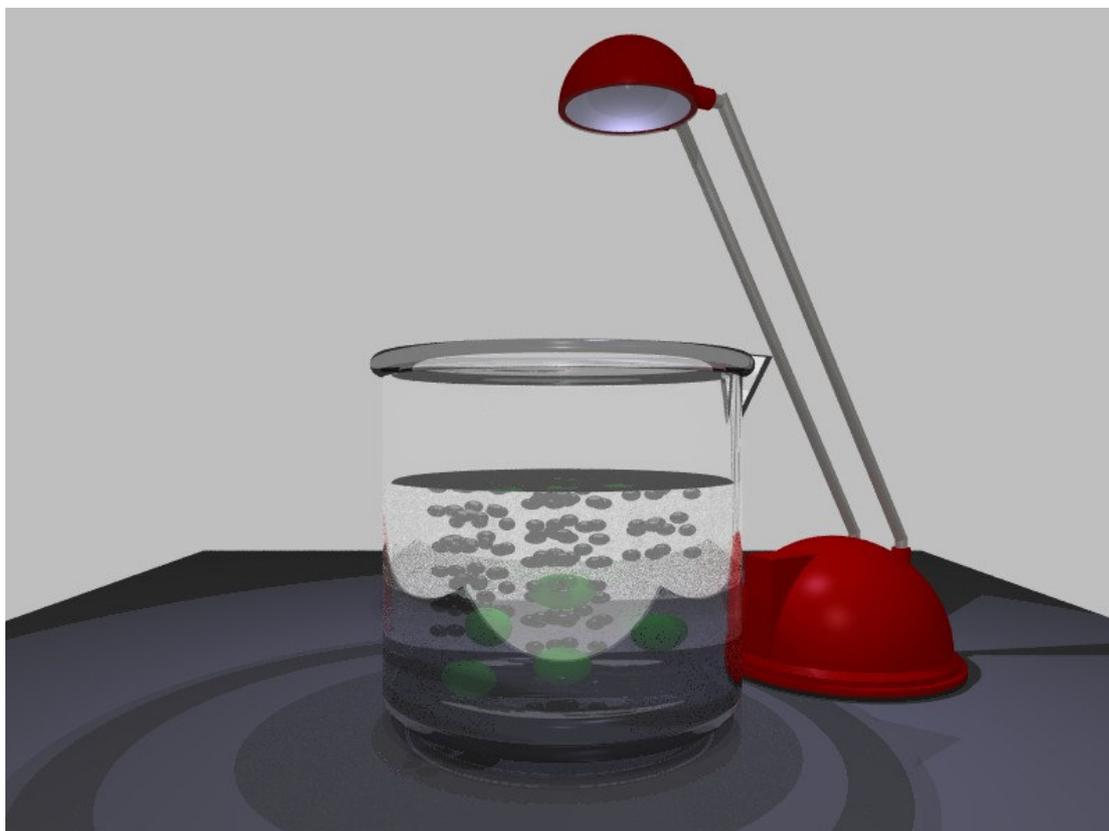


Fundamentals of Photocatalytic Water Splitting by Visible Light



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21st March 2004

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Preface

During the last years the main goal of research on photocatalysis was to find the best photocatalyst. This was pursued by trial and error methods. In order to get a more structured view of photocatalysis, fundamental knowledge in quantummechanics is needed. Also the mechanism for the splitting of water needs to be obtained. Therefore we tried to develop the basic understanding of these subjects and to combine them for engineering a suitable photocatalyst.

Table of Contents

<i>Preface</i>	2
<i>Table of Contents</i>	3
1 Introduction	4
2 The bandgap of solid materials	6
2.1 The primary effect; electronegativity	6
2.2 The secondary effect: bonding	7
2.2.1 Band structures	7
2.2.2 Bonding situation in pure semiconductors	8
2.2.3 Bonding situation in chalcogenoids	8
3 Trends in current research	11
3.1 The bonding situation in titaniumdioxide (TiO₂)	11
3.2 Explanation of several catalysts	12
4 Mechanistic Understanding	14
4.1 Introduction	14
4.2 Dissociative adsorption of water	14
4.2.1 Adsorption of one water molecule on TiO ₂ (110)-surface	14
4.2.2 Multilayer adsorption of water	15
4.3 The use of co-catalysts	15
4.3.1 Platinum	15
4.3.2 Nickel(II)oxide (NiO)	16
5 Properties of a good photocatalyst	18
6 Conclusions	19
7 Recommendations	20
8 Acknowledgements	21
9 Literature	22

1 Introduction

Recently, the community is considering evolution from an oil-based economy to a hydrogen-based economy due to the limitation of the earth's reserve of fossil fuels. The current way to produce hydrogen is still via fossil fuels. The main production route treats carbon (charcoal) with steam to produce synthetic gas. Carbon dioxide is produced as by-product through this route. To overcome this problem water can be dissected into hydrogen and oxygen. The production of one hydrogen molecule costs 2.43 eV^1 , which is too high to be generated by heating water. Another energy source that can be used is electricity, but a disadvantage is that the energy costs are very high. A cheap alternative on the other hand is sunlight. At this point photocatalysis can play an important role. The definition of photocatalysis is: A change in the rate of chemical reactions or their generation under the action of light in the presence of substances -called photocatalysts- that absorb light quanta and are involved in the chemical transformations of the reaction participants.²

The definition of a photocatalyst is: A substance that is able to produce, by absorption of light quanta, chemical transformations of the reaction participants, repeatedly coming with them into the intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions.²

