Development of photocatalytic functional coatings via magnetron sputtering deposition and their integration into a laboratory-scale water treatment reactor

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> Manchester Metropolitan University Faculty of Science and Engineering, Department of Engineering Surface Engineering group

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Declaration

This is to certify that the material contained in this thesis has been produced by author and has not been accepted in substance for any other degree and is not currently submitted in candidature for any other academic award.

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Abstract

Photocatalysis is an advanced oxidation process that only requires a photocatalyst, an appropriate light source and water to decompose a wide variety of pollutants. In recent years, it has been extensively studied for environmental wastewater treatment applications. Although promising, it has yet to be globally adopted, as it faces many challenges; namely cost, complexity and efficiency. To achieve this goal, two strategies have been employed in the present thesis. First, photocatalytic thin films were produced by pulsed DC magnetron sputtering, a method of high industrial relevance, onto substrates specifically selected to improve the performance of immobilised systems. Second, the deposition process was scaled-up and the thin films were integrated into laboratory scale water treatment systems.

Titanium dioxide (or titania) is, to date, the most popular photocatalyst due to its stability, low toxicity and low cost. When deposited by reactive magnetron sputtering, titania often requires substrate bias or annealing to be photocatalytic. In this present work, crystalline titanium dioxide was successfully deposited on woven stainless-steel in a one step process, using low pressure and high-power deposition conditions. Anatase and rutile polymorphs were identified by XRD analysis, whilst Raman mapping indicated excellent coating coverage of the mesh substrate. The pseudo first rate order constant was as high as $5.3 \times 10^{-5} s^{-1}$, for methylene blue degradation, and the performance was maintained over 10 consecutives cycling experiments.

Large sheets of photocatalytic titania coated mesh were produced in a one-step process and integrated in a bespoke laboratory-scale photocatalytic reactor. The reactor was built from inexpensive and readily available consumer market parts, to facilitate a widespread adoption of such water treatment methods. The influence of variable parameters was studied, using a DOE template, to maximize the degradation rate of methylene blue, leading to the removal of more than 90% of the model pollutant after 5 h. This substrate/catalyst combination proved to be effective at degrading methylene blue, with no evident performance degradation after 10 repeated cycles, equivalent to 360 h of consecutive use.

A bismuth titanate composite photocatalyst was investigated as an alternative to the conventionally used titanium dioxide, to tackle the well-known drawbacks of fast chargecarrier recombination and low quantum efficiency of titania. Optimum deposition and annealing conditions were identified, to deposit bismuth titanate coatings by reactive magnetron sputtering. Bismuth titanate proved to be more efficient at decomposing methylene blue under UV light, with a pseudo first rate order constant of 1.40 and 0.52 $(10^{-5}s^{-1})$ for bismuth titanate and titania coatings on glass substrates, respectively. Moreover, the reusability assessment of bismuth titanate thin films revealed an incremental performance increase after each consecutive test, leading to a 6-fold increase in photocatalytic activity. This behaviour was investigated by XPS and TRPL analysis and attributed to the formation of oxygen vacancies under UV irradiation. The oxygen vacancies-rich bismuth titanate was termed "black bismuth titanate" due to its dark colour, as opposed to the opaque white colour of the pristine one.

Glass stirring rods were coated with bismuth titanate and integrated in the bespoke laboratory-scale photocatalytic reactor. Dye degradation tests carried out in the presence of scavengers and revealed that photocatalytic reactions were driven by superoxide and holes, when using pristine bismuth titanate and by superoxide, electrons and holes, when using black bismuth titanate. Finally, the reactor was used to successfully degrade levofloxacin, a reserve antibiotic, which was verified by UV-Vis spectroscopy and inhibition zone test in the presence of three different pathogens.

Overall, this piece of work describes the use of reactive magnetron sputtering to deposit efficient photocatalytic coatings, under optimised deposition conditions. These photocatalysts were then integrated in a laboratory-scale water treatment reactor, which was optimised to maximise the photocatalytic activity of the system. The results of this work address the technical viability and economic feasibility challenges faced by photocatalytic waste treatment.

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Nomenclature

AC	Alternating Current	MD	Movchan and Demchishin
AFM	Atomic Force Microscopy	MFC	Mass Flow Controller
ANOVA	Analysis Of Variance	ΜΟ	Methyl Orange
BG	Band Gap	OII	Orange II
BSE	Back Scattered Electron	OVAT	One Variable At a Time
ВТА		DDCDC	Pharmaceuticals and Personal
	Bismuth Titanate	Bismuth Fitanate FFCFS	Care Products
BBTA	Black Bismuth Titanate	pDC	Pulsed Direct Current
СВ	Conduction Band	PDF	Powder Diffraction File
CCD		DECUD	Plasma Enhanced Chemical
CCD	Charge Coupled Device	PECVD	Vapour Deposition
CFU	Colonies Forming Units	PEM	Plasma Emission Monitoring
CEUDMG	Closed-Field Unbalanced	DI	D1 (1)
CFUBMS	Magnetron Sputtering	РL	Photoluminescence
CQ	Collisional Quenching	PMMA	Poly(methyl methacrylate)
CDEC	Chemical Reactor	DOM	Polyoxymethylene
CREC	Engineering Centre	FUN	
CSD	Chemical Solution Depositon	PVC	Polyvinyl Chloride
CVD	Chemical Vapour Deposition	PVD	Physical Vapour Deposition
DC	Direct Current	RF	Radio Frequency
DNA	Deoxyribonucleic Acid	RhB	Rhodamine B
DOE	Design Of Experiment	RPM	Rotations Per Minute
EDV	Energy-Dispersive X-ray	DOG	Reactive Oxygen Species
EDX	spectroscopy	KU5	
FEG	Field Emission Gun	SE2	Secondary Electrons
FIB	Focused Ion Beam	SEM	Scanning Electron Microscopy
FOM	Figure Of Merit	SO	Sodium Oxalate
GC-MS	Gas Chromatography–Mass	SN	Sodium Nitrato
	Spectrometry		Soululli Initiate

