-Ni/TiO₂; and (c) x-NiPd/TiO₂ and x-PdNi/TiO₂

5.2.2 HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

The HRTEM analysis shows significant changes in the size, morphology and dispersion of the metal nanoparticles between mono- and bimetallic samples, as



Figure 5.4: UV-Visible absorption spectra of $1-PdNi/TiO_2$ and $1-Pd/TiO_2$ samples.

shown in the Figure 5.5, 5.6 and 5.7. In the monometallic samples, (Pd/TiO_2) most of the Pd NPs are spherical with an average size of 13 nm. However, some Pd NPs agglomeration was also observed. In general the number of Pd NPs in an aggregate does not exceeded 3, and the aggregate size is around 20 nm, Figure 5.5

In the case of co-modification with Pd and Ni, both shape and size of NPs depend on the metal ratio. On one hand, for the $PdNi/TiO_2$ photocatalyst with the ratio Pd/Ni=10, large aggregates of metal NPs were observed with an average size > 20nm as shown in Figure 5.7. Such aggregates are constituted of numerous individual grains with an average size <7 nm, see Figure 5.7 b and c. On the other hand, when nickel is the predominant metal in the sample (Pd/Ni=0.1), small and spherical NPs where observed with an average size of 6 nm, see Figure 5.6. It is clear that the size of the NPs decreases with an increase of nickel loading. It must be highlighted that NPs aggregation was not observed.

For the bimetallic samples, the elemental analysis revels the presence of both Ni and Pd signals. For the monometallic samples, the corresponding signals were



Figure 5.5: HRTEM of 1-Pd/TiO₂ samples.



Figure 5.6: HRTEM of 1-NiPd/TiO₂ samples.

detected, even that of nickel, proofing the nickel existence on the samples. Nickel NPs in the samples Ni/TiO_2 were not observed by HRTEM probably because of the proximity of the atomic number of Ni and Ti, which makes difficult to

distinguish them by contrast.



Figure 5.7: HRTEM of 1-PdNi/TiO₂ samples.

5.2.3 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

The surface composition and oxidation states of all elements (Pd, Ni, O, Ti, and C species) in samples were analyzed using X-ray Photoelectron Spectroscopy. A comparison of the spectrum Pd3d of the mono- and bimetallic samples is presented in Figure 5.8.

The Pd3d core-level energy of the samples Pd/TiO₂ and PdNi/TiO₂ are the same (334.7 eV) while this of NiPd/TiO₂ is shifted to higher values (335.5 eV). The fit of the signals show four contributions: metallic Pd Fujiwara *et al.* [2016]; Yui *et al.* [2011], intermediate Pd oxidation (PdOx) Gabasch *et al.* [2006]; Ouyang *et al.* [2015], PdO Gabasch *et al.* [2006], and ionic Pd²⁺ Fujiwara *et al.* [2016], with a BE of 334.5, 335.5, 336.7 and 337.7 ± 0.2 eV, associated to 3d_{3/5}, respectively. The samples Pd/TiO₂ and PdNi/TiO₂ are mainly composed by metallic Pd (\approx 51%). In both samples a strong contribution of PdOx is observed (36-38%), which can be attributed to PdOx-TiO₂ interaction and/or substoichiometric PdOx (x<1).



Figure 5.8: XPS spectra of the Pd3d core level of: a) $PdNi/TiO_2$, b) Pd/TiO_2 , and c) $NiPd/TiO_2$.

PdO concentration exhibited by such samples is around 9% indicating a slight oxidation of the surface NPs by air contact.

For the sample NiPd/TiO₂ the fit of the Pd3d spectrum reveals mostly a contribution of PdOx, PdO, and only a small peak corresponding to Pd⁰. Studies of Ni-Pd total energy calculations have reported a clear preference for a Ni

core-Pd shell structure Zhang *et al.* [2010], therefore the intermediate Pd contribution can be endorsed to substoichiometric PdOx (x < 1) mainly. The interaction with Ni, whose concentration is 10 times higher than Pd, can be the cause of substoichiometric PdOx.

The Ni2p spectra of NiPd/TiO₂ and Ni/TiO₂ samples exhibit $2p_{1/2}$ and $2p_{3/2}$ binding energies at 873.4 and 855.7 eV respectively. These binding energies and the shake-up satellite peaks, observed at 6 eV above the main Ni $2p_{1/2}$ and $2p_{3/2}$ lines, indicate the presence of NiO nanoparticles. Nevertheless, the fit of Ni 2p signal shows a small amount of Ni⁰, see Figure 5.8. Solvated electrons are very strong reducing species able to reduce Ni ions, and the applied dose is sufficient to reduce all the Ni²⁺ precursor present in the suspension. However, it is well known that Nickel is very sensitive to air contact, which is the cause of the partial oxidation of NPs during the drying step of the synthesis.

