Tutor/s

Dr. Javier Fernández
Departament de Química de Materials i Química Física

Dr. Bernardí Bayarri
Departament de Engenieria Química i Química analítica

Grau de Química

Treball Final de Grau

Reduction and characterization of the band-gap of TiO_2 nanoparticles

Reducció i caracterització del band-gap de nanopartícules de TiO_2

Antía Cela i Junyent

Gener 2022

Universitat de Barcelona
B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

En qüestions de ciència, l'autoritat de milers no val l'humil raonament d'un simple individu.

Galileo Galilei.

En primer lloc vull agrair al Javier Fernàndez i a la Noemí Gavieiro per haver-me ajudat durant el desembolupament del treball. Sens dubte també agrair a Bernardí Bayarri i a Thais per haver-me donat un cop de mà sempre que ho he necessitat. Així mateix al departament de Ciència de Materials i Química Física de la UB, el CPT i el CCiTUB per haver-me proporcionat totes les instal·lacions, materials i equips necessaris per dur a terme tots els experiments i caracteritzacions.

Al Carlos per haver-me fet companyia durant aquest projecte i a la Yaiza per ajudar-me.

Altrament agrair a tota la meva família, en especial als meus pares, al meu germà i a la Megan per haver cregut en mi, a la Paula per estar al meu costat durant tot el transcurs de la universitat i als meus amics que m'han ajudat a oblidar el que he donat per recordar el que he rebut.

REPORT

CONTENTS

1. SUMMARY

Water contamination is one of the main challenges we face. It consists on the release of substances into groundwater, lakes, streams, rivers and oceans to the extent that substances interfere with the beneficial use of water or with the natural functioning of ecosystems. [1]

Most of this pollutants can degrade by reacting with photocatalyst of TiO_2 nanoparticles (NPs).[2] The problem is that TiO_2 NPs require the absorption of ultraviolet radiation and it only represents a small percentage of sunlight. Therefore the decomposition has a very low performance. This fact is due to it has a large band gap (approc 3eV) and therefore it needs to absorb large amound of light energy to be able to produce photocatalysis.

To improve this performance TiO_2 NPs will be synthesized and thermal and chemical treatments to synthesize black TiO_2 will be performed that has a smaller band gap, which can produce photocatalysis absorbing lower wavelengths (from UV to visible regions), representing a high percentage of sunlight.

Keywords: Nanoparticles, photocatalysis, titanium oxide, band gap

2. RESUM

La contaminació d'aigua es un dels principals reptes als que ens enfrentem. Aquesta consisteix en l'alliberament de substàncies en l'aigua subterrània o en llacs, rierols, rius, estuaris i oceans fins al punt en què les substàncies interfereixen amb l'ús beneficiós de l'aigua o amb el funcionament natural dels ecosistemes.[1]

Molts d'aquests contaminants poden degradar-se reaccionant amb un fotocatalitzador de nanopartícules de TiO_2. [2] El problema d'aquest és que per a degradar-los necessita absorbir radiació ultravioleta i, només representa un petit percentatge de la llum solar, per tant la descomposició te un rendiment molt baix. Aquest fet es degut a que te una banda prohibida (band gap) gran (3eV aprox) i aleshores necessita absorbir llum de gran quantitat d'energia per a produir forocatalisis.

Per a millorar aquest rendiment se sintetitzaran nanopartícules de TiO_2 i s'aplicaran tractaments tèrmics i químics per a sintetitzar black TiO_2, que al tenir menor banda prohibida, és capaç de produïr la fotocatalització absorvint longituds d'ona de menor energia (desde l'UV fins a la regió visible), el que representa un elevat percentatge de la llum solar.

Paraules clau: Nanopartícules, fotocatalització, òxid de titani, banda prohibida

3. INTRODUCTION

Water is a vital natural resource for most living beings, and it's indispensible for all ecosystems. There is currently a water crisis in some regions of the world and it may spreadbecause of the higher consumption and wasting, the irregular distribution of water in the world, climate changes, etc.[3] Morover, the increasing production, the use and elimination of chemical products, industry, agriculture and common household conveniences [4] have caused the appearance of organic pollutants into water.[5]

So it is possible that all residual water from cities has some kind of contamination presenting a direct threat to people's health.[1]

One way to reduce or avoid this problem, efficiently and ecologically, is degrading these organic pollutants by reacting them with photocatalysts of TiO_2 nanoparticles (NPs). [2]

To be efficient, however, black TiO_2 is needed because pristine TiO_2 reacts when UV light is applied and little amount of degradation is obtained naturally (because it only represents a small percentage of sunlight). That fact is because to produce pollutants' descomposition the metal oxide neets to absorb light energy equal to or greater than it's band gap.[6] Pristine TiO_2 is a semiconductor with a certain crystalline structure. By inducing defects in its crystalline structure we obtain Black TiO_2. These defects are reflected in the appearance of discrete energy levels inside the band gap that allows a lower energy requirement to overcome the band gap.[2]

Then, black TiO_2 has the ability to quantitatively degrade pollutants with sunlight.

3.1. WATER POLLUTANTS

Water can be contaminated with lots of substances like biodegradable organic waste, toxic chemicals, petroleum, radiactive substances, etc. [1]

Domestic sewage water is the principal cause of diseases. But there is also the risk of depleting oxygen water due to the degradation of organic substances found in it. That produces a risk to lakes and streams because high oxygen levels are required for fish and other aquatic organisms to survive.[1]

3.2 NANOMATERIALS

Nanomaterials are considerated all materials of dimensions between 1 and 100nm. Below 1nm we are in the quantic measure and above 100nm in the macroscopic measure.

The term nanotechnology was coined in 1974 by Professor Norio Taniguchi, from Tokyo Science University, to describe manipulation on a very small scale (10^{-9}m).[7]

Still, the use of metallic nanoparticles seems to have started with the beginning of glass making in Egypt and Mesopotamia in the XIV and XIII centuries BCE. [7]

Currently, the interest in the synthesis of nanomaterials has increased due to its optical characteristics, magnetic, electrical, mechanical [8], chemical and physical properties.