HPLC	High Performance Liquid	SZM	Structure Zone Model
	Chromatography		
	High Resolution	TEM	Transmission Flootron
HRTEM	Transmission Electron		Microscowy
	Microscopy		Microscopy
ICDD	International Centre for	ТМР	1 Undrown Tomas
	Diffraction Data		4-nydroxy-1empo
IC	Internal Conversion	TOC	Total Organic Carbon
ΙΡΑ	Isopropul Alashal	TRLP	Time Resolved
IPA	ізоргоруї Асопог		Photoluminescence
IR	Infrared	TSA	Trypton Soya Agar
ISC	Intersystem Crossing	TSB	Trpyton Soya Broth
150	International Organization for	UV	Liltrovialat
ISO	Standardization	U V	Olliaviolet
ja	Atom flux	UV-Vis	Ultraviolet-Visible
ICPDS	Joint Committee on Powder	VR	Valence Band
JCIDS	Diffraction Standards	۷D	valence Dand
ji	Ion flux	WHO	World Health Organization
KA	Kelly and Arnell	WLI	White Light Interferometry
Kn	Knudsen Number	WWTP	Wastewater Treatment plant
I C-MS	Liquid Chromatography-	VPS	X-ray Photoelectron
	Mass Spectrometry	лгэ	Spectroscopy
I CPR_I	Low-Cost Photocatalytic	VRD	X-ray Diffraction
LUI K-I	Reactor I	AND	A-ray Diffaction
LCPR-II	Low-Cost Photocatalytic	VAC	Vitaina Almaining Compt
	Reactor II	IAG	
MB	Methylene Blue		

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P. Dutra, M. Grao, M. Ratova, C. Amorim, A. Santosa, P. Kelly, 'TiO₂-Graphene photocatalytic nanocomposites prepared through a DC Magnetron Sputtering system', Journal of Environmental Sciences.

Part 1. Background and context

Chapter 1. Introduction

The primary goal of this research was to build an efficient laboratory-scale photocatalytic reactor, for wastewater treatment. The photocatalysts were produced by magnetron sputtering, as it is already widely used to produce coatings on an industrial scale, for various applications. This chapter lays out the different approaches, which were studied, to transition from a "bench scale" to a "laboratory scale" wastewater treatment system. This chapter also provides an overview of the work, including background information and motivation, a description of the main research, and information about the thesis layout.

The chapter is structured as follows: Background and motivation for this work are provided in Section 1.1, research and aims are described in Section 1.2 while Section 1.3 lays out the thesis structure.

1.1. Background and motivation

In 2015, 844 million people still lacked basic access to drinking water while 711 million people used inadequately treated sewer connections [1]. As a result, one child dies from contaminated water every two minutes [2]. These deaths are preventable and call for new and reliable methods to treat unsanitary water. According to the data published by the World Health Organisation (WHO), in 2017 almost a third of the global population did not have access to safely managed, available and uncontaminated drinking-water services (World Health Organization, 2019). It is predicted that by 2025, half of the world's population will be living in water stressed areas. Use and consumption of unsanitary water is known to result in rapid spread of diarrhoea, cholera, dysentery, typhoid, and polio, thriving and praying on the most vulnerable populations. In the near future, water scarcity and imbalance is predicted to be one of the many consequences of climate change [8]–[10]. Pollutants found in wastewater come in all shapes and sizes: metallic ions, microplastics, bacteria, hydrocarbons, nitrates, ammonia, textile dyes, pharmaceuticals compounds, pesticides [11]–[13].

Their origin can be traced back to pharmaceuticals and personal care product (PPCPs) consumption [14] and industrial discharges which may contaminate surface water, ground water and soil. The main reason wastes are not safely treated is due to a lack of efficient and economical treatment technologies. Wastewater treatment plants were not originally designed to eliminate such a complex and diverse group of hazardous compounds. Those wastes are disastrous to the environment, but they keep being produced to support the industrialization of countries, whose economy and development rely on the manufacturing plants and factories.

Although there is a wide variety of wastewater treatment plants, they typically operate with the same sequential steps. First, wastewater undergoes a pre-treatment phase, where solid bulky wastes are removed and flowed into a primary sedimentation tank. Floating fats and sediments are removed and treated in sludge treatment facilities, while the remaining effluent is channelled into a secondary sedimentation tank [15]. The organic load in the wastewater is then considerably reduced through the use of biological processes, such as activated sludges. The final tertiary step focuses on the inactivation of microorganisms and decomposition of pharmaceuticals, personal care products, pesticides etc. It is usually achieved through chlorination, UV radiation and ozonation [15]. Unfortunately, not only are those additional steps expensive, but they are not always sufficient.

The textile industry is one of the economic pillars of many developing countries, especially in southeast Asia. The dying process of cotton, synthetic and woollen fibres is extremely inefficient and as 700,000 tons of dyes are produced every year, nearly a third is lost to the environment, making up ~20% of total industrial wastewater [16]. These untreated highly soluble dyes are released in water effluents and represent a potentially hazardous and toxic danger to the environment. As previously stated, wastewater treatment plants often rely on chlorination to disinfect the water. The main issue with this approach is that, although chlorine is powerful antimicrobial agent, it also reacts with colorants, such as dyes, and forms toxic and/or mutagenic compounds, which are then released in wastewater treatment plants effluents[17]–[19]. Antibiotic resistance is another area of concern when considering wastewater treatment; it relates to the capacity for microorganisms (e.g., bacteria) to survive the usually damaging or lethal effects of antibiotic compounds. Whilst antibiotic resistance has always developed naturally, the anthropogenic and overuse of antibiotics has resulted in a significant increase in resistant microorganisms capable of causing deadly infections across the world.