Based on the latter, structural model for each system was proposed, see Figure 5.10. A more detailed explanation about these models will be given in the discussion of the results.



Figure 5.9: Fitting of Ni2p core level of $NiPd/TiO_2$ sample.



Figure 5.10: Proposed structural model of the systems: a) Ni/TiO_2 , b) Pd/TiO_2 , c) $NiPd/TiO_2$, and d) $PdNi/TiO_2$. At left of each model a scheme of structural surface formation is presented.

5.2.4 TIME RESOLVED MICROWAVE CONDUCTIVITY

The effect of surface modification of TiO₂ with metal NPs on the charge-carrier kinetics was examined by TRMC. For all the samples, the TRMC signals were obtained. However for clear discussion and understanding, only the most representative TRMC signals and data (I_{max} , I_{40}/I_{max} , and k_D) are shown in Figure 5.11 and Table 5.1. The TRMC signals were displayed in double logarithm plots with a time scale from 0 to 1000 ns.

In comparison with bare titania, all the modified samples display a lower maximum (I_{max}). Three phenomena linked to metal deposition and corresponding to the lost of charge-carriers during the pulse can be responsible for this I_{max} reduction: a) shield effect by NPs, b) surface recombination centers induced by the synthesis method, and c) fast electron scavenging by the metal (<10 ns). Therefore,



Figure 5.11: **TRMC signal of the modified samples and bare TiO**₂. The signals were induced by 355 nm light pulses at 1.2 mJ.cm⁻² excitation density. (a) 1-PdNi/TiO₂ and (b) 1-NiPd/TiO₂.

to understand which of these three phenomena has the largest contribution on I_{max} reduction a detailed analysis of the signal decay is required.

The short-range decay for the modified samples is faster than bare TiO₂. The latter can be easily observed in the Table 5.1, where I_{40}/I_{max} values are presented. For that range, a faster decay can be explained by: a) a larger recombination rate

	Imax (mV)	$\mathbf{I}_{40}/\mathbf{I}_{max}$	\mathbf{k}_D
TiO_2	233	0.64	0.186
0.5-NiPd	152	0.39	0.158
0.5-Pd real	126	0.34	0.360
0.5-Ni	158	0.45	0.197
1-PdNi	131	0.53	0.217
1-Ni real	169	0.54	0.187
1-Pd	156	0.65	0.216

Table 5.1: TRMC parameters for bare titania and modified samples.

of charge-carriers, which may be caused by surface defects generated during metal deposition b) electron trapping by the metal. To discern between the two above causes, the analysis of long-range decay is also necessary.

The photocatalyst containing mainly palladium (0.5- Pd_{real}/TiO_2 , 1- $PdNi/TiO_2$ and 1- Pd/TiO_2) exhibit higher k_D value compared to bare TiO₂. While the samples with higher amount of nickel (0.5-Nireal/TiO₂, 1-Ni/TiO₂ and 1-NiPd/TiO₂) show either a lower or similar value of k_D compared to bare titanium. The higher K_D value of the modified samples (compared to that of bare titanium) leads to consider the hypothesis of trapping electron by the metal, because it is the only phenomenon that can induce a change in the long-range decay. The influence of the surface defects in the recombination of charge-carriers should not have an effect on the k_D value. In that context, TRMC profiles support the idea that the palladium NPs in the samples improve the capacity to scavenge electrons.

5.3 Photocatalytic hydrogen production test

The generation of hydrogen was the reaction selected to evaluated the effect of the metal NPs on titania surface. The evaluation was realized with different irradiation sources: (1) polychromatic light and (2) monochromatic light (action spectra).

5.3.1 Hydrogen generation under mercury lamp irradiation

The activity of the PdNi/TiO₂, NiPd/TiO₂, Ni/TiO₂ and Pd/TiO₂ photocatalysts for H₂ production was initially evaluated using batch set-up conditions (50vol% of aqueous methanol under UV irradiation), previously described in detail in the experimental section. The reaction displays a zero order kinetics.