The use of photocatalysis is shown in the pictures below:

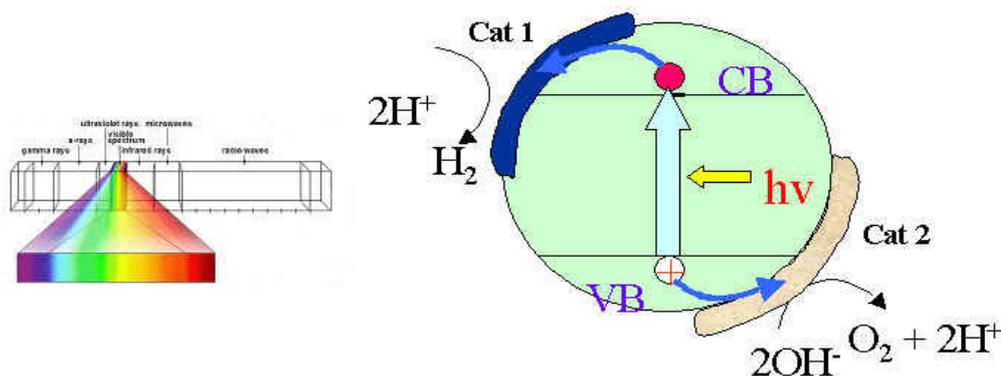


Figure 1.1: The conversion of a photon into an electron-hole pair with a photocatalyst. This electron hole pair can be used for redox reactions like the splitting of water..¹

The photocatalyst uses a photon to excite an electron from the valence band to the conduction band: resulting in an excited state. The two protons, which are needed to generate hydrogen gas, can use the electrons that are excited in the photocatalyst. The hole in the valence band can be filled with an electron produced by the oxygen generation. Additional catalysts can catalyse the two half-reactions. A requirement for the photo-catalyst is to have a bandgap higher than 2.43 eV , which is the energy needed for the splitting of water.

The goal is to split water into hydrogen and oxygen by the use of redox-reaction. Cat 1 facilitates hydrogen generation and cat 2 the oxygen creation. To enhance the speed of the reaction two things must happen. First, the association of protons needs to be quick and second, the electron generation needs to be high. The latter could be achieved by reducing the bandgap to a wavelength where the intensity in sunlight is very high.¹

A lot of research has been done to create a photocatalyst with an optimal bandgap, but little is done on the fundamental understanding of bandgap engineering and the mechanism. This report shows more insight into the problem of photocatalysis and can be seen as a preliminary study to a more fundamental approach towards photocatalysts.

The report is structured as follows: Section 2 describes the insight in the bandgap of materials. Section 3 discusses the current trends in research. Section 4 considers the mechanistic understanding of water adsorption on a TiO₂ rutile 110-surface. Section 5 discusses the properties for an optimal photocatalyst. Section 6 states the conclusion.

2 The bandgap of solid materials

In the introduction was stated that the bandgap of a material decides whether it can function as a photo-catalyst or not. To understand the bandgap in these materials, it is necessary to get a better understanding of the nature of this bandgap and thus the nature of the chemical bonding situation in these materials.

Bonding occurs because of overlap between the atomic orbitals present in the crystal structure. This process leads to several molecular orbitals that are grouped in bands. The bands that are filled with electrons are called the valence band and the empty bands are named conduction band. The energy difference between the conduction band and the valence band is called the bandgap.³

If the valence band cannot be completely filled with electrons, no bandgap will be present and the material is called a metal. If the valence band is completely filled with electrons and the bandgap lies between 0 and 5 eV, it will be called a semiconductor. A material with a bandgap higher than 5 eV is called an insulator. A closer look at the energy level reveals that for the splitting of water a semiconductor is needed as photo-catalyst. The next step is to change the bandgap of a material. Roughly two effects contribute to the width of the bandgap:^{3,4}

1. The primary effect; electronegativity
2. The secondary effect; bonding situation.

2.1 The primary effect; electronegativity

This primary effect contributes more to the width of the bandgap than the secondary effect. An ionic material consists of cations and anions. This means that in an inorganic material the bonding between the atoms is caused by a charge-separated state on which the valence electrons are located on the more electronegative ion. The reason for this localisation is that the more electronegative atom needs electrons to fulfil the octet rule, therefore stabilizing the negative charge at this ion. This also means that electrons are more stabilised by a more electronegative atom. In short, fluorine stabilises the electrons more than oxygen and oxygen more than nitrogen. The same explanation can be given for cations, leading to more stabilisation of the holes by yttrium than calcium and calcium more than sodium. This effect is shown in figure 2.1.^{4,5}

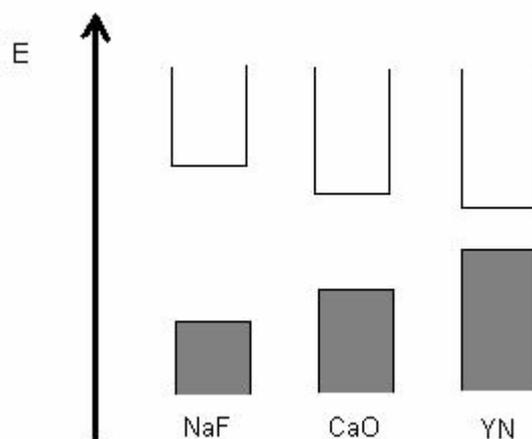


Figure 2.1: The distance between filled and empty bands will increase with increasing electronegativity