As such, the WHO has declared antimicrobial resistance one of the top ten global public health threats facing humanity [20]. Traces of antibiotics will inevitably make their way into the wastewater system as a result of human and animal excretion, due to incomplete metabolism, and disposal of unused drug wastes from pharmaceutical manufacturing processes [21]. In addition to this, wastewater provide an ideal location for bacterial growth due to the abundance of organic matter, presence of oxygen and nitrate, stable temperatures and adequate pH [21]. These conditions in addition to sub-inhibitory traces of antibiotics can result in, and even increase rates relating to evolution and transfer of resistance in and between bacteria [22], [23], which can result in large numbers of antibiotic resistant bacteria being discharged into other water systems. As such, removing antibiotics from wastewater is of critical importance. Antibiotics in concentrations ranging from µg.L⁻¹ to ng.L⁻¹ were detected in wastewater treatment plant effluents in Japan [24], United Kingdom [25], Sweden [26], Croatia [27], Spain [28], China [29], Slovakia [30], Germany [31], Finland [31], Ireland [31], Norway [31], and Portugal [31].

Conventional wastewater treatment plants (WWTP) are simply not designed to treat the massive and diverse loads of organic contaminants originating from industrial/agricultural discharges and homes. These inefficient WWTPs need to adapt to these new pollutants, which calls for new advanced water treatment technology, such as photocatalysis.

1.2. Research aims

This section summarises the research goals and objectives of this project and aims at characterising the contributions of this work. The goal of this thesis is to produce a laboratory-scale wastewater treatment photocatalytic reactor, based on functional photocatalytic coatings deposited by magnetron sputtering. Therefore, the project was subdivided into the following research directions:

- 1. Optimisation of the deposition conditions, to produce, in a one-step process, photocatalytic TiO_2 deposited onto stainless steel mesh.
- 2. Build an affordable laboratory-scale photocatalytic reactor, integrate the TiO₂-coated mesh in the reactor and optimise the operating conditions to improve the reaction yield.

- 3. Produce a novel bismuth titanate photocatalyst by co-sputtering, characterise it and compare its performances to the well-established TiO₂.
- 4. Integrate the bismuth titanate photocatalyst in the bespoke photocatalytic reactor, optimise the operating conditions based on previous experiments and test the reactor against a pollutant of concern.

In this thesis two different approaches were adopted to produce a laboratory scale photocatalytic reactor. The first one consists in improving the deposition process of a tried and tested photocatalyst, TiO₂, to make it as easy and inexpensive as possible to produce. The second one consists in producing a more efficient photocatalyst using a more complex and expensive deposition process. In both cases, the photocatalysts were successfully integrated in an affordable, bespoke, proof-of-concept wastewater treatment reactor. These two approaches used in this thesis are illustrated Figure 1.



Figure 1. Flowchart of the scientific approach used in this Thesis.

1.3. Thesis structure

The thesis is divided into four parts, which are further divided into 10 chapters and the appendices. Part I presents the background information and research relevant to the thesis contributions and findings. Part II describes the analytical and experimental techniques used in this project for the thin film production and characterization. Part III provides an extensive description of the results obtained during this work. Part IV outlines the main findings of the work and suggests some possibilities for future research.

A more detailed description of the thesis structure is as follows:

In Chapter 1, the background and motivations of this thesis are defined, with an overview of the research aims and contributions.

In Chapter 2, the main principles of photocatalysis are introduced, the mechanisms are described and TiO_2 , the most popular photocatalyst, is reviewed. This chapter also gives a description of promising TiO_2 alternatives and of the current state of photocatalytic reactor research.

In Chapter 3, an overview of different thin film deposition techniques and of the mechanisms involved in thin film growth is presented. The chapter also focuses on magnetron sputtering and vacuum technologies.

In Chapter 4, an overview of the different statistical analysis tools used in this thesis is given, more details are provided in the Annexe.

In Chapter 5, the deposition chamber used to produce the coatings is described and an overview of the analytical tools used to characterise them is given.

In Chapter 6, deposition parameters are investigated, to produce photocatalytic TiO₂ coatings on stainless steel mesh, by reactive magnetron sputtering, in a one-step process.

In Chapter 7, large sheets of TiO_2 coated stainless steel mesh are integrated in a bespoke laboratory-scale photocatalytic reactor and the several parameters are investigated to optimise the photocatalytic degradation process.

In Chapter 8, a novel bismuth titanate photocatalyst was produced by reactive cosputtering, its characteristics and photocatalytic performances were investigated and compared to those of TiO_2

In Chapter 9, the bismuth titanate photocatalyst was coated onto stirring glass rods, integrated into the previously optimised photocatalytic reactor and its ability to decompose antibiotics was assessed.

In Chapter 10, results are summarised and discussed, and further research work suggestions are given.

8

Chapter 2. Photocatalysis

In this chapter the phenomenon of semiconductor photocatalysis and titanium dioxide as one of the widely used photocatalytic materials are introduced. The chapter provides an overview of the mechanisms involved in photocatalysis, alternative photocatalysts and on different types of existing photocatalytic reactors. The chapter introduces the main advantages and drawbacks of using titanium dioxide as a photocatalyst and briefly reviews the methods of improving its efficiency that are intended to be used in terms of this work.