Titanium dioxide nanoparticles (TiO_2 NPs) are among the most often used nanoparticles.[9]

The most important point of these materials is that number of atoms on the surface increased, creating a greater contact surface.

3.3 PHOTOCATALYSIS

Photocatalysis is a process for the use of solar energy to stock photons' energy in chemical blonds. [10]

Its development has been the focus of considerable attention in the recent years since it is used in a variety of applications across a broad range of research areas, especially environmental and energy-related fields. [11]

The capacity of photocatalyst to absorb visble light is a requisit to perform an efficient photocatalysis in natural conditions.[10]

There are tree types of material: conductor, semiconductor and insulator. Theise differ according to the distance between the conduction and the valence band (band gap). Most photocatalysts, though, are semiconductors due to their electronic structure, like TiO_2. [12]

The band gap is the difference in energy between the Valence Band (VB) and Conduction Band (CB).

Without excitation, both electrons and holes are in the VB. When semiconductors are excited by an energy equal to or greater than its band gap, electrons are promoted from VB to CB. [6] Photocatalysis consists on the formation of photogenerated charge carriers (hole and electron) (eq. 1) that are produced after the absorption of light (the energy that excites electrons). [11] The photogenerated holes in the valence band diffuse to the surface of TiO_2 and react with the adsorbed water molecules, forming hydroxyl radicals (• OH) (eq. 2) The generated voids and hydroxyl roots oxidize the organic molecules close to the TiO_2 surface .

At the same time, electrons in the conduction band participate in the reduction process, reacting with molecular oxygen to produce superoxide radical anions (O_2 • -). (eq 3) These free radicals will cause the degradation of pollutants with a redox reaction. [13]

$$\text{Photocatalyst} + h\nu \longrightarrow h_{VB}^{+} + e_{CB}^{-} \tag{1}$$

$$h_{VB}^{+} + H_2O \longrightarrow {}^{*}OH\ (\text{hydroxyl radical}) + H^{+} \tag{2}$$

$$e_{CB}^{-} + O_2 \longrightarrow O_2^{-*}\ (\text{superoxide radical}) \tag{3}$$

$$^{*}OH + \text{pollutant} \longrightarrow H_2O + CO_2 \tag{4}$$

$$O_2^{-*} + \text{pollutant} \longrightarrow H_2O + CO_2 \tag{5}$$

Equation (1) Formation of electrons (e^-) and holes (h^+), (2) Formation of hidroxyl radical, (3) Formation of superoxide radical, (4) and (5) degradation of pollutants by radicals. (Made with ChemDraw)

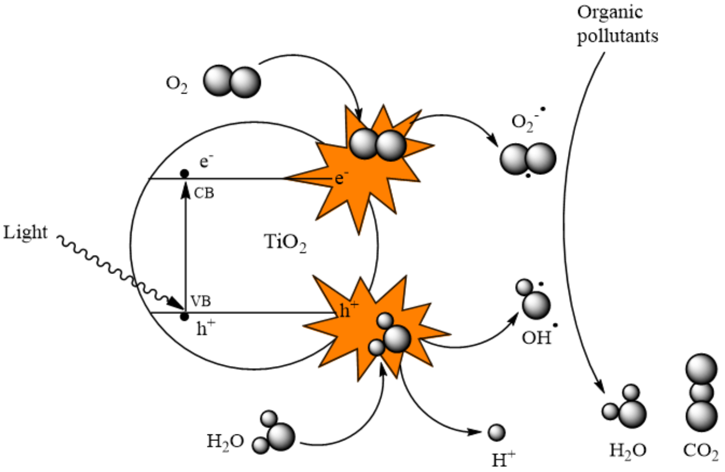


Figure 1: Photocatalytic process in semiconductors. (Made with ChemDraw)

3.4 TITANIUM DIOXIDE (TiO_2) AS A PHOTOCATALYSER

Titanium dioxide (TiO_2) belongs to the transition metal oxide family.

In the beginning of the 20th century, the production industry began to manufacture large amounts of TiO_2 to replace toxic lead oxides as pigments for white paint. Currently, the annual production of TiO_2 exceeds 4 million tons. [14]

It is considered very similar to an ideal semiconductor for photocatalysis due to its high stability, its safety for humans and the environment and due to its low cost [15] since it is the ninth most abundant element on the earth.[16]

3.4.1 Structures

There are four commonly polymorphs of TiO_2 appearing in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic) [14]

Brookite unit cell is composed of 8 TiO_2 units and is formed by TiO_6 octahedra that share edges. As it has a more complicated structure, it is not usually used for experimental research [17], so the focus will be seton anastase and rutile. Rutile unit cell is composed by 6 atoms and anatase by 12 atoms. In both cases Ti atoms are coordinated to 6 O atoms, and O atoms are coordinated to 3 Ti atoms.[18] The basic unit-cell structures of these tree phases are shown in Fig. 2

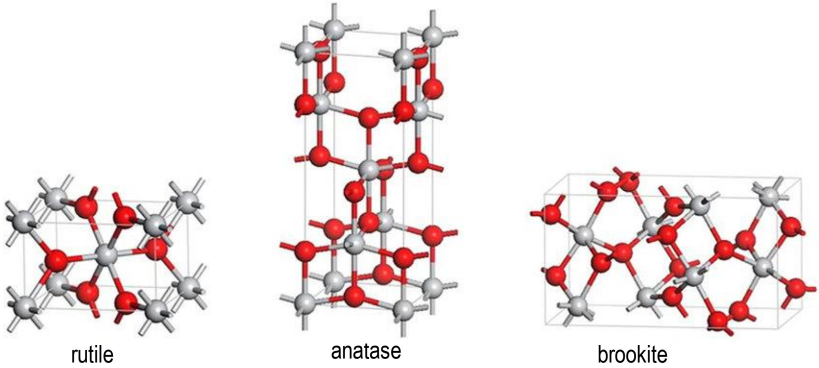


Figure 2: crystalline structures of TiO_2 rutile, anatase and brookite respectively. E.Baranowska-Wojcik et al tri. Biological trace element research 193 (2020), 118-129.