2.2 The secondary effect: bonding

The secondary effect is mainly the overlap between several atomic orbitals and the filling of the resulting bands with electrons. The secondary effect determines, whether a material is a metal, semiconductor or an insulator. Before discussing the actual bonding situation, first the creation of bands according to the most common quantum mechanical theories will be described. Then, there will be a closer look at the bonding situation in semiconductors.³

2.2.1 Band structures

In contrast to chemistry of single molecules where a discrete level of orbitals is present, solid state chemistry gives rise to band structures. The reason is that, in solid-state chemistry, also nearest neighbour interactions, next-nearest neighbour interactions, and so forth, have to be taken into account. Quantum mechanically this leads to nearly inseparable discrete energy levels, which is shown in figure 2.2. Each energy level can be filled with two electrons according to Hund's rule. The fact that bands are constructed by discrete energy levels will be neglected in the remainder of this report.³

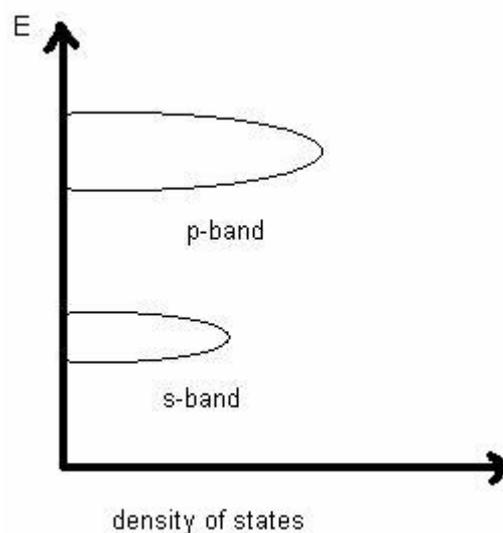


Figure 2.2: Instead of molecular orbitals bands will be formed in a crystal structure³

The bands are created by overlap of several atomic orbitals, but which atomic orbitals of the atoms contribute to the bands? Only the valence shell of the atoms plays an essential role in bonding, as for every bonding situation. Because the semiconductors lie in the range needed for a photo-catalyst, these are the most important and therefore only the bonding situations for semiconductors will be discussed. There are two kinds of semiconductors: Pure solids, like silicium or germanium and chalcogenoids, which are for example metaloxides, metalsulfides and metalfluorides.³

2.2.2 Bonding situation in pure semiconductors

The main materials used as pure semiconductors are located in group 13 and 14 of the periodic table. The bandgap of these materials are less influenced by the primary effect discussed in chapter 2.1. The bandgap of these materials are mostly influenced by the following factors:

- Configuration in the crystal lattice
- Amount of electrons in the valance shell
- Hybridisation of the orbitals

This report focuses on the last two effects. The first can be seen as the influence the crystal structure has on the conductive properties. This effect is difficult to predict and will not be discussed further. The second effect is quite trivial. If more electrons are present, more orbitals will be filled. The third is less trivial. In molecular chemistry the bonding orbitals are lowered in energy due to hybridisation of the s- and p-orbitals to sp^3 -orbitals. This is also the case for the pure semiconductors, but there is a slight difference, namely they have d-orbitals. If the energy of the s-, p- and d-orbitals are close together, hybridisation can occur resulting in nine lower lying sp^3d^5 -orbitals, shown in figure 2.3.³

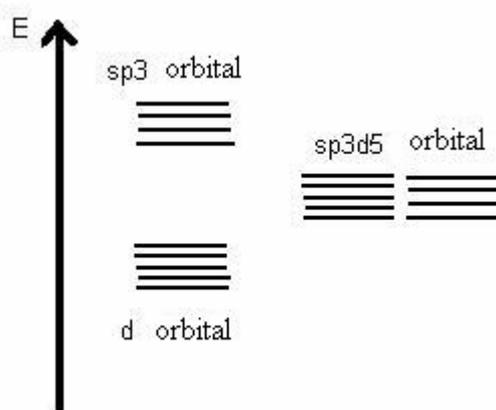


Figure 2.3: Hybridisation between sp^3 orbitals and d orbitals will lower the valence band and increase the bandgap³

This hybridisation leads to a lower lying valence band and thus to a larger bandgap. Semiconduction can be obtained by doping the material with atoms that have either more or less valence electrons.³

2.2.3 Bonding situation in chalcogenoids

Because the chalcogenoids consist of a metal with a heteroatom, the bonding situation is more difficult than in pure semiconductors. First of all, due to a combination of more than one element, the primary effect plays a role. Second, there is ligand field splitting, because transition metals are mainly used in this class of semiconductors. The last effect is due to aggregation of the crystal, like Rb_9O_2 . The valence electrons can be delocalised, which will lead to a conducting material. Some examples of transition metal oxides of the third row in the periodic table are shown in table 2.1.³

Table 2.1: Examples of transition metal oxides³

Compound	Structure	Stoichiometrics (x)	Electrical Properties
CaO _x	Rock salt	1	Isolator
TiO _x	Rock salt	0.65-1.25	Metal
VO _x	Rock salt	0.79-1.29	Metal
MnO _x	Rock salt	1-1.15	Semiconductor
FeO _x	Rock salt	1.04-1.17	Semiconductor
CoO _x	Rock salt	1-1.01	Semiconductor
NiO _x	Rock salt	1-1.001	Semiconductor
CuO _x	PtS	1	Semiconductor
ZnO _x	Wurzite	Light Zn excess	Wide gap n-type Semiconductor

The striking result is that TiO and VO are metallic conductors. The explanation for this is that the resulting d-band is only partly filled due to lack of electrons on the vanadium and titanium atoms. An example for the bonding situation of these third row oxides is shown in figure 2.4.