The chapter is structured as follows. Section 2.1 provides an introduction to semiconductor physics, Section 2.2 presents the advanced oxidation processes, with a focus on photocatalysis. The most popular photocatalyst, titanium dioxide, is presented in Section 2.3, while interesting alternatives are discussed in Section 2.4. Finally, Section 2.5 provides an overview of the existing models of photocatalytic reactors.

2.1. Semiconductors

A semiconductor can be defined by its electrical resistivity which is typically in the range of 10^{-2} and 10^9 (Ω ·m) and lies between those of metals and dielectric materials, but it can also be defined by its band gap which lies between 0 and 4 eV [32]. In solid state materials, the band theory states that electrons populate energy levels called "bands" following the Fermi–Dirac distribution. Bands of high and low energy are usually disregarded for being inert as they are generally completely empty or filled with electrons, respectively. The most interesting bands are those close to the Fermi level, which can be defined as a level which has a 50% chance to be occupied at any temperature [33]. Materials with a zero bandgap are considered conductors, as their valence and conductance bands overlap at the Fermi level, granting mobility to the electrons. Materials with a bandgap higher than 4 eV are considered insulators and with such a large band gap, electrons from the valence band cannot make the jump to the conduction band.



Figure 2. Band structure of different types of solid-state materials

On the other hand, the small bandgap of semiconductors can be crossed by electrons, provided they receive a thermal or optical excitation of sufficient energy. As a result, the normally empty conduction band is populated by electrons, while the normally fully populated valence band has unoccupied states [34].

These unoccupied states are referred to as holes, and with their corresponding thermally or photo generated electrons, are referred to as electron-hole pairs or excitons. Semiconductors with a fermi level halfway through the valence band and the conduction band are called intrinsic semi-conductors, while those with a fermi level close to the valence band or conduction band are respectively called p-type and n-type semi-conductors [35]. These different band configurations are summarised for each type of solide-state material in Figure 2.

2.2. Advanced oxidation processes

The Fenton reactions, catalytic ozonation and photocatalysis are advanced oxidation processes used to treat organic pollutants present in water. Advanced oxidation processes (AOPs) can be defined as set of chemical treatment used to decompose organic compounds in water and wastewater by oxidation utilising highly reactive species; OH^{\bullet} in particular, to oxidize recalcitrant toxic compounds into less harmful products and eventually mineralize them.

Hydroxyl radicals are highly reactive species, with little selectivity, attacking most organic compounds with high constant rates ranging from 10^6 to 10^9 M⁻¹.s⁻¹[36]. *OH*[•] reacts with saturated and unsaturated organic compounds by hydrogen abstraction (1) or electron abstraction (2) followed by deprotonation (3). Comparatively, ozone which is an oxidiser commonly used in water treatment plants, has a kinetic constant rates for organic compounds ranging from 10^{-2} to 10^5 M⁻¹.s⁻¹[37].

$$RH + OH^{\bullet} = R^{\bullet} + H_2 O \tag{1}$$

$$RH + OH^{\bullet} = RH^{+} + OH^{-} \tag{2}$$

$$RH^+ = R^{\bullet} + H^+ \tag{3}$$

2.2.1. Fenton oxidation process

The Fenton reaction was discovered by H.J.H Fenton in 1984 and is based on the reaction between hydrogen peroxide (H_2O_2) and ferrous oxides $(Fe^{2+})[38]$, [39]. The general reaction can be summarised by a rapid decomposition of hydrogen peroxide by ferrous oxides into ferric ions Fe^{3+} and hydroxyl radicals (4). The hydroxyl radicals can then oxidise organic pollutants into less harmful compounds until they are finally mineralised (5). This reaction is widely used to remove organic compounds from contaminated wastewater [38]. The main advantages of the Fenton reaction are the simplicity of the process, the reaction's high yield and the inexpensiveness of the reagent. However, to work effectively the reaction's pH has to be maintained at an acidic level. Furthermore, it suffers from scalability issues and from excessive iron sludge production [40]. To overcome these limitations, modifications to the

process have been researched such as the heterogeneous Fenton reaction, the fluidized-bed Fenton process and the electro- Fenton process [38], [40].

$$H_2O_2 + Fe^{2+} + H^+ = Fe^{3+} + HO^{\bullet} + H_2O \tag{4}$$

$$HO' + pollutant = degradation \ products \tag{5}$$

2.2.2. Catalytic ozonation

As explained previously in 2.2, ozone's oxidation potential for organic compounds is not as strong as hydroxyl radicals, meaning it cannot completely mineralise some organic compounds which can lead to an accumulation of potentially dangerous by-products. To overcome this weakness, a catalyst can be added to the process to enhance the degradation of organic compounds. The surface of the catalyst is used to favour the decomposition of ozone into hydroxyl radicals which are more suitable for organic compound mineralisation [41]. The catalytic ozonation can be homogeneous using transition metal ions or heterogeneous solid ceramic catalysts.