Firstly, the surface modification of TiO_2 with metal NPs leads to a H₂ rates production higher than that of bare TiO_2 , as shown in Figure 5.12. It is not a surprising result because it is well know that bare TiO_2 is an inefficient material for photocatalytic hydrogen generation. The above is commonly attributed to high hydrogen overpotential resulting in the rapid electron-hole recombination, reducing the number of charge-carriers available for the photoreaction. In both mono- and bimetallic samples, the efficiency of these changes is according the amount and the type of the metal NPs.

On one hand, the activity of Ni/TiO₂ samples is almost the same (around 60 μ mol/h) for the samples containing ≤ 0.5 w%, see Figure 5.12a. The increase of metal loading leads to a decreasing in the hydrogen generation. On the other hand, as shown in Figure 5.12b, the palladium photocatalyst exhibits an optimum amount of metal loading around 0.5w%.

The main purpose of this work is to study the effect of the bimetallic modification compared with its monometallic components. An improvement of hydrogen production was achieved using the bimetallic samples compare to the monometallic ones, as shown in Figure 5.13. However just two of the samples $(0.5-NiPd/TiO_2$ and $1-PdNi/TiO_2$) show a true synergistic effect, that is, the whole amount of obtained hydrogen for such samples is greater than the simple sum of its parts.



Figure 5.12: \mathbf{H}_2 production rates for modified samples and bare titania. \mathbf{R}_{H_2} from 50vol% aqueous methanol.

5.3.2 ACTION SPECTRA MEASUREMENTS

In order to better elucidate the origin of the enhanced photoactivity of the modified materials, the generation of hydrogen was studied as a function of the irradiation wavelength.

A comparison of the absorption and action spectra (apparent quantum efficiency) for three different samples $(1-Ni_{real}/TiO_2, 1-PdNi/TiO_2 \text{ and } 1-Pd/TiO_2)$ was measured in the range 320-440 nm (with intervals of 30 nm), Figure 5.14.

Bare titania shows the lowest AQE. Its action spectra profile does not follow the absorption spectrum. According the absorption spectrum, the bare titanium absorbs a large amount of photons at wavelength <350 nm. However, measuring action spectra show an optimum at wavelength of 355 nm and below of that



Figure 5.13: Comparison of H_2 production rates of bimetallic samples with its respecting parts.

wavelength the activity to produce hydrogen decreases. The modified samples exhibit a higher AQE than bare TiO_2 , and they display different action spectra profile.

The sample $1-Ni_{real}/TiO_2$ shows an action spectrum shape similar than absorption spectrum, while the action spectra of the other two samples $(1-PdNi/TiO_2)$ and $1-Pd/TiO_2$) show different profiles compared to their absorption spectra.

For the sample 1-PdNi/TiO₂, high AQE values were obtained using 320 and 355 nm irradiation wavelengths, being the optimum one 355 nm. The AQE value decreases considerably at wavelength ≥ 380 nm. A similar results was obtained with sample 1-Pd/TiO₂, however for this sample also a significant AQE at 380 nm was observed. The activity around 400 nm suggests that a large amount of Pd nanoparticles are deposited on the rutile phase, which has an absorption edge around 410 nm.



Figure 5.14: Absorption- and action spectra of modified samples. a) TiO₂, b) 1-PdNi/TiO₂, c) 1-Pd/TiO₂, and d) 1-Ni_{real}/TiO₂

5.3.3 DISCUSSION

The results show that modification of bare titania with metal NPs has an influence on its conventional light absorption, electronics properties, and photocatalytic activity. In photocatalysis, it is generally accepted that the generation of hydrogen depends of the efficiency of the deposited metal to trap electrons in order to avoid their recombination with the holes. However, our results show that titania by itself can absorb UV photons and generate a large amount of electrons available to carry out the photocatalytic process to generate hydrogen. However the amount of the hydrogen produced is negligible. An opposite effect was observed with the modified sample, which generated a larger amount of hydrogen than bare TiO_2 , even though the charge-carriers generated by the modified samples were less than those generated by bare TiO_2 . That point reveals that the two first steps of the process (photons absorption and charge-carriers separation) are proper to the photocatalytic process, while the third step (hydrogen production) involves a catalytic process where the metals NPs act as actives sites. This hypothesis is well supported by the integral analysis of the DRS, TRMC and action spectra results, where the absorption of photons, the generation of charge-carriers and the efficiency to produce hydrogen are respectively observed.