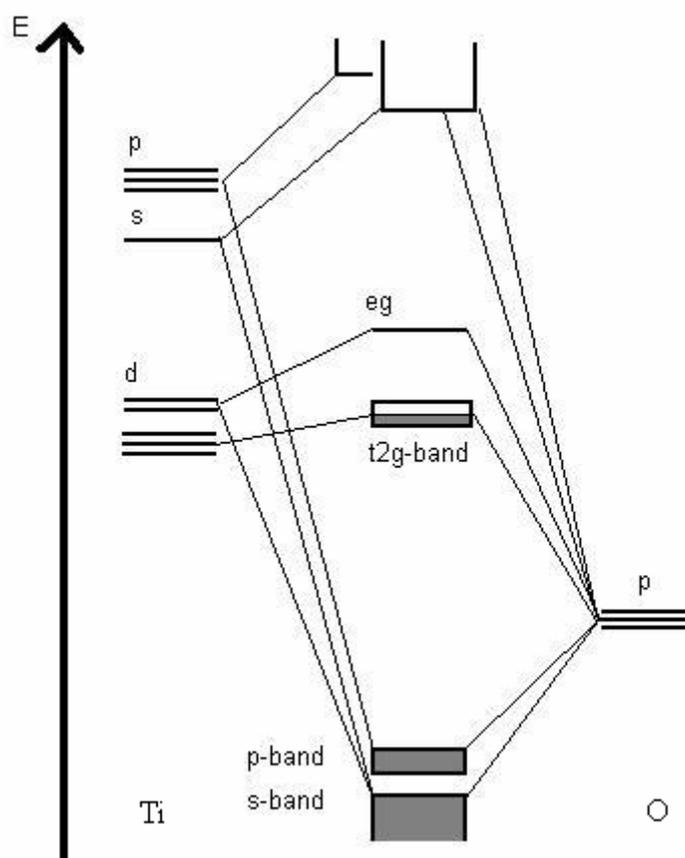


Figure 2.4: In the band structure for TiO a partially filled t_{2g} band can be seen. This gives TiO its metallic properties.³

The t_{2g}-band mainly belongs to the metal because the energy level of this band corresponds more to the metal than the oxygen. This means that the lack of electrons in this band results from a lack of d-electrons at the metal. The only difference in bonding comes from the difference in amount of electrons in the valence shell of the metal. This means that the t_{2g}-band is filled with electrons when one goes from titanium towards nickel.

Conduction in these crystals proceeds via a hopping mechanism. The speed of conduction is related to the perfection of the lattice. More imperfections lead towards a lower conduction rate.³

3 Trends in current research

The emphasis in current research lies more on developing a good photo-catalyst than understanding it. The papers contain a lot of data obtained by screening a wide range of catalysts. To obtain more insight into designing a photocatalyst with an optimal bandgap and good mechanistic properties, one should analyse and understand the materials already available. This section focuses on the understanding how the bandgap can be engineered. First, the photocatalyst that is most examined, TiO_2 , is discussed in greater detail. Other catalysts are analysed, with the information obtained from TiO_2 .

3.1 The bonding situation in titaniumdioxide (TiO_2)

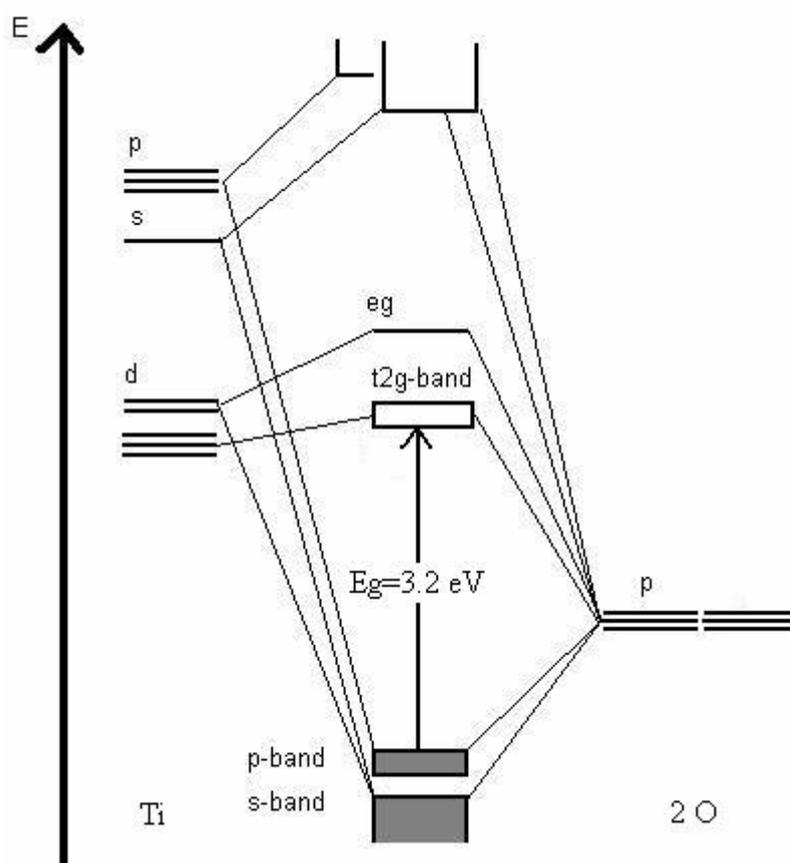


Figure 2.5: The empty t2g and completely filled p-band of TiO_2 makes it a semi-conductor with a bandgap of 3.2 eV. This is in the ultraviolet region.