The phenomenon of photocatalysis was first reported by Fujishima and Honda in 1972, who discovered that water splitting could be achieved by irradiating a TiO₂ electrode with UV light in a photoelectrochemical cell [42]. Photocatalysis quickly found numerous applications, other than water electrolysis, such as air/water purification, self-cleaning coatings, nonspotting glass, self-sterilising coatings, cancer treatment, selective synthesis of organic compounds etc. [43]–[48]. When exposed to a light source of appropriate wavelength (hv >Eg), a photocatalyst can generate excitons, which react with ambient water or oxygen molecules to form radical species (Figure 3). The electrons and holes are produced in the photocatalyst's conduction and valence bands, respectively (6). These mobile charge carriers then diffuse to the surface of the catalysts and react with ambient adsorbed oxygen and water, to produce radical species (7), (8). These radical species can either produce other radical species (9), (10), (11), or directly oxidise organic pollutants, until complete mineralisation is achieved via the reactions described in 2.2. Contrary to the Fenton oxidation process and to catalytic ozonation, photocatalysis does not require any chemical, *i.e.*, peroxide or ozone, to produce reactive radical species and decompose organic pollutants. Photocatalysis only requires a photocatalyst, water and a source of irradiation to decompose pollutants, which make it a method of choice for large scale wastewater treatment applications. Although photocatalysis it a promising process, there is still a lot of room for improvement, as mobile carrier recombination and limited light absorption spectrum are highly detrimental to the catalyst reaction yields [49], [50]. Furthermore, the photocatalytic degradation of organic compounds may result in the production of intermediary species with higher toxicity than the original pollutant, as has been demonstrated by S. Rodriguez et.al [51].



Figure 3. Radical species produced by a light activated photocatalyst

 $Photocatalyst + h\nu \to h_{VB}^+ + e_{CB}^- \tag{6}$

 $h_{VB}^{+} + H_2 O \to H^+ + OH^{\bullet} \tag{7}$

$$e_{CB}^{-} + O_2 \to O_2^{\bullet -} \tag{8}$$

$$O_2^{\bullet-} + 2H^+ \to H_2O_2 \tag{9}$$

$$H_2 O_2 + H^+ + e_{CB}^- \to OH^\bullet + H_2 O$$
 (10)

$$H_2 O_2 + e_{CB}^- \to OH^\bullet + OH^- \tag{11}$$

2.2.4. Photocatalytic degradation of organic pollutants

Dyes, antibiotics, drugs, personal care products, endocrine disruptors, pesticides, and many other contaminants are found in traces in municipal wastewater and sometimes in higher concentrations in industrial effluents [52]. Continuous exposure to such chemicals, even in trace concentrations are of concern, as they can be the source of serious health hazards [53]. Photocatalysis has shown promise as an efficient, economical and environment-friendly method to treat such chemicals [50], [54].

Photocatalytic water or air treatment is mainly driven by radical species, O_2^{*-} and OH^* , also known as reactive oxygen species (ROS). Hydroxyl radicals in particular are highly reactive species, believed to play a major role in the photocatalytic oxidation of organic compounds [55]. Their high reactivity toward organic molecules is attributed to their oxidation potential, second to only fluorine ions (Table 1), with reaction rate constants usually of the order of 10^{6} - 10^{9} mol.L⁻¹.s⁻¹[54]. These ROS react with contaminants within the vicinity of the photocatalyst's surface, by initiating several sequential reactions, ultimately resulting in the mineralisation of organic pollutants. These reactions include (but are not limited to): breaking double bonds, degrading hydrocarbons, cause epoxidation, opening aromatic ring, radical polymerization, and formation of secondary radicals. The high reactivity and non-selectivity of ROS make photocatalysis a versatile tool, which can be employed to eliminate potentially harmful organic compound present in water.
Species	Oxidation potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Permanganate	1.68
Chlorine dioxide	1.58
Chlorine	1.36
Dioxygen	1.26

Table 1. Oxidation potential of different oxidative agents [54].

Methylene blue is the most studied dye in the field of photocatalysis, yielding close to 10000 results, when using the Sciencedirect.com research engine with the keywords "photocatalysis" and "methylene blue". It is in fact used as a standard for activity assessment of photocatalytic materials under UV (ISO 10678:2010) [56].

It belongs to the thiazine dye family, which are characterised by a ring of four carbon, one nitrogen and one sulphur atoms. Its popularity among researchers, as a model pollutant, may be attributed to its stability, inexpensiveness and simple concentration monitoring when in solution, via UV-Vis spectroscopy.

Ammar Houas *et al.* studied the degradation of methylene blue in water, by P25 under UV light irradiation and reported the final mineralisation products, after 1000 hours, to be sulphate ions, nitrate ions, carbon dioxide and water molecules [57]. Degussa (Evonik) P25, is a widely used titanium dioxide photocatalyst, popular due to its high photocatalytic activity and is used as a de-facto standard photocatalyst. P25 is composed of anatase and rutile crystallites, with ratio varying from 70:30 to 80:20 [58]. Total mineralisation via photocatalysis of complex organic compounds is a time dependent process and produces many intermediary products. These intermediates may be more toxic than their original molecule and need to be considered carefully [59]. In the case of methylene blue, mineralisation is believed to be hydroxyl radical driven, initiated by the cleavage of the $C - S^+ = C$ functional group, shown in Figure 4 (a, b), and followed by dissociation of the two aromatic rings (Figure 4 (c, d)) [57]. Eventually, the constant attack of hydroxyl radicals will lead to the loss of functional groups in intermediary products (Figure 4 (e, f, g, h)), until only simple molecules remain.



Figure 4. Photocatalytic degradation pathway of MB [57].

2.2.5. Photocatalytic inactivation of microorganisms

According to the World Health Organisation (WHO), developing countries, especially rural areas, are the most vulnerable to infectious diseases caused by hazardous microorganisms [60]. The pathogens' origins can usually be traced back to water contamination by human or animal faeces. These pathogens belong to 4 main groups of microorganisms: bacteria, viruses, protozoa and parasitic worms [60]. Therefore, photocatalysis has the potential to improve the quality of drinking water, providing significant worldwide health benefits, especially in developing countries. Photocatalysis has been shown to be an effective method to inactivate all of these groups [61]. However, the time required to inactivate these pathogens varies greatly, from one microorganism to another, and seems to depend on the cell wall properties.