Rutile is stable at most temperatures and pressures (at 60 KBar), TiO_2 (II) is the thermodynamically stable phase), but its photocatalytic activity is very poor. In contrast, anatase, despite having a slightly higher band gap, has a higher photocatalytic activity due to the high mobility of electrons, the low dielectric constant, low density and lower deposition temperature.[15]

Despite this, the highest catalytic activity is found by having a mixture of the two phases due to the synergy effect between the anatase and rutile particles, which enhances the life time of the charge carriers [19], [20],

Table 1 shows different characteristics of rutile, anatase and brookite.[15], [18], [21]

	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorombic
Lattice constants (Å)	a = b = 4,5936 c = 2,9587	a = b = 3,784 c = 9,515	a = 9,184 b = 5,447 c = 5,154
Density	4,13	3,79	3,99
Dielectric Constant	6,62	6,04	7,89
Band gap (eV)	3,02	3,2	2,96

Table 1: Crystal properties of Rutile, anatase and brookite polymorphs

3.4.2 Colours TiO_2

Reducing the bandgap we enlarge the wavelength absorbed by TiO_2. There are diferents ways to do that which are based on defects on its crystalline structure like doping with other elements, making a reduction, sensitizing with dyes, and coupling with metal or nonmetal nanoparticles or different semiconductor materials, etc. [22] Depending on the treatment we apply to TiO_2 or what dopants we add, it will adopt different colors.

The pure one is white TiO_2, but it’s the large bandgap (aprox 3 eV) limits its light absorption [23] (100-400nm) [24]

Yellow TiO_2 can be obtained through nitrogen dopping [9] or by self-assembly processes induced by evaporation of ethanol. The bonds Ti-Ti formed at the interface causes a decrease of surface oxygen atoms in the TiO_2 structural unit, which alters the electronic structure and extends the light absorption to ~550 nm. [23]

Blue TiO_2 can be synthesized by Ti^{3+} self-doped TiO_{2-x} NPs with abundant defects

using a simple solvothermal approach, extending the light absorption to ~664nm. [25]

Red TiO_2 can be obtained through nitrogen dopping, extending the absorption up to about 700 nm covering the entire spectrum of visible light. [9]

Grey TiO_2, applying aluminium doping and N2 reduction treatmen can enhance absorption less than 450nm. [25]

Black TiO_2 is the most studied because it can absorb wavelengths from UV to visible.

3.4.2.1 Black TiO_2

Black titanium dioxide was discovered in 2011, and is one of the most studied photocatalysts to this day. Many synthetic pathways have been developed for black TiO_2 because it has much higher activity than pristine TiO_2 in various applications.[26]

This improvement in photoactivity is given by defects such as Ti^{3+} and oxygen vacancies, which create non-paired electrons that can excite to the CB. [26]

Nevertheless, excess defects can act as charge recombination centers, leading to a decrease in photocatalytic activity.

3.4.3 Limitations of TiO2 as photocatalyst

Photocatalysis is based on the separation of electron-hole that allows the formation of free radicals, which cause the degradation of pollutants. One of the main limitations is the recombination of the photogenerated electron and the hole (equation 2) that happens in a short time, releasing energy in the form of heat or photons. [6]

$$h_{VB}^{+} + e_{CB}^{-} \rightarrow \text{energy} \qquad (6)$$

Equation 6: Recombination of holes (h^+) and photogenerated electrons (e^-).

This would lead to a decrease in the performance of photocatalyitc activity. Methods to avoid this limitation are being studied, an example is the incorporation of titanium oxide in carbon black. The better promoting effect could be attributed to the larger pores of carbon black that allow faster diffusion of adsorbed organic matter from carbon black to TiO_2 and the high electrical conductivity of carbon black that can reduce the recombination of electrons and holes generated in TiO_2. [23]

Another limitation is that photogenerated electrons and holes are involved in the production of hydrogen through the division of water (equation 3) Although there is a low possibility of this happening.

$$2H^+ + 2e_{CB}^- \rightarrow H_2 \qquad (7)$$

$$2H_2O + 4h_{VB}^+ \rightarrow O_2 + 4H^+ \qquad (8)$$

Equations (7) Oxidation of H+ to form H_2 by photogenerated electrons (e-), (8) Reduction of water to form O_2 by photogenerated holes (h+)

3.4.4 Aplications

The absortion potential of TiO_2 has been used in many fields like fotodegradation [5], solar cells [5], self-cleaning coattings [5], organic reactions [27], photocatalytic sensors [28], foodstuffs [9]... Thats's because of the high refractive index [29] and stability [22], it's non-toxicity [30] and broadband energy [31].

Solar energy is a renewable source that is available in abundance and at no cost. Of the solar radiation that reaches the earth, 49.4% is found to infrared radiation (from 700nm to over 1mm), the 42,3% to visible light (400-700nm) and the 8% to ultraviolet radiation (100-400nm). [32]

Pure TiO_2 is a white crystalline solid that absorbs the ultraviolet radiation, that is why for most applications it is necessary to apply a subsequent treatment to make the most of natural light. This produces a saving of energy that leads to a decrease in pollution and saving money.