The titanium has no electrons in its valence shell when it is in the oxidation state of +4, resulting in an empty t2g-band. The bandgap is the gap between the filled p-band (valence band) and the empty t2g-band (conduction band). This molecular orbital diagram can be seen as a standard for transition metals.

3.2 Explanation of several catalysts

Some catalysts will be analysed with the aid of the previous chapters. This analysis leads to several tricks that can be applied to engineer the bandgap.

As shown in figure 3.1 the use of additional metals can lower the bandgap of the initial compound. Bismuth is used as a so-called co-metal. The $6s^2$ -orbitals of bismuth lie higher in energy than the p-band of the oxygen. This can be visualised by putting some extra layers on top of the valence band and will only happen if the orbitals from the co-metal correspond to the p-band of the oxygen.

The bandgap for BiTaO_4 is larger than BiNbO_4 because tantalum has a higher atomic number and thus a higher valence shell, 5d vs. 4d, than niobium.⁶

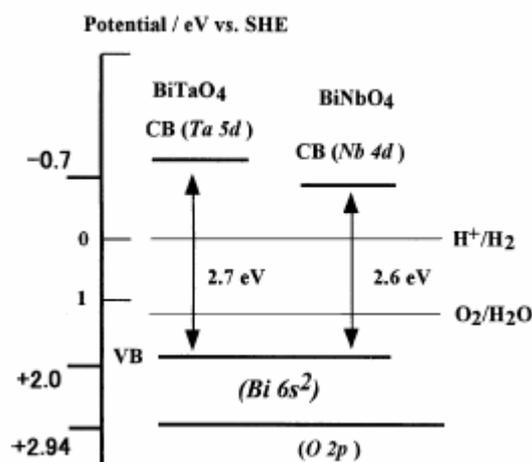


Figure 3.1: The bandgap changes because the filled $6s^2$ band of Bismuth lies on top of the $2p$ band of oxygen. This way the bandgap can be decreased.⁶

A second trend is shown in figure 3.2. Two parameters are shown in this figure. The first is an addition of a co-metal, Indium, and the second is a shift down the fourth column of the periodic table.⁷

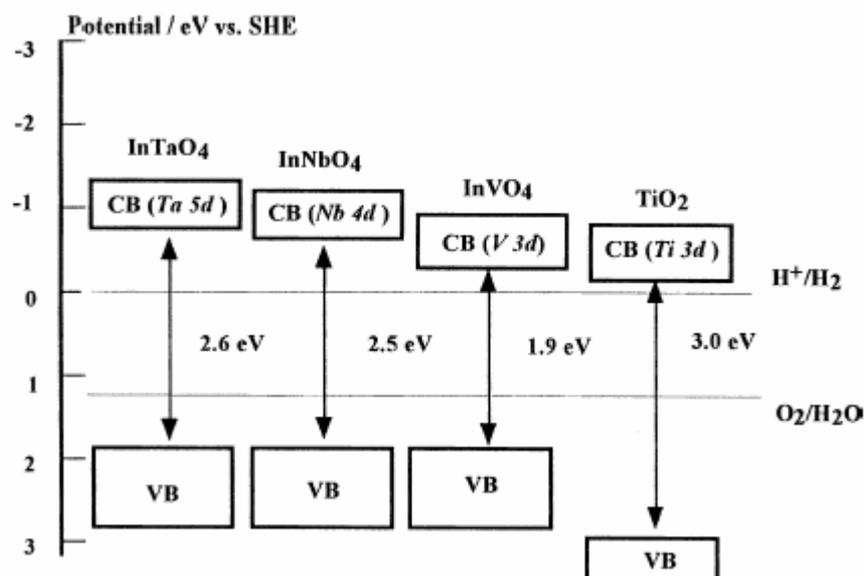


Figure 3.2: The change in bandgap can be in the valence band as well as the conduction band by replacing or adding different metals.⁷

The molecular orbital scheme shown in the previous section for TiO₂ can also be applied to V₂O₅ (V⁵⁺ cation). For this compound the conduction band is constructed from 3d-orbitals of the metal and the valence band from the p-orbitals of oxygen. The only difference is a consequence of the higher lying d-orbitals in vanadium.

Going from V₂O₅ to InVO₄ the crystal structure changes. In this latter two lattices are present, namely the octahedral InO₆ and the tetrahedral VO₄.⁷ The molecular orbital diagram of InVO₄ can thus be seen as a summation of the two separate diagrams. In the molecular orbital diagram the valence band of InO₆ lies higher than the valence band of the VO₄, meaning that if summation occurs, the resulting valence band of InVO₄ will be higher than the one of V₂O₅. The second trend is the shift down the fourth column of the periodic table. The explanation is quite trivial. The 5d-orbital lies higher in energy than the 3d-orbital. Therefore the conduction band becomes higher in energy and the bandgap larger.