Also in photocatalysis, the efficiency of the metals for scavenging electrons is sensitive to the size of the metal NPs. Usually small size of metal NPs are desired to trap a large amount of electrons. But according our results, the effect of the cluster size does not seem to play a key role in the hydrogen production. The samples $1-NiPd/TiO_2$ and $1-Pd/TiO_2$, with small particles (<10 nm), were not the best photocatalysts to produce hydrogen. While, the sample $1-PdNi/TiO_2$ showed the highest activity, despite of large size of metal NPs (around 8 times larger).

Although, it has been demonstrated that electron trapping is beneficial for H_2 generation, our results show clearly that the ability of metal NPs to trap electrons is not their principal role. Our integral study provides evidence that the key role of metallic NPs is to act as good active site for the recombination of atomic hydrogen. For example, TRMC results of Ni/TiO₂ samples do not show to be a good electron scavengers, even so a considerable amount of H_2 was generated by these samples.

The samples containing mostly Pd show a good efficiency to trap electrons, even the sample 1-PdNi/TiO₂, which shows larger size of nanoparticles. However, it is well known that larger particles are less efficient in trapping electrons coming from the CB of the semiconductor. In order to explain such behavior, it is necessary to take into account the XPS results. The XPS results reveal the presence of Pd, PdO_x and PdO. For the samples rich in Pd, Pd NPs are assumed to in interaction with TiO₂ surface through the Pd-O bonds. Therefore, PdO_x species must be mainly located at the interface of Pd and TiO₂. The Pd atoms at the middle layers of the particles should mainly exist in the metallic state. Finally, PdO species are located as a thin layer covering the NPs. Then, the strong interaction between PdO_x and TiO₂ surface can be responsible in the photogenerated electrons scavenging. When the amount of Ni increases in the samples, the interaction between PdO_x and TiO_2 surface decreases, consequently the NPs become less efficient to scavenger the CB electrons. Our TRMC results support the latter explanation.

Although, the mount of electrons trapped by the samples rich in Ni is negligible, the generated hydrogen is considerable, proving again that metallic NPs act as recombination center of atomic hydrogen.

For bimetallic samples an appreciable improvement for hydrogen production was observed. The rate of hydrogen production for 1-PdNi/TiO₂ and 0.5-NiPd/TiO₂ photocatalyst is around 50% higher than the sum of the H₂ amount obtained with the their monometallic counterparts. This improvement can be attributed to a synergetic effect of the two metals acting as active sites. The difference in the efficiency of the latter samples (1-PdNi/TiO₂ and 0.5-NiPd/TiO₂) is because of PdO_x between TiO₂ surface and metallic Pd. The presence of PdO_x is beneficial for electron scavenging, in that way the recombination of electrons and holes on TiO₂ surface is avoided, as shown Figure 5.15. The above mentioned results and conclusions confirm that electron scavenging is beneficial to H₂ generation, but it is not the main role of the metallic NPs. The main role of metal NPs, according our results, is to recombine the atomic hydrogen. It means that metal NPs are catalytic sites.



Figure 5.15: Schematic representation of the mechanisms proposed to explain the role of metal NPs (Pd-Ni) in the photocatalytic H_2 generation. a) PdNi/TiO₂ and b) NiPd/TiO₂

5.3.4 CONCLUSION

Ni and/or Pd NPs were synthesized on P25 TiO_2 by radiolysis. The characterization of the samples show an extended absorption of spectra of titanium dioxide to the visible region. A remarkable difference in the size of the metal NPs was found as function of the metal ratio. Large size of NPs are obtained in bimetallic samples when Pd is the predominant metal. A partial oxidation of both Ni and Pd was observed.

The surface modification of TiO_2 with Pd and Ni NPs resulted in an increase of the photocatalytic activity for hydrogen production using a methanol-water solution under UV light. The highest production of hydrogen was obtained with the PdNi/TiO₂ photocatalyst, which was explained in terms of a synergetic effect induced by the presence on Pd^0 -PdO-PdO_x NPs and Ni⁰-NiO clusters on TiO₂, acting as recombination sites for atomic hydrogen conversion to molecular hydrogen.

CONCLUSIONS & PERSPECTIVES

* General conclusion

In this work, we have studied the effect of surface modification of titanium dioxide with ions or metal NPs on its photocatalytic activity.

The *adsorption of nickel* ions on titania had an effect on the absorption of light in the visible region. The kinetics of charge-carriers were not modified under excitation at 355 nm, but under visible light excitation (wavelengths 460-500 nm) free electrons in the CB of TiO₂ were detected by TRMC. TiO₂ modified with Ni²⁺ ions showed small improvement in phenol degradation kinetics either under visible or under UV irradiation.