3.4.2 Synthethic methods

There are many methods for the preparation of nanocrystalline TiO_2, the most common are the precipitation, hydrothermal and solvothermal, sol-gel, combustion, microemulsion, gasphase, spray pyrolysis method among others, etc. [14]

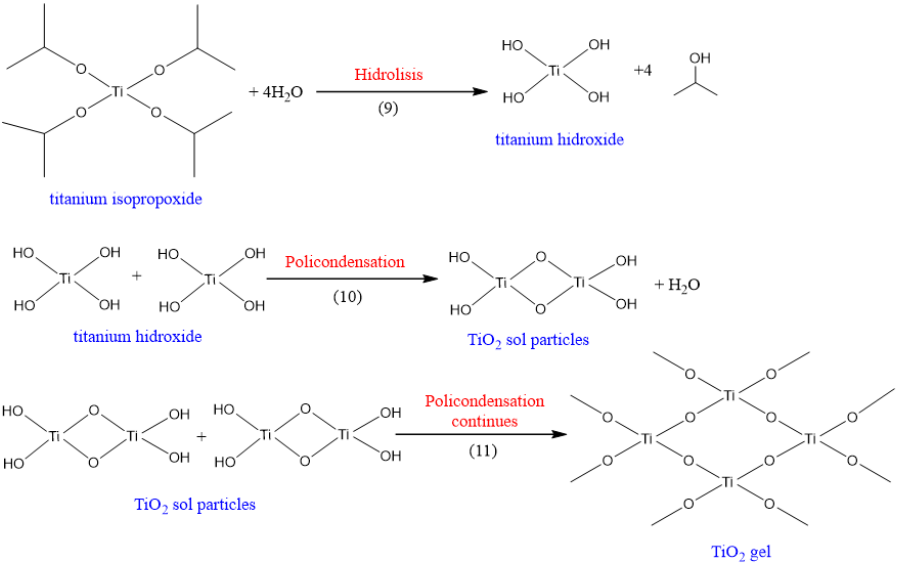
The size of the particles and the physical and chemical properties will depend on the preparation method used. [33]

For photocatalytic applications the most common methods are the sol-gel and solvothermal methods (hydrothermal and solvothermal methods) [33]

Solvothermal method: Chemical reactions are carried out in aqueous media (hydrothermal method) or organic (solvothermal method) [34] under pressures produced at low temperatures. Normally it requires a subsequent heat treatment for the crystallization of the material. These methods are useful to control the size and morphology of the particles, the crystalline phase and the chemistry of the surface, regulating the composition of the solution, the reaction temperature and the pressure. [33]

Sol-gel method: There are two types of route for this method: without alkoxide, which uses inorganic salts, and with alkoxide (the most common), which uses metal alkoxides as the starting material. In any of these cases, this method has many advantages over other manufacturing techniques such as purity, homogeneity, flexibility in the induction of dopants, easy processing, control in stoichiometry and composition.

The precursor in an organic solvent is hydrolyzed, forming a colloidal suspension in which the dispersed particles are found, called sol. [14], [35] As the solvent evaporates, the dispersed particles come into contact, completing the polymerization reaction, thus obtaining a gel. This gel is heated to eliminate the organic compounds obtaining a gel with the metallic oxide. The resulting gel is stable for only a short period of time and solidifies. [35], [36]



Equations (9) Hydrolysis, (10) Polycondensation and formation of sol (11) End of polycondensation and formation of the gel. (Made with ChemDraw)

3.4.2.1 Reduction methods

Since 2011, many synthetic routes have been explored for obtaining black TiO_2. The amount of methods to synthesize black TiO_2 has increased, but hydrogenation is still the most studied route. The hydrogenation method is simple and direct, which is based on introducing defects in the structure of TiO2 by heating to 900ºC under a reducing atmosphere consisting of H_2, H_2 / Ar, H_2 / N_2 or Ar. [33] This defects can be induced by reductor metals, plasma or ionothermic assisted process, $NaBH_4$ reduction, laser ablation, etc. [37], [38] (figure 3) Most of the methods are based on the reduction of pristine TiO_2, where red represents the reductant. (eq. 12)

$$TiO_2 + Red \rightarrow TiO_{2-x} + RedO_x \qquad (12)$$

Equation 12: TiO_2 most common reduction reaction

The various synthesis methods discovered so far broaden the horizon on how black TiO_2 can be synthesized. A new approach to induce photocatalysis of TiO_2 activated by visible light is by substituting oxygen for ions (N^{3+}, C^{4+}, S^{4+}, X (F, Cl, Br)) leading to a narrowing of the band gap. [14]

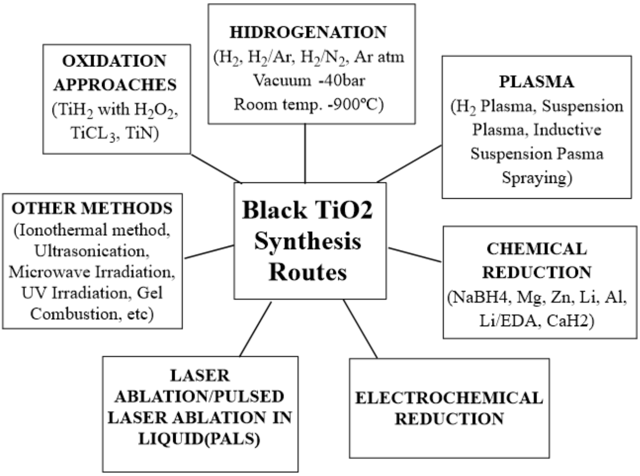


Figure 3: The various synthetic methods of black TiO_2. (Made with ChemDraw)

4. OBJECTIVES

The main objective of this PROJECT is to synthesize titanium oxide NPs and reduce the band gap with reduction routes following the steps shown below:

- Synthesis of TiO2 nanoparticles by the sol-gel method.
- Determination of the crystalline structure.
- Obtaining black TiO2 from reduction treatments.
- Characterization of the TiO2 obtained.
- Photocatalysis efficiency of the TiO2 obtained.

5. EXPERIMENTAL SECTION

5.1. MATERIALS AND METHODS

The chemicals used in these experiments were isopropanol (≥99,5%, Sigma-Aldrich) o ethanol absolute (Codex Panreac), Titanium (IV) isopropoxide (97%, Aldrich), nitric acid pure (69%, Labkem), sulfamethoxazole (Sigma Aldrich).

The formation of TiO_2 was made using a 100ºC oven and a 500ºC oven and for the TiO_2 reduction the equipment used was N_2 oven. All products obtained were analised by Photocatalysis, Raman and HPLC. SEM analysis was supposed to be used to characterize the size of the powder however because of unavailability of the equipment, the results are not obtained at the moment of the presentation of the report. They will be shown during the oral presentation.