A last example deals with the addition of Yttrium and rare earth metals, shown in table 3.1.⁸

Table 3.1: Comparison of bandgaps of several bismuth modified photocatalysts⁸

photocatalyst	type of structure	band gap eV
Bi ₂ RNbO ₇		
R = Y	pyrochlore	2.03
R = Ce	pyrochlore	2.10
R = Gd	pyrochlore	2.13
R = Sm	pyrochlore	2.21
R = Nd	pyrochlore	2.25
R = Pr	pyrochlore	2.26
R = La	pyrochlore	2.38
TiO ₂ (P25)	anatase+rutile	3.22

As concluded earlier, bismuth gives a lower bandgap for niobium oxide because the 6s² raises the valence band in energy. Because the metals are from the d and f block the conduction band is altered and the valence band remains the same. The addition of Yttrium lowers the conduction band the most, probably due to the lower position of the 4d-orbitals with respect to the 4f-orbitals. A closer look at the table reveals that addition of the first element in the f-block, Lanthanum, results in the highest bandgap. The reason is that Lanthanum has an empty f-block and empty orbitals have a higher energy than orbitals that are filled, resulting in a higher bandgap. This effect also explains why cerium gives the lowest bandgap. But for the remaining compounds this reasoning contradicts the trend observed.

The difference between praseodymium and cerium can be seen as a summation of two effects. The first effect is increased attraction that is due to more protons in the praseodymium nucleus than in the cerium nucleus. Therefore the electrons of praseodymium feel a more positive charge. But this effect is not enough to account for the energy increase due to electrostatic repulsion between the electrons. After summation of the two, the net result is a higher conduction band for the praseodymium.

The previous reasons also explain the bandgap effect seen in the compounds with neodymium, samarium and gadolinium respectively. Here the attractive effect from the nucleus becomes higher, because neodymium, samarium and gadolinium have more protons in their nucleus. The effect of the electron-electron repulsion is lower than this attraction because the electrons cannot get into the orbital otherwise.

4 Mechanistic Understanding

4.1 Introduction

To create a good catalyst with high photo-catalytic activity a well-designed bandgap is not the only criterion. Another is the understanding of the reaction that takes place. Several questions come to mind:

- How does water adsorb on the catalyst?
- How does water dissociate?
- Is the use of co-catalysts necessary?
- How does this co-catalyst work?
- Where are the electrons and holes generated?
- How does the electron flow proceed from catalyst to reagents?
- Where are the gasses generated?

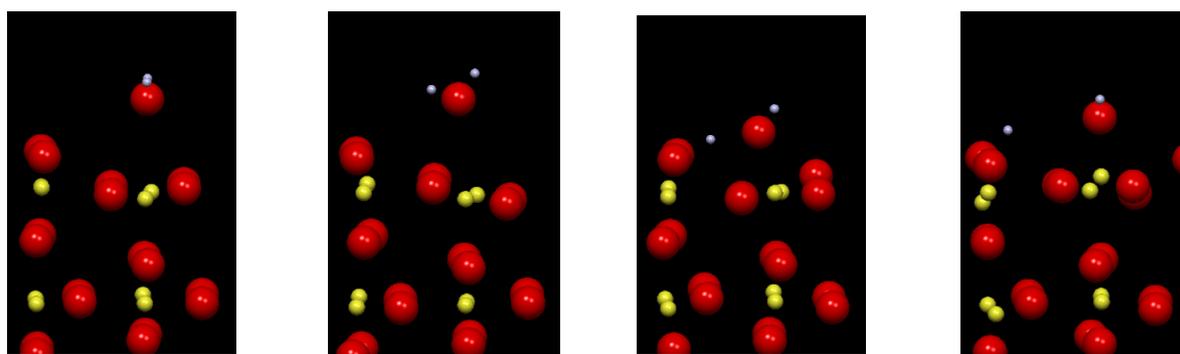
These questions will be discussed in the following sections.

4.2 Dissociative adsorption of water

The adsorption of water on TiO_2 (110) surface is first explained for adsorption of one molecule and then for multilayer adsorption.

4.2.1 Adsorption of one water molecule on TiO_2 (110)-surface

P.J.D. Lindan's group has done a lot of research on the prediction of adsorption of water. This group is able to calculate the adsorption of water onto a TiO_2 (110)-surface. These studies show that water partially adsorbs dissociatively onto the surface.¹⁰ First results show that two surface sites play an important role in the adsorption process, namely the five-fold coordinated titanium site and the bridging oxygen site. The process is given below in figure 4.1.⁹



In figure 4.1a the oxygen of a water molecule is pulled towards the five-fold coordinated titanium site. This effect continues in figure 4.1b, but now the hydrogen is directed to the bridging oxygen via hydrogen bonding. This hydrogen bonding becomes increasingly stronger and eventually results in complete heterolytic dissociation of the water molecule into a hydroxyl anion and a proton, that coordinates to the the bridging oxygen, figure 4.1c. The resulting hydroxyl anion coordinates to the titanium, but is still connected to the lost proton

due to hydrogen bonding. This leads to an equilibrated state between the proton on the bridging oxygen and the hydroxyl anion on the titanium, figure 4.1d.⁹ The formation of the hydrogen bond between the oxygen atom that is adsorbed onto the titanium and the proton on the bridging oxygen, provides the stability of the dissociative adsorption.¹⁰ This equilibrium will be shifted towards more dissociative water adsorption, if the hydrogen bond is reduced in strength, for example by increasing the distance. Replacing the titanium with a larger atom, such as tin, can give the desired result and leads to more dissociatively adsorbed water.¹¹

4.2.2 Multilayer adsorption of water

From the studies of Lindan's group, it is clear that about a quarter of a monolayer water dissociates on the surface. The remaining water is physisorbed. The fact that only a portion of the water dissociates is not completely clear to us. A possible explanation is that an optimisation can occur between the broken water bonds and the created hydrogen bonds of the bridging hydroxyl and the other water molecules.⁹

At monolayer coverage dissociated water molecules are still present, therefore proton conduction can occur.¹² This means that the protons are not located on an exact location at the surface but are delocalised. This makes production of hydrogen gas troublesome. Because the chance that two protons and two electrons will combine is larger if the protons are localised on the surface. This can be done by using co-catalysts.