The *deposition of metal nanoparticles* (mono and bimetallic NPs) on the TiO_2 was successfully performed by radiolysis method. The metal ions were reduced until the zero valence, however in the case of Ni and Pd NPs, they were sensitive to the contact with air, and partially oxidized.

The morphology of the metal NPs was spherical and the size varied with the deposited metal. The size of the gold NPs in the Au/TiO₂ system was around of 18 nm. In the sample Pd/TiO₂, the size of Pd NPs was around 7 nm. The Ni NPs on TiO₂ were quite difficult to observe by HRTEM, because of the close atomic number of Ni and Ti, and/or the small size of Ni clusters. The addition of a second metal had an impact on the size of the metal NPs. In case of the sample NiAu/TiO₂, the presence of nickel induced a reduction of the size of Au NPs. The size of gold NPs were < 9 nm.

The size of the Pd NPs in the sample NiPd/TiO₂ was sensitive to the ratio PdNi. Large aggregates of metal NPs were observed with an average size > 20 nm when the ratio PdNi=10. In contrast, small Pd NPs (<7 nm) were obtained with the ratio NiPd=0.1.

The *photocatalytic process* was influenced by the presence of metal NPs on titanium dioxide under UV irradiation, but this effect depends on different factors such as: metal, size, and morphology of the metal NPs. The first step of the photocatalytic process, e.i. the photo absorption, is slightly influenced at wavelength shorter than 380 nm by the presence of metal NPs. Although this effect is not obvious in the DRS characterization. When the study was complemented with TRMC results, it revealed that the presence of metal NPs induced lower light absorption by TiO_2 . However since the metal loading is low, this effect is small.

In the second step of the photocatalytic process, charge-carrier dynamics was influenced (or not) depending on the type of deposited metal:

- Nickel clusters did not influence the dynamics of the charge-carriers, and this was attributed to the oxidation of nickel clusters to NiO by air contact. Then, the electron injection from TiO₂ to NiO was not thermodynamically possible, as supported by TRMC results.
- 2. Gold NPs did not act as scavengers of the photoexcited electrons due to their large size (mean diameter of 18 nm). However, the lifetime of the free photoexcited electrons was longer in the presence of Au NPs. The long lifetime of the electrons was apparently explained by hole trapping as a consequence of the presence of Au NPs.
- 3. Palladium NPs scavenged the photogenerated electrons. This is due to the intermediate Pd oxidation (PdO_x) .
- 4. Ni-Au NPs also acted as electron scavengers, however since the observed segregation between Ni and Au, the electron scavenging was attributed mainly to Au because in those samples the size of Au NPs was smaller than in the metallic gold.
- For Ni-Pd system, the NPs ability to scavenge the electrons increases with the increasing of the Pd loading. An opposite effect is obtained with increasing the Ni loading.

The photoactivity of the modified samples were tested in the degradation of phenol under UV irradiation. No improvement was obtained even for the samples where electron scavenging by the metal NPs were observed. Then metal NPs were considered as an impurity on the TiO_2 surface. Titania was the only participant in the oxidation of phenol.

Contrarily, the generation of hydrogen was improved with metal NPs deposition. Bare TiO₂ was not efficient to produce hydrogen even if titania could absorb photons and generate the electron-hole pair as DRS and TRMC characterization respectively revealed. The production of hydrogen was promoted by adding small amounts of metals to TiO₂ surface, even with those metals (Ni and Au) which did not show any capacity to scavenge electrons from TiO₂ CB. Our results suggested that the hydrogen generation involved photocatalytic and catalytic processes. Photoexcited electrons and holes, induced by TiO₂ excitation, are responsible of the oxidation of alcohol/water and the reduction of protons, respectively. The atomic hydrogen is recombined on the surface of metal NPs. The amount of hydrogen generated depends on the efficiency of the metal NPs to recombine the atomic hydrogen. Bimetallic NPs (Ni-Au and Ni-Pd) on TiO₂ were much more active than the monometallic NPs, due to the synergetic effect obtained with two deposited metals on the surface of TiO₂. Bimetallic NPs become better recombination centers compared to their monometallic counterparts.

The modification of TiO_2 with metal NPs induces a strong influence in the photon absorption in the visible region. However the study of the charge carrier dynamics at wavelengths longer than 430 nm does not reveal separation of charge-carriers. Then, the absorption under visible light was considered a consequence of the incorporation of the optical transitions or the plasmon proper to metal NPs.