5.2 SYNTHESIS OF TIO_2 NPS

For the TiO_2 NPs synthesis, the sol-gel method has been used. 100mL of organic solvent (isopropanol or ethanol) are added in a 250mL beaker (solution B) and a mechanical stirrer. It is then covered with parafilm paper because TTiP is very sensitive to humidity. The beaker where the formation of the sol-gel occurs has been covered to prevent it from reacting with moisture and thus obtain smaller TiO_2 particles.. In a separatory funnel of 250mL add a 50mL solution of the same organic solvent used previously and 50mL of TTiP (solution A). A hole is made in the parafilm paper of the same size as the tip of the separatory funnel and this tip is placed inside the hole to decrease the amount of moisture that comes into contact with solution A. Solution A is dropped onto drop B dropwise with constant stirring. When finishing the drop by drop, the parafilm paper is removed and two drops of HNO_3 are added to control the pH of the solution; the high concentration of ions on the surface of the nanoparticles increases the charge on the surface of the nanoparticles and reduces the possibility of coagulation of the particles. It is left to warm to 100ºC with constant stirring to eliminate the remaining moisture. After about 2 hours, the solution is no longer liquid and becomes somewhat viscous. This is when the gel forms. It is necessary to avoid the formation of a very viscous gel to be able to do the dialysis. Once the gel is obtained, it is added to a dialysis bag and left in deionized water to achieve a neutral medium in the gel without the need to change the volume of this gel. This step is achieved by measuring the pH of the water with pH Test Paper and changing it when it is acidic. When the water has a constant pH = 7, the dialysis will be over.

The TiO_2 formed inside the dialysis bag is added to an evaporating porcelain dish and left in the oven at 100ºC for 4 hours. Once the dry powder is obtained, it is crushed with a mortar to separate the agglomerated particles and obtain more contact surface for the following heat treatments: In the first one, it is necessary to stabilize its crystalline structure: the solid is heated at 500ºC for 4 hours under oxidant atmosphere (normal air). The others are used to form defects in the solid.

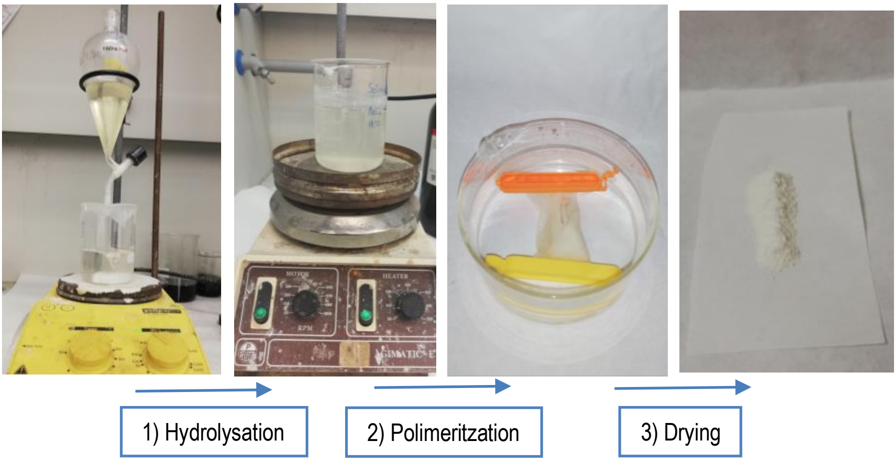


Figure 4: Sol-gel synthesis steps

$$Ti(PrO_4) + H_2O \xrightarrow[1]{} Ti(OH)_4 \xrightarrow[2]{} TiO_2 \cdot H_2O \xrightarrow[3]{\Delta} TiO_2$$

Equation 13: Sol-gel synthesis reaction (Made with ChemDraw)

Other variations, such as the addition of 20 ml of deionized water substituting dialysis, have been tried to form a precipitate that helps gel formation through a polymerization reaction.

5.2.1 Reduction of TiO_2 powders

The reduction treatments applied to TiO_2 are carried out to form defects in the solid. The first treatment is done by heating to 500ºC under a reducing atmosphere of N_2 to create oxygen vacancies, which reduces the band gap. This treatment has been performed with a duration of 4, 8 and 12 hours. (figure 5)

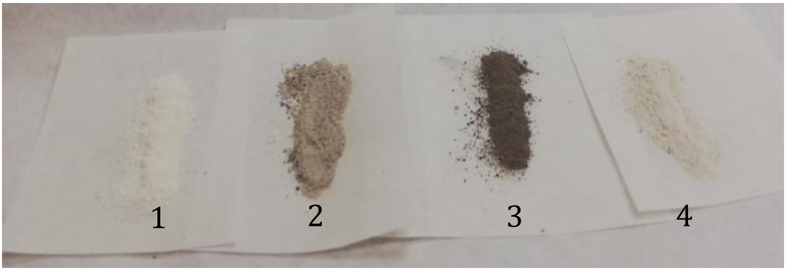


Figure 5: TiO_2 synthesized by sol-gel method after heat treatment under oxidant atmosphere (1) and after treatment under reductant atmosphere: 4h (2), 8h (3), 12h (4)

The other treatment consists of mixing 1g of TiO_2 and different amounts of ascorbic acid (AA) with defined volumes of deionized water: 4 different AA-modified photocatalysts were prepared containing 0.050, 0.100, 0.250 and 0.500% by weight of AA (0, 0005g, 0.001g, 0.0025g, 0.005g AA). [33]

First, each 1g of AA was dissolved in 0.1L of H2O: in 0.05mL, 0.1mL, 0.25mL and 0.5mL respectively (solution C) and 4 equal solutions of 1g of TiO2 in 5mL of H20 (solution D). [39] Once both solutions are made, each C solution is mixed with a D solution. It is constantly stirred for 30 minutes (figure 6).

Figure 6: AA reduction treatment. On the left is the solution less concentrated in AA (yellow) and on the right the most concentrated in AA (orange).