4.3 The use of co-catalysts

As explained in the foregoing section the use of co-catalysts is necessary to localise the protons for the formation of hydrogen gas. This section will deal with two co-catalysts. First we take a closer look at platinum¹³, second we will focus on nickel(II)oxide.^{14, 15}

4.3.1 Platinum

Platinum is mainly used as a catalyst for the hydrogenation of alkenes and other double or triple bonds. The main reason to use platinum for these reactions is that hydrogen binds easily to its surface. If platinum is coated onto the surface of the photocatalyst, the protons will transfer to the platinum surface via proton conduction. If this happens, a second problem will arise; how will the electrons be transferred to the platinum surface to facilitate the reactions of the protons to hydrogen gas?

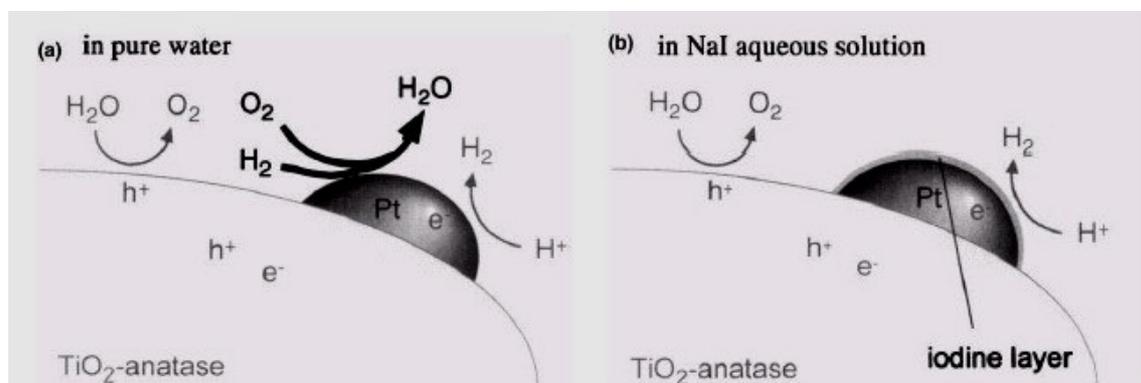


Figure 4.2: A platinum co-catalyst also catalyses the reverse reaction. This can be prevented by adding an iodine layer on the platinum surface¹³

Platinum is a metal and the property of a metal is that it can conduct electrons. This means that the electrons generated in the photocatalyst are transferred to the surface via conduction through the platinum.

Platinum catalyses the forgoing and reverse reaction. This means if hydrogen is produced it will immediately react with oxygen to water. This problem can be solved by adding iodine to the reaction mixture. The iodine forms a layer on the platinum surface and prevents the production of water on the platinum surface. On the other hand, hydrogen gas can still be produced. The necessary electrons are transferred via tunnelling through the iodine layer, as seen in figure 4.2.¹³

4.3.2 Nickel(II)oxide (NiO)

In literature it is stated that water splitting is enhanced by the addition of nickeloxide onto the surface. They prove that hydrogen gas is formed on the nickeloxide surface and the oxygen is released from the photocatalyst surface. The reason why nickeloxide provides higher hydrogen evolution is not clear. Domen et al. give two suggestions for electron conduction within the catalyst.

1. One-photon scheme
2. Two-photon scheme

The two mechanisms are shown in figure 4.3.¹⁵

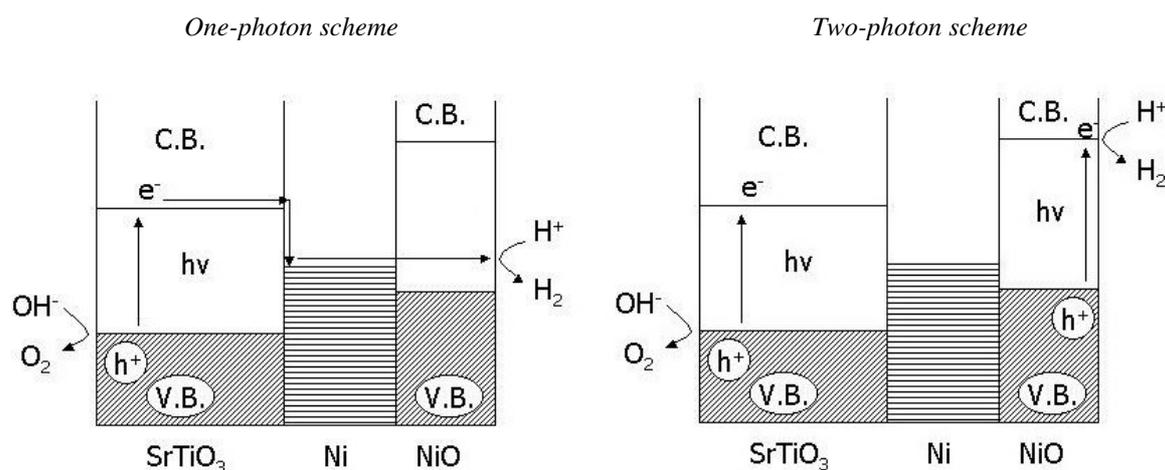


Figure 4.3: Two mechanisms with a NiO co-catalyst. The first alternative uses one photon to excite an electron. This electron is conducted to nickel and tunnels through nickel-oxide to the surface. The second mechanism needs two excitations to achieve the same: photocatalytic water splitting.