The samples containing gold $(Au/TiO_2 \text{ and } NiAu/TiO_2)$ presented photocatalytic response under visible light for the oxidation of phenol and 2-propanol. This was explained by the LSPR proper of gold NPs. Action spectra experiments showed that the oxidation of 2-propanol was photo-induced by the LSPR. No TRMC signal was detected when the samples were irradiated at the LSPR wavelengths of gold suggesting that there is no injection of electron from the gold NPs to TiO₂. Therefore we proposed that both reduction and oxidation reactions happen at the surface of gold NPs. The samples NiAu/TiO₂ were much more active than Au/TiO_2 . The samples Ni/TiO₂ did not show any activity under visible light, and considering the few amount of Au in the bimetallic samples, we propose a synergetic effect between Ni species and Au NPs leading to higher photocatalytic activity for degradation of phenol or 2-propanol.

Hydrogen was not generated under visible light ($\lambda > 450$ nm) because, at this wavelength, the electron-hole pair is not created in TiO₂.

Thus, the results of our integral study lead us to argue that the main role of the metal NPs in H_2 generation is to act as recombination center (promoter) of atomic hydrogen. This conclusion suggests a change in the focus, in which the goal is to identify better promoters instead of better scavengers. Bimetallic systems, mainly base on inexpensive metals such as Ni, have shown to be better promoters compared to the monometallic ones. Thus, the costs of the photocatalyst preparation are relatively low for future applications. These bimetallic NPs can also have applications in catalysis and electrocatalysis.

* Perspectives

The obtained results open lead to the following perspectives:

- 1. It is a great interest to continue to explore bimetallic systems mainly based on inexpensive metals such Co, Ni and Cu for photocatalysis, and mainly for H₂ generation. For example, a deep study of Co-Au, Cu-Au, Co-Cu and their single metal counterparts will be interesting to investigate, in order to know if in all those cases a synergetic effect is obtained and to try to understand origin of this synergetic effect. In particular, the system Cu-Au has already been studied in our group and a synergetic effect has been obtained for photocatalytic oxidation reactions and TRMC study has shown that Cu-Au nanoparticles scavenge electrons better that monometallic Au and Cu Hai *et al.* [2013]. It will be interesting to study the photocatalytic activity of this system for reduction reactions and H₂ generation.
- 2. The bimetallic NPs Ni-Au or Ni-Pd can be deposited on inorganic semiconductors with small a band gap in order to produce hydrogen using visible

light. Inorganic semiconductors can also be replaced by another materials able to split the water molecule and to reduce the protons to atomic hydrogen, for example a conducting polymer. Indeed, our research group has shown that conjugated polymer nanostructures are a new class of photocatalysts very active under visible light Ghosh *et al.* [2015].

3. In this work, it was demonstrated that the gold plasmon plays an important role in the oxidation of 2-propanol under visible light. The photocatalytic activity increase considerably with the presence of a transition metal. A deep study is suggested in order to understand how the transition metal affects the gold plasmon leading to higher photocatalytic activity.

ANNEXES

DETERMINATION OF H₂ MEASURED BY GC

* Pressure Correction

The head space of the reactor (Figure) is important in quantification of hydrogen generated.

The correction is calculated using the following equation:

$$x = \frac{A \cdot a \cdot Z}{[y - (22.4\frac{298}{275} \cdot 1000 \cdot A \cdot a)]}$$
(5.1)

were:

 \boldsymbol{x} is the amount of H₂ [mol]

A is the are obtained by GC measured

 \boldsymbol{a} is the slope from GC calibration curve the value for the used GC was 4.67 x 10^{-12}

 \boldsymbol{Z} head space [mL]

 \boldsymbol{y} sample injected [mL]

The temperature at which measurements were made 25 $^{\circ}\mathrm{C}$

* Apparent quantum efficiency (AQE

$$AQE = \left(\frac{reaction \ rate}{light \ flux}\right) \cdot 100 \tag{5.2}$$

* Reaction rate (r) $[mol \cdot s^{-1}]$ this take into account the rates of e⁻ and h⁺ consumption by the number of reaction electron in H₂ evolution, and is calculated as follow:

$$r = \frac{n \cdot reaction \ rate}{3600} \tag{5.3}$$

n=2 reaction electron number for H_2 evolution (methanol decomposition)

* Light flux $[mol \cdot s^{-1}]$

$$Light \ flux = \frac{Intensity}{Energy \ of \ 1 \ mol \ photon}$$
(5.4)

where

Light intensity $[J \cdot s^{-1}]$ this is measured directly in the lamp Energy of 1 mol photon(\mathbf{E}') $[J \cdot mol^{-1}]$

$$E' = 6.022 \times 10^{23} \cdot \left[\frac{6.63 \times 10^{-34} \cdot 3 \times 10^8}{\lambda \times 10^{-9}}\right]$$
(5.5)