During this time the mixture takes on a deep yellow color depending on the AA concentration. Then the TiO_2 is washed with deionized water and left in the oven at 100ºC to eliminate the water (figure 7). [37]

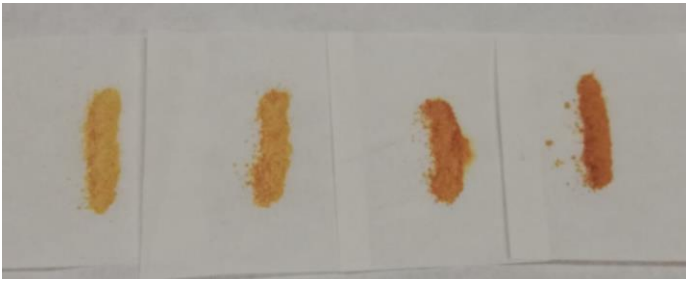


Figure 7: AA reduction treatment after dry. On the left is the solution less concentrated in AA (yellow) and on the right the most concentrated in AA (orange)

In previous experimental studies [39], [40] AA has been used as a TiO_2 modifier and it has been found that the photocatalytic activity of TiO_2 increases through the formation of a surface charge transfer complex on the TiO_2 particles. [33]

$$\underset{\text{ascorbic acid}}{C_6H_8O_6} \longrightarrow \underset{\text{ascorbate}}{C_6H_7O_6^- + H^+} \qquad (14)$$

$$\underset{\text{ascorbate}}{C_6H_7O_6^-} \longleftrightarrow \underset{\text{dehydroascorbic acid}}{C_6H_6O_6 + H^+ + 2e^-} \qquad (15)$$

$$Ti^{4+} + 1e^- \longleftrightarrow Ti^{3+} \qquad (16)$$

Equations (14) Ascorbic accid desprotonation, (15) Ascorbic acid oxidation, (16) Ti^{4+} reduction (Made with Chemdraw)

5.3 PHOTOCATALYTIC DEGRADATION OF SULFAMETHOXAZOLE BY TIO2

To verify the effectiveness of TiO_2 in photocatalysis, a solar simulation camera (Xenoterm-1500RF, CCI) has been used, which has a 1.5kW xenon lamp (it is the radiation source) with a spectrum of approximately 450nm. In a 600mL beaker (reactor), 500mL of a 3mg / L sulfamethoxazole solution (SMX) was added. A sample (M1) of approx 1mL is taken before adding the TiO2 (photocatalyst) to see which part of the solution adsorbs. Then 0.125g of TiO2 is added, stirred for 15 minutes and another sample (M2) is taken to verify that the SMX does not degrade in the absence of light. The xenon lamp is lit, it is left under constant stirring for 15 minutes and another sample (M3) is taken. After 15 minutes you take the M4, after 20 minutes the M5, after 30 minutes the M6, you wait another half hour to take the M7 and to take the M8 and M9 you wait 40 minutes for each (Figure 8).

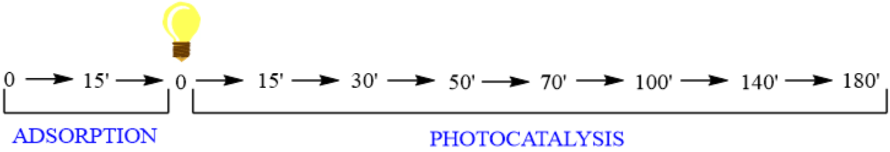


Figure 8: Scheme of the sampling during the degradation test (Made with ChemDraw)

This experiment was carried out with TiO_2 synthesized by ethanol, TiO_2 synthesized by isopropanol, with TiO_2 reduced in the N_2 oven for 4 hours, 8 hours and 12 hours and with TiO_2 reduced with ascorbic acid.

Figure 9: Experimental set-up of the photodegradation of sulfamethoxazole in aqueous suspension of TiO_2 inside a Solar Simulator

5.4 CHARACTERIZATION

To characterize the TiO_2 synthesized with the sol-gel method, a scanning electron microscope (SEM) equipment, an integrating sphere, and High-performance liquid chromatography (HPLC) have been used.

5.4.1 SEM

To perform this microstructural characterization, a QUANTA250 electron microscope (SEM) was used, whose working voltatge was 20kV. The samples were coated with C (graphite) to make them conductive and allow a correct observation in the SEM. It has been possible to obtain TiO2 synthetized with ethanol particles size. (Figure 10).

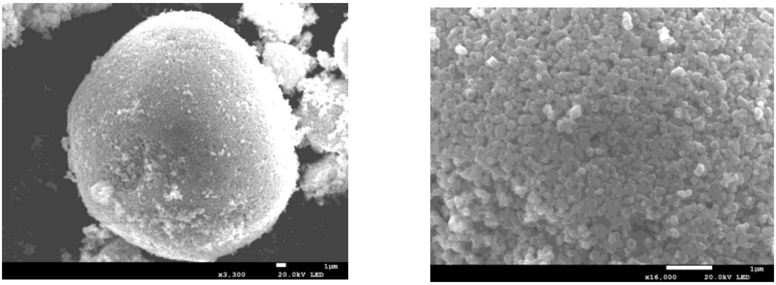


Figure 10: SEM pictures of TiO_2 NPs synthesized by sol-gel with etanol

5.4.2 Band gap

The optical properties were evaluated by measuring the transmittance and reflectance spectra, by using an integrating sphere (Bentham PV300 EQE system), using monochromated light from a Xe and quartz halogen dual lamp source through the 300-1100 nm range, and collecting the transmitted (or reflected) light with an InGaAs photodetector.

The sample has been successfully dissolved in isopropanol, ethanol or cyclohexanol and at diferent cancentrations (0,24; 0,48; 0,96 and 2 g/L) but none has been validated.

5.4.3 Photocatalysis

The results of photocatalysis are studied with High-performance liquid chromatography (HPLC). Chromatography is based on the different affinity between substances as a consequence of their polarity. There is a mobile phase (which carries the compound that will be characterizated) and a fixed phase (through which the mobile phase passes).