First the strontium-titanium oxide is excited with a photon to give rise to an excited state. The electron in the conduction band can be stabilised by electron transfer to the nickel and via tunnelling it can be transformed to the surface, where it can react with the protons.

In the two-photon scheme, the strontium-titanium oxide is again excited resulting in an excited state. Second the nickel oxide adsorbs a photon and gives rise to an excited state of the nickel oxide. The electron in the excited state of the nickel oxide facilitates the creation of hydrogen gas. The oxygen is generated by the hole in the valence band of the strontium-titanium oxide just like the one-photon mechanism. But there is a striking difference between these mechanisms. If the hole is used in the first mechanism, the system will return towards its normal state. But in the two-photon mechanism the use of the hole gives rise to a negative charge on the titanium-dioxide and a positive charge on the nickel oxide. This state is clearly an excited one and therefore wants to relax to its normal state.¹⁵

Both mechanisms seem reasonable, but the first is probably more realistic because after reaction the system does not contain any charge-separated state, which is the case for the two-photon mechanism.

Nickel oxide in its pure form is also used as mechano-catalyst for the generation of hydrogen and oxygen gas from water. A comparison between the mechano-catalytic system and the photocatalytic system results in a 6 times more productive photocatalyst than used as a mechano-catalyst.¹⁴

5 Properties of a good photocatalyst

This report covered several properties of the photocatalyst. This section states a list of properties we think that are important to create a good photocatalyst for water splitting.

- The bandgap should be between 2.43 eV and 3.2 eV
- The valence band should be lower than the oxygen oxidation potential
- The conduction band should be higher than the hydrogen reduction potential
- The aid of a co-catalyst for hydrogen generation is necessary
- The photocatalyst must be able to split water in protons and hydroxyl anions
- The generation of water from molecular oxygen and hydrogen must be reduced
- Electron transport to the surface is necessary

6 Conclusions

In literature a lot of research is reported in which an attempt is made to create a photocatalyst with the highest activity. To create a large number of catalysts and screen them for their activity, is the general applied method. We think a more fundamental approach is better than simple screening. Therefore we tried to give more insight into the subject of photocatalysis.

The first step in creating a suitable catalyst is to tune the bandgap in such a way that it lies between 2.43 and 3.2 eV. The following properties of the bandgap can be tuned:

- The primary effect: Electronegativity
- The secondary effect: Bonding situations.

The secondary effect can be used to modify the bandgap in the desired direction, the valence band needs to be lower in energy than the oxidation potential of oxygen and subsequently the conduction band needs to be higher than the reduction potential of hydrogen.

Because the reaction proceeds via half reactions using ions, it is preferable that the photocatalyst splits water heterolytically into a proton and a hydroxyl anion. This can be facilitated by metaloxides. A metal atom of larger size results in more dissociation of water, because hydrogen bonding is less strong between the proton on the bridging oxygen and the hydroxyl anion on the five-fold titanium site. The larger metal also leads to less proton conduction and thus to more localisation of the protons. Because proton conduction is always present, a co-catalyst is necessary to create hydrogen gas. Several co-catalysts are possible, two of them are:

- Platinum
- Nickel(II) oxide

A problem with platinum is that also the reaction between oxygen and hydrogen is catalysed, which leads to water. This reaction can be suppressed by iodine. The reason that nickel(II) oxide as co-catalyst gives higher hydrogen evolution is not clear.

The most important catalysts are titanium-dioxide and its derivatives.

7 Recommendations

As stated earlier, it is preferable that the catalyst splits the water. Therefore we recommend that the photocatalyst needs to be a metal oxide. Second we need a semiconductor of which the bandgap lies in the desired region. This can be tuned by addition of other atoms in the crystal.

If we use a metal oxide, proton conduction is a problem that arises. Therefore we need a co-catalyst to locate the protons and facilitate hydrogen formation. Nickel(II) oxide is a option.

According to us the best option for a photocatalyst is titanium-dioxide doped with bismuth and nickel(II) oxide as co-catalyst.

But before this catalyst can be screened, one must discover which mechanism, one-photon or the two-photon mechanism, is responsible for the hydrogen formation. Using monochromatic light that only induces the modified titanium-dioxide can give more insight in this mechanism. If this leads to the two-photon mechanism, then we recommend that nickel(II) oxide should not be used as a co-catalyst because the next step is to alter the co-catalyst, which is not logical. It is possibly better then to use platinum as co-catalyst instead.

We also recommend investigating the penetration depth of light into the catalyst. We think that the Lambert-Beer law doesn't hold for solids, because it is difficult to express the concentration in volumetric units.

The diffusion length for the holes and electrons is another factor that should be examined.

8 Acknowledgements

We would like to thank the following people for their constructive support during this project. First we would like to thank Dr. H.T. Hintzen for his comments about bandgap engineering. Second Dr. Ir. C.F.J. Flipse for his help concerning the mechanistic understanding of the hydrogen and oxygen formation. And last but not least, Prof. Dr. J.W. Niemantsverdriet, for the supervision of our project.

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