Microorganisms with a complex and/or thick wall structure have shown more resistance to photocatalysis; generally, protozoa are considered the most resistant, followed by spores, viruses, fungi and bacteria [61]. Resistance to photocatalysis varies among different domains of pathogens, but also within different domains. For example, Gram-positive bacteria tend to be more resistant to photocatalysis than Gram-negative ones, as a result of their different cell wall structure. The former generally consist of numerous layers of peptidoglycan and teichoic acid, while the latter consist of a few layers of peptidoglycan surrounded by a second lipidic membrane [61].

The inactivation mechanism of microorganisms through photocatalytic treatments is not completely understood. However, in bacteria, photogenerated radicals are believed to puncture the membrane, via oxidation-reduction reactions, leading to cells spilling their content and eventually dying. S. Pigeot-Rémy *et al.* examined this particular mechanism in *E. coli* cells, in the presence of P25 under UV-A irradiation, using transmission electron microscopy (Figure 5) [62]. After 80 min of treatment, displayed in Figure 5a, the integrity of the cell wall seems disrupted, most likely due to its lipid components being oxidised, by radical species [62]. After 180 min, the cell walls seem to succumb to the radical's attack, rupturing (Figure 5b), and spilling the cell's content (Figure 5c) [62].



Figure 5. TEM micrographs of E. coli cells suspended in water solution with P25 (0.25 g.L⁻¹) after: (a) 80 min, (b) and (c) 180 min of UV-A (3.45 mW.cm⁻²) exposure; with (1) cell's membrane, (2) cell's content and (3) P25 [62].

A bacterium can be visualised as a complex machine, kept alive and active by thousands of intricate processes. Antibiotics used against these pathogens specifically aim to disrupt this complex machine by interfering with its metabolism, slowing its growth or attacking its DNA. As a response, by pure random chance, bacteria can evolve to express proteins, able to bind and inactivate a specific antibiotic and/or use efflux pumps to eject it from its system before it can do damage [63].

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Unlike antibiotics, photocatalysis does not target any specific essential process in bacteria; membranes tend to be preferentially attacked, as they are the most exposed component. Bacteria cannot, to this day, develop efficient resistance against it, but it doesn't mean that they do not possess defence mechanisms. Under oxidative stress, bacteria are known to produce enzymes, namely superoxide dismutase, catalase and peroxidase; these proteins bind to radical species, forming harmless compounds [61], [62]. Although these ubiquitous natural defences against oxidative stress slow the inactivation process, they eventually are overwhelmed by the sheer abundance of radical species.

The main drawback of non-specific targeting of bacteria is that as they are punctured, radical species react with the cell's content (cytoplasm, organelle, DNA etc.). Consequently, fewer radicals are available to react with other viable bacteria membranes, giving them time to repair themselves and eventually, slowing the inactivation process [61].

Photocatalysis has shown promises in the inactivation of microorganisms from contaminated water, but the process has yet to be fully understood and efforts should be undertaken to improve the reaction kinetic. Although there is no specific bacterial protection against radical attack, the inactivation process can be severely slowed down, rendering it non-applicable in large scale process.

2.3. Titanium dioxide

Titanium (Ti) is a metal recognised for its mechanical properties, high strength to weight ratio, high melting point, resistance to corrosion, biocompatibility and abundance; it is ranked 9th most abundant element in the earth's crust [64]. Given titanium's refractory properties, it is commonly used for high temperature applications as an alloy in jets, missiles and aircrafts, while it is used in laboratories and medical equipment for its biocompatibility and inertness [64]. As an oxide, titanium dioxide (TiO₂) or "titania", has a naturally white opaque colour, in its powder form and is characterised by a broad-spectrum reflectance. Titania is inexpensive, biocompatible, abundant, stable and non-toxic, and thus, is well suited for large scale industrial applications. Hence, it is extensively used as a pigment in sunscreens, paints, ointments, toothpaste and as a food additive [64], [65]. Most importantly, it is a N-type semiconductor, whose photocatalytic properties were first discovered by Fujishima and Honda in 1972 [42].

Ever since it has been used for various applications, such as: hydrogen production by water splitting, dye-sensitised solar cells, air/water purification, self-cleaning coatings, non-spotting glass, self-sterilising coating etc. [48], [66]. Titania has three polymorphs, which are all photocatalytic: anatase, rutile and brookite; on the other hand, amorphous TiO₂ is not. Anatase and brookite are both metastable, while rutile is a stable polymorph. Consequently, the transition from either anatase or brookite to rutile is irreversible and occurs at high temperatures [67]. Although brookite shares characteristics similar to anatase and rutile, it is hard to synthesise and produce on a large scale [68]; therefore, it will not be discussed in this work. As illustrated in Figure 6, both anatase and rutile belong to a tetragonal crystal system, composed of TiO₆ octahedron. However, they differ in their arrangements, with anatase's octahedron sharing four edges with each other, whilst rutile's share two [67], [69], [70].



Figure 6. Illustration of anatase and rutile crystalline structures [67].

In crystalline TiO₂, the bandgap energy value is determined by the difference between the highest occupied and lowest unoccupied molecular orbitals, Ti (3d) and O (2p), respectively. This energy gap (E_g) is estimated to be of ~3.2 and ~3.0 eV for anatase and rutile, respectively. Hence, when crystalline TiO₂ is excited by a photon hv (> E_g), an electron-hole pair is generated, initiating photocatalytic reactions. Although anatase possesses a higher bandgap, it is generally accepted as the most active of the two. This is most likely a consequence of anatase's Fermi level being ~ 0.1 eV higher than rutile's, and its smaller average grain size [71], [72]. In the former case, photogenerated charge carriers have a higher redox potential and, in the latter, it tends to have a higher specific surface area.