Determination of H_2 measured by MS

To quantify the amount of hydrogen generated during the photoreaction by MS it was necessary to calibrated the equipment. For that different amount of a gases mix (hydrogen, oxygen, nitrogen) was injected to the system. In each injection the amount of H_2 (ppm) was known. The graphic obtain is show in Figure 5.16. The average of the constant signal (red circle) values were calculated. After using those values the linear calibration graph was generated, see Figure 5.17



Figure 5.16: MS signal for generated H_2 calibration curve. To obtain this graph different amount of mix gases with a determinate amount of H_2 was injected to MS equipment.

The signals recover during the photocatalytic test can been converted to partial fraction (Figure 5.18) using the liner equation from the calibration curve.

The amount of hydrogen (n_{H_2}) is calculated using the following equation:

$$x_{ppm} = \frac{n_{H_2}}{n_{total}} \tag{5.6}$$

where

 x_{ppm} is the fraction times $1E^{-}6$



Figure 5.17: Calibration curve of H_2 . A linear regration was fitted

 n_{total} is the total moles of the different gases inside of the reactor. It can be calculated using the ideal gas law at standard conditions. The volume in the head space of the reactor was 130 mL.



Figure 5.18: The signals recover during the photocatalytic test and converted to partial fraction.

FRICKE DOSIMETRY

 60 Co-rays, photons with energies of 1.17 and 1.33 MeV (1 eV = $1.6 \mathrm{x} 10^{-19} \mathrm{J})$

The reaction involved in the Fricke dosimeter is the radiation-induced oxidation of ferrous ion to ferric ion (Fe²⁺ \rightarrow Fe³⁺) at low pH and in the presence of oxygen. The standard dosimeter solution contains 10⁻³ M ferrous sulfate or ferrous ammonium sulfate, 10⁻³ M NaCl in 0,4 M of H₂SO₄ (pH 0,46) and is saturated with air.

Water radiolysis

$$H_2O \to H^{\bullet}, OH^{\bullet}, e_{ag}^-, H_3O^+, H_2O_2, HO_2^-, OH$$
 (5.7)

$$H_2O \to H^{\bullet}, OH^{\bullet}, e_{aq}^-, H_3O^+, H_2O_2, HO_2^-, OH$$
 (5.8)

In presence of Fe^{2+} and oxygen

$$Fe^{2+} + H_2O_2 \to Fe^{3+} + OH^{\bullet} OH$$
 (5.9)

$$Fe^{2+} + \bullet OH \to Fe^{3+} + - OH \tag{5.10}$$

and

$$H^{\bullet} + O_2 \to HO_2^- \tag{5.11}$$

$$Fe^{2+} + HO_2^- \to Fe^{3+} + H_2O_2$$
 (5.12)

Acid medium (H_2SO_4) is used to scavenge the eaq- and to follow the hydroxyl radical presence by the oxidation of ferrous ion.

The yield of Fe^{3+} is:

$$G(Fe^{3+}) = 2G(H_2O_2) + G(^{\bullet}OH) + 3G(H^{\bullet}) = 15.6(ions/100eV)$$
(5.13)

$$G(Fe^{3+}) = 15.6/9.65 \times 10^6 = 1.62 \times 10^{-6} \text{ mol.} J^{-1}$$

The number of formed ions per cm3 in the irradiation conditions is: n= G x ($\Delta E/100$) with G[=] ion/100 eV and E[=] eV/cm3 where the moles of the formed ions per litter (or kg) is:

C= G x ΔE with G[=] mol.J⁻¹ and E[=] J.kg⁻¹ [=] Gy

Thus, we measure the formed Fe^{3+} concentration by absorption spectrophotometry. We measure the DO from the irradiated solutions at 304 nm (maximum Fe^{3+} absorption).