MET degradation was monitored by HPLC (1200 Infinity Series from Agilent) under the following conditions: C18 reverse phase column (SEA18 5 µm 15 × 0.46 cm from Teknokroma), a mixture of H_2O acidified to pH = 3 with orthophosphoric acid and acetonitrile (Reag. Ph. Eur.) as the mobile phase, injected with a flow-rate of 0.850 mL min−1, and a Waters 996 photodiode array detector using the Empower Pro software 2002 Water Co., working at max- imum UV absorbance (270 nm). In order to remove the catalyst, before the analysis, samples were filtered with a polyethersulfone membrane filter of 0.45 µm.

In Figure 11, the percentage of SMX remaining with respect to the reaction time is shown. From minute -15 to 0, the concentration of SMX is constant, which means that this SMX is not adsorbed by the reagent or reacts with air. The results show that TiO_2 synthesized with isopropanol has better photocatalytic activity than TiO_2 synthesized with ethanol. Also that the reduction in the N_2 furnace is more effective during 8h than not during 4h.

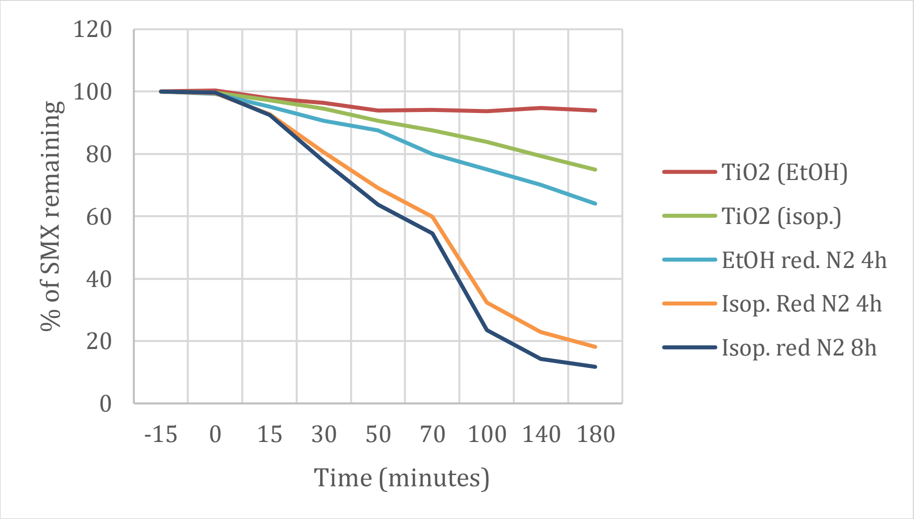


Figure 11: Decomposition of the SMX in% vs reaction time

10. CONCLUSIONS

Although the obtention of black TiO_2 NPs by chemical reduction with AA in solution was not achieved, the following conclusions can be obtained:

- Sol-gel is an efficient and scalable method for the synthesis of TiO_2 NPs.
- TiO_2 at nanometricsize with ethanol has been successfully synthesized.
- N_2 treatment is very effective but the difference in photocatalytic activity between the samples reduced at differents times does not exceed 5% yield.
- Through reduction treatment with AA, yellow-orange TiO_2 has been obtained but on the other hand black TiO_2 not.

11. REFERENCES AND NOTES

1. Britannica, The Information Architects of Encyclopaedia. "water pollution". Encyclopedia Britannica, 9 Jan. 2022, https://www.britannica.com/facts/water-pollution. Accessed 9 January 2022.
2. Sébastien S. Les soignants face à la mort. *Rev Infirm*. 2012;1(180):39-41.
3. Salud OM de la. The World Health Report 2005: Make every mother and child count The World Health Report 2005. *World Heal Rep*. Published online 2005.
4. Kolpin DW, Furlong ET, Meyer MT, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environ Sci Technol*. 2002;36(6):1202-1211.
5. Schneider J, Matsuoka M, Takeuchi M, et al. Schneider et al. - 2014 - Understanding TiO 2 Photocatalysis Mechanisms and Materials(2).pdf. *Chem Rev*. 2014;114(9):9919−9986
6 . Ni M, Leung MKH, Leung DYC, Sumathy K. A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. *Renew Sustain Energy Rev*. 2007;11(3):401-425.
7. Schaming D, Remita H. Nanotechnology: from the ancient time to nowadays. *Found Chem*. 2015;17(3):187-205.
8. Biju V. Chemical modifications and bioconjugate reactions of nanomaterials for sensing, imaging, drug delivery and therapy. *Chem Soc Rev*. 2014;43(3):744-764.
9. Baranowska-Wójcik E, Szwajgier D, Oleszczuk P, Winiarska-Mieczan A. Effects of Titanium Dioxide Nanoparticles Exposure on Human Health—a Review. *Biol Trace Elem Res*. 2020;193(1):118-129.
10. Liu G, Yin LC, Wang J, et al. A red anatase TiO 2 photocatalyst for solar energy conversion. *Energy Environ Sci*. 2012;5(11):9603-9610.
11. Nakata K, Fujishima A. TiO 2 photocatalysis: Design and applications. *J Photochem Photobiol C Photochem Rev*. 2012;13(3):169-189.
12. R. Ameta, M. S. Solanki, S. Benjamin, and S. C. Ameta, *Advances Oxidation Processes for Waste Water Treatment: Emerging Green Chemical Technology*. Udaipur, Rajasthan: Academic Press, 2018
13. Fujishima A, Zhang X, Tryk DA. TiO2 photocatalysis and related surface phenomena. *Surf Sci Rep*. 2008;63(12):515-582.
14. Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium dioxide. *Prog Solid State Chem*. 2004;32(1-2):33-177.
15. Gupta SM, Tripathi M. A review of TiO2 nanoparticles. *Chinese Sci Bull*. 2011;56(16):1639-1657.
16. Hashimoto K, Irie H, Fujishima A. TiO 2 photocatalysis: A historical overview and future prospects. *Japanese J Appl Physics, Part 1 Regul Pap Short Notes Rev Pap*. 2005;44(12):8269-8285.
17. Thompson TL, Yates JT. Surface science studies of the photoactivation of TIO2 - New photochemical processes. *Chem Rev*. 2006;106(10):4428-4453.
18. Mo S Di, Ching WY. Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. *Phys Rev B*. 1995;51(19):13023-13032.
19. Luttrell T, Halpegamage S, Tao J, Kramer A, Sutter E, Batzill M. Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO2 films. *Sci Rep*. 2015;4:1-8.
20. Bacsa RR, Kiwi J. Effect of rutile phase on the photocatalytic properties of nanocrystalline titania during the degradation of p-coumaric acid. *Appl Catal B Environ*. 1998;16(1):19-29.
21. Baur WH. Atomabstände und Bindungswinkel im Brookit, TiO 2 . *Acta Crystallogr*. 1961;14(3):214-216.
22. Ullattil SG, Narendranath SB, Pillai SC, Periyat P. Black TiO2 Nanomaterials: A Review of Recent Advances. *Chem Eng J*. 2018;343(January):708-736.