2.3.1. Photon absorption

Most photon absorption events in photocatalytic reactions typically occur in the bulk of the material. Titanium dioxide's surface electronic structure is distinctly different from its bulk, and different excitation events can take place. However, these differences need only be considered when the surface-to-volume ratio of the material is important, *i.e.*, nanoparticles <10 nm in size. Considering the thicknesses of the coatings involved in this work, varying from hundreds of nanometres to microns, it is reasonable to assume, that most photon absorption events occur in the material's bulk. The bulk optical properties of both anatase and rutile are well-documented, with energies for valence to conduction band transitions occurring are at \sim 3.2 and \sim 3.0 eV, respectively [73]–[75]. Hence, the maximum wavelength required to photo generate electron-hole pairs is ~387 and ~413 nm for anatase and rutile, respectively. In other words, as a photocatalyst, anatase can only utilise UV light, whilst rutile can utilise UV light plus a fraction of the visible light spectrum. However, electron photogenerated in anatase crystals have a higher reduction potential, which improves their transfer from the photocatalyst to the adsorbed molecules. As illustrated in Figure 7, more than 90 % of the solar spectrum is composed of visible and infrared light, while ultraviolet represents less than 5 % of the spectrum [76]. Hence, on its own, titanium dioxide is an ill-suited photocatalyst for outdoor, solar applications.



Figure 7. Solar spectrum [76].

2.3.2. Charge transport and trapping

Upon exposure to photons of sufficient energy ($hv > E_g$), electrons from the valence band can cross the band gap energy threshold, through inter-band transitions, to the conduction band. As a result, electrons and holes are photogenerated in the valence and conduction bands, respectively, forming electron-hole pairs. Ideally, these photogenerated species should diffuse to the surface of crystalline titanium dioxide, to initiate a charge transfer, through redox reactions, with adsorbed O₂ and H₂O molecules, forming radical species; this is a fundamental step to every photocatalytic reaction. However, prior to the charge transfer, these electron hole pairs can recombine during the diffusion step, in the catalyst's bulk or surface, releasing energy as light or heat. Consequently, as shown in Figure 8, recombination and charge transfer events are competing for the consumption of photogenerated species; the former being detrimental to photocatalytic reactions, while the latter is beneficial. It is estimated that less than 10 % of the photogenerated charge carriers are used for redox reactions, while the rest are recombined and radiated away as heat and light [77].



Figure 8. Schematic representation of the photogenerated charge carrier's movements in TiO2.

Although practical, this simplified representation (Figure 8), doesn't reflect the complexity of the mechanisms involved in photocatalysis. In materials sciences, crystalline materials are defined by their highly ordered atomic structure, extending in all directions. However, real crystalline materials do have defects such as: vacancies, interstitial atoms, substitution atoms, dislocations and grain boundaries. In TiO₂, such defects can act as traps for the photogenerated species by allowing mid-gap energy states to exist in the band gap. When a defect traps either photogenerated specie, it is referred to as shallow trap, if the next most probable event is re-excitation [34]. On the other hand, if the next most probable event is the capture of the opposite photogenerated specie, it is referred to as a deep trap or recombination centre [34]. In general, deep traps are located near the middle of the bandgap, whereas shallow traps are located near the valence and conduction bands. The behaviour of the defects is a direct consequence of their position in the bandgap. For example, an e_{CB}^- trapped in a defect located in the middle of the bandgap of an anatase crystal would require an energy of ~1.6 eV to be re-excited toward the CB, while an e_{CB}^- trapped in a defect near the conduction band would only require ~0.1 eV.

Hence, a charge carrier trapped in shallow trap has a higher probability of being reexcited before an opposite charge carrier gets trapped as well; and vice-versa for the deep trap. Overall, recombination centres or deep traps are detrimental to photocatalytic processes, as they prevent charge transfer, and ultimately redox reactions from occurring. Unlike deep traps, shallow traps can be beneficial to photocatalytic reactions as they promote charge carrier separation, and ultimately prevent recombination events [77].

Kohtani *et al.* developed a model of the different pathways undertaken by photogenerated species in anatase crystals, summarised in Table 2 [78]. When TiO₂ is excited by a photon hv of sufficient energy ($\geq 3.2 \text{ eV}$), an electron-hole pair is generated (12). Photogenerated electrons can either diffuse to the surface of TiO₂, to react with adsorbed electron acceptors to form radical species, (16) or be trapped by Ti⁴⁺ defect sites (13). These trapped electron acceptors (7). Similarly, holes diffuse to the surface of photocatalyst to be trapped by surface hole trap sites (14), (15). Then, they either react with adsorbed electron donors to form radical species (18) or recombine with captured electrons (19), (20) or trapped electrons from other defect sites (22), (21). The time scales of these different events are laid out in Table 2, and highlight that on average, recombination events are orders of magnitudes faster than charge transfer events, and thus, they are more likely to occur. Charge carrier kinetics is highly influenced by crystalline phase(s), crystallinity, specific surface area, and defects; exploring and understanding their relationships are essential to design more efficient photocatalysts [77], [78].