$$DO = E \times l \times C \tag{5.14}$$

where E=2204 L· mol⁻¹· cm⁻¹, l = 1 cm and C= molar concentration [mol.L⁻¹] The radiation dose can be found by:

$$D = \Delta E = \frac{DO}{E \cdot l} \frac{1}{G} = [Gy] \tag{5.15}$$

And the dose rate $(d = \frac{D}{t})$ as follow

$$d = \frac{DO}{E \cdot l \cdot G \cdot t} = \left[\frac{Gy}{h}\right] \tag{5.16}$$

$$d = \frac{1}{2204 \cdot 1 \cdot 1.62E^{-6}} \frac{DO}{t} \tag{5.17}$$

$$d = \frac{280 \times DO}{t} = \left[\frac{Gy}{h}\right] \tag{5.18}$$

Table 5.2: Fricke solution		
Concentration	Substance	
$10^{-3} {\rm M}$	Fe ²⁺ , Mohr salt: $Fe(NH_4)_2(SO_4)_2(H_20)_6$	
0.4 M	H_2SO_4	
$10^{-3} \mathrm{M}$	NaCl	

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Titre: Synthèse et caractérisation de nouveaux photocatalyseurs modifiés pour des applications environnementales et énergétiques

Mots clés : Photocatalyse, Action spectra, TRMC, Radiolyse, Ni-Au/TiO₂

Sciences chimiques : molécules,

matériaux, instrumentation

Résumé : Notre travail présente la modification du TiO₂ commercial P25 par des NPs mono- et bimétalliques (Ni, Au, Ni-Au, Pd et Ni-Pd), leur caractérisation et leur évaluation photocatalytique. Cette étude complète relie les trois étapes principales du procédé photocatalytique: (1) l'absorption de la lumière (génération des paires électron-trou), (2) la dynamique des porteurs de charge et (3) l'efficacité photocatalytique. Les NPs métalliques ont été synthétisées directement sur la surface de TiO₂ par rayonnement gamma. La caractérisation exhaustive a été faite par Microscopie Electronique à (MET-HR). Transmission Haute Résolution Diffraction des Rayons X (DRX), Analyse Dispersive en Energie de RX (EDS), Spectrométrie Photoélectronique X (XPS), Spectroscopie UV-vis en Réflexion Diffuse (DRS) et Time Resolved Microwave Conductivity (TRMC). Les échantillons ont été testés, sous illumination UV-Visible poly et monochromatique (Action Spectra),

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par les réactions photocatalytiques suivantes: (1) dégradation du phénol et du 2-propanol, (2) production d'hydrogène et (3) oxydation et réduction du Pb^{2+} .

Les résultats montrent que les systèmes bimétalliques sont plus actifs que leurs homologues monométalliques respectifs. Nos résultats nous conduisent à affirmer que le rôle principal des NPs métalliques est, dans le cas de la production d'hydrogène photocatalytique, sur l'aspect catalytique. Cette étude ne rejette pas les arguments classiques des NPs métalliques agissant comme piégeurs d'électrons, mais montre que ce n'est pas leur rôle principal. Les échantillons Au/TiO2 et Ni-Au/TiO₂ ont montré une activité photocatalytique dans la dégradation des composés organiques sous illumination visible. Ceci a été expliqué par l'effet plasmonique des NPs d'Au.

Title: Synthesis and characterization of new modified photocatalysts for environmental and energy applications.

Keywords : Photocatalysis, Action spectra, TRMC, Radiolysis, Ni-Au/TiO₂

Abstract : Our study presents the modification of TiO₂ P25 with mono- and bimetallic NPs (Ni, Au, Ni-Au, Pd and Ni-Pd), their characterization and their photocatalytic evaluation. Our integral study links the three main step of the photocatalytic process: (1) absorption of light (generation of electron-hole pair), (2) dynamics of charge-carriers and (3) efficiency of the photocatalytic activity. The metal NPs were synthetized, directly on the surface of TiO₂, by gamma radiation. The exhaustive characterization was done through High Resolution Transmission Microscopy (HRTEM), X-ray diffraction (XRD), Energy-Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron (XPS), and UV-vis Spectroscopy Diffuse Reflectance Spectroscopy (DRS) and Time Resolved Microwave Conductivity (TRMC). The samples were tested using UV and visible polychromatic and monochromatic (action spectra)

light in the following photocatalytic reactions: (1) phenol and 2- propanol degradation, (2) hydrogen production and (3) Pb^{2+} oxidation and reduction. The results show that bimetallic systems are more active that their respective counterparts. Our results lead us to argue that the main role of the metal NPs is, in photocatalytic hydrogen generation, acting as catalytic site. This study does not reject the typical arguments that the metal NPs act as a scavenger of

electrons, however our integral study shows that it is not the main role of the metal NPs. The Au/TiO_2 and Ni-Au/TiO₂ samples showed photoactivity in the organic compound degradation under visible light. It was attributed to the plasmon effect, which is characteristic of gold NPs.