23. Wang J, Zhao Y, Xu X, Feng X, Yu J, Li T. A facile interfacial assembling strategy for synthesizing yellow TiO 2 flakes with a narrowed bandgap . *RSC Adv*. 2015;5(72):58176-58183.
24. Rajaraman TS, Parikh SP, Gandhi VG. Black TiO2: A review of its properties and conflicting trends. *Chem Eng J*. 2020;389:123918.
25. Zhu Q, Peng Y, Lin L, et al. Stable blue TiO2-x nanoparticles for efficient visible light photocatalysts. *J Mater Chem A*. 2014;2(12):4429-4437.
26. Liu Y, Chen P, Fan Y, et al. Grey rutile TiO2 with long-term photocatalytic activity synthesized via two-step calcination. *Nanomaterials*. 2020;10(5).
27. Mao CC, Weng HS. Promoting effect of adding carbon black to TiO2 for aqueous photocatalytic degradation of methyl orange. *Chem Eng J*. 2009;155(3):744-749.
28. Lang X, Chen X, Zhao J. Heterogeneous visible light photocatalysis for selective organic transformations. *Chem Soc Rev*. 2014;43(1):473-486.
29. Evans CC, Liu C, Suntivich J. TiO2 Nanophotonic Sensors for Efficient Integrated Evanescent Raman Spectroscopy. *ACS Photonics*. 2016;3(9):1662-1669.
30. Mont FW, Kim JK, Schubert MF, Schubert EF, Siegel RW. High-refractive-index Ti O2 -nanoparticle-loaded encapsulants for light-emitting diodes. *J Appl Phys*. 2008;103(8).
31. Shi H, Magaye R, Castranova V, Zhao J. Titanium dioxide nanoparticles: A review of current toxicological data. *Part Fibre Toxicol*. 2013;10(1).
32. Riu J, Maroto A, Rius FX. Nanosensors in environmental analysis. *Talanta*. 2006;69(2 SPEC. ISS.):288-301.
31. Fondriest Environmental, Inc. "Solar Radiation and Photosynethically Active Radiation." Fundamentals of Environmental Measurements. 21 Mar. 2014. Web. < https://www.fondriest.com/environmental-measurements/parameters/weather/solar-radiation/ >.
32. Žunič V, Vukomanović M, Škapin SD, Suvorov D, Kovač J. Photocatalytic properties of TiO2 and TiO2/Pt: A sol-precipitation, sonochemical and hydrothermal approach. *Ultrason Sonochem*. 2014;21(1):367-375.
33. Xu LH, Patil DS, Yang J, Xiao J. Metal Oxide Nanostructures: Synthesis, Properties, and Applications. *J Nanotechnol*. 2015;2015(May 2014).
34. Yin S, Fujishiro Y, Wu J, Aki M, Sato T. Synthesis and photocatalytic properties of fibrous titania by solvothermal reactions. *J Mater Process Technol*. 2003;137(1-3 SPEC):45-48.
35. Sakka S. Sol-Gel Process and Applications. *Handb Adv Ceram Mater Appl Process Prop Second Ed*. Published online 2013:883-910.
36. Mert EH, Yalçin Y, Kiliç M, San N, Çinar Z. Surface modification of TiO2 with ascorbic acid for heterogeneous photocatalysis: Theory and experiment. *J Adv Oxid Technol*. 2008;11(2):199-207.
37. Liu Y, Tian L, Tan X, Li X, Chen X. Synthesis, properties, and applications of black titanium dioxide nanomaterials. *Sci Bull*. 2017;62(6):431-441.
38. Wajid Shah M, Zhu Y, Fan X, et al. Facile Synthesis of Defective TiO 2-x Nanocrystals with High Surface Area and Tailoring Bandgap for Visible-light Photocatalysis. *Sci Rep*. 2015;5(July):1-8. doi:10.1038/srep15804
39. Rajh T, Nedeljkovic JM, Chen LX, Poluektov O, Thurnauer MC. Improving optical and charge separation properties of nanocrystalline TiO2 by surface modification with vitamin C. *J Phys Chem B*. 1999;103(18):3515-3519.
40. Lana-Villarreal T, Rodes A, Pérez JM, Gómez R. A spectroscopic and electrochemical approach to the study of the interactions and photoinduced electron transfer between catechol and anatase nanoparticles in aqueous solution. *J Am Chem Soc*. 2005;127(36):12601-12611. doi:10.1021/ja052798y

12. ACRONYMS

NPs: Nanoparticles

UV: Ultraviolet

nm: Nanometre

VB: Valence band

CB: Conduction band

h^+: Positive holes

e^-: Photogenerated electrons

mL: millilitre

TTIP: Titanium (IV) isopropoxide

AA: Ascorbic acid

SMX: Sulfamethoxazole

SEM: Scanning electron microscope

kV: Kilovolt

FESEM: Field Emission Scanning Electron Microscope

HPLC: High-performance liquid chromatography

µm: Micrometre