Reaction	Time scale (s)	Equation No.			
Electron-hole pair photogeneration					
$TiO_2 + hv \rightarrow h_{VB}^+ + e_{CB}^-$	<10 ⁻¹³	(12)			
Electron and hole trapping					
$Ti^{4+}_{ds} + e^{CB} \to Ti^{3+}_{ds}$	$10^{-10} - 5 \times 10^{-13}$	(13)			
$Ti - OH_s + h_{VB}^+ \rightarrow Ti - OH_s^{\bullet+}$	$<1-2 \times 10^{-13}$	(14)			
$Ti-O-Ti_s+h_{VB}^+\to Ti-O-Ti_s^{\bullet+}$	$<1-2 \times 10^{-13}$	(15)			
Radical species formation via charge transfer					
$e_{CB}^- + A_{ads} \to A_{ads}^{\bullet -}$	>10 ⁻⁸	(16)			
$Ti_{ds}^{3+} + A_{ads} \rightarrow Ti_{ds}^{4+} + A_{ads}^{\bullet-}$	Slow process	(17)			
$Ti - O - Ti_s^{\bullet +} + D_{ads} \rightarrow Ti - O - Ti_s + D_{ads}^{\bullet +}$	$10^{-8} - 10^{-10}$	(18)			
Recombination events					
$Ti - OH_s^{\bullet +} + e_{CB}^- \to Ti - OH_s$	$10^{-11} - 10^{-12}$	(19)			
$Ti - O - Ti_s^{\bullet +} + e_{CB}^- \rightarrow Ti - O - Ti_s$	$10^{-11} - 10^{-12}$	(20)			
$Ti - OH_s^{\bullet +} + Ti_{ds}^{3+} \rightarrow Ti_{ds}^{4+} + Ti - OH_s$	>2 × 10 ⁻⁸	(21)			
$Ti-O-Ti_s^{\bullet+}+Ti_{ds}^{3+}\rightarrow Ti_{ds}^{4+}+Ti-O-Ti_s$	>2 × 10 ⁻⁸	(22)			

Table 2. Steps involved in the early stage a photocatalytic reaction in anatase TiO₂ [78].

ds: defect site; s: surface; CB: conduction band; VB: valence band; A: electron acceptor (ex: O₂); D: electron donor (ex: H₂O), ads: adsorbed

2.3.3. Titanium dioxide modification

As explained in 2.3.1 and 2.3.2, crystalline titanium dioxide is hindered by its lack of visible light absorption and high charge carrier recombination rate. Fortunately, it can be modified to extend the former and/or the latter. Such feats can be achieved by doping or co-doping titanium dioxide with non-metal, transition metal, noble metals or combining it with other photocatalysts. Table 3 summarises the three most popular categories of elements used to dope TiO_2 .

- Non-metal doping is usually carried out with elements having an atomic radius similar to oxygen, such as boron, carbon, and nitrogen [79], [80]. These dopants are thought to distort the TiO₂ lattice via oxygen atom substitution or by interstitial site occupation, ultimately creating mid-gap states. Substitutions tend to introduce local states right above the valence band, making them good acceptors and improving visible light absorption [81]. On the other hand, interstitial sites tend to form shallow donor Ti³⁺ states, right below the conduction band, improving charge carrier separation [81].
- Noble metals can be defined as a group of metals resistant to corrosion and oxidation. In the field of catalysis, they are praised for their stability, selectivity and ability to change their oxidation state [82]. Unfortunately, as their name suggests, they are rather expensive and in short supply, and although efforts have been made to find alternatives, in many cases, they are irreplaceable. In the context of photocatalysis, their enhancement is thought to be attributed to surface plasmon resonance (SPR) effects and Schottky barrier [83], [84]. SPR is a light induced collective electron oscillation, occurring at the surface of metal nanoparticles when in contact with a dielectric or semiconductor [83]. This photogenerated localised electric field induces the formation of electrons, which can be transferred to the conduction band of TiO₂. Noble metals exhibit SPR effects under visible light, which would explain the enhanced visible light activity of noble-metal-doped TiO_2 [83], [84]. The junction between the semiconductor and the noble metal is also believed to produce an electric field known as a Schottky barrier. The misalignment of the metal and semiconductor Fermi levels caused by the junction is rectified by a flow of electrons from the semiconductor to the metal, until equilibrium is reached. Hence, the populated (metal) and depleted (semiconductor) layers of the junction produce a permanent electric field, forcing the photogenerated species into different direction and ultimately preventing recombination events [83].

• Alternatively, titanium dioxide can also be doped with transition metals, which can be a cost effective way to replace noble metals [85], [86]. However, the improved photocatalytic performances arise from different mechanisms and therefore often do not match the levels of activity of noble metals. Visible light absorption can be enabled via charge transfer between the Ti (3d) or O (2p) orbitals of TiO₂ and the d level of transition metals [87]. Additionally, transition metals ions can form shallow traps near the conduction and/or valence band, inhibiting charge-carrier recombination [88].

Doping is an interesting approach to improve TiO₂, but it comes with a few caveats. Introducing impurities through doping can produce shallow traps, inhibiting charge-carrier recombination, but they may also produce deep traps, which have the opposite effect [79]. Consequently, not only does the nature of the dopant matter, so does its concentration, as it can both supress and enhance photocatalytic activity. Likewise, dopants used to promote bandgap redshift, often promote recombination centres; in a way, some photocatalytic activity under UV light is traded for some under visible light [79]. Dopants may also supress or hinder the crystallisation process, due to lattice deformation, thereby requiring more energy to form crystalline structures. Finally, metal-doped photocatalysts tend to be thermally unstable, while non-metal doped photocatalysts are prone to dopant leeching when annealed [89].

Doping element		Reference
	Non-metals	
В		[90], [91]
С		[92], [93]
Ν		[94], [95]
	Noble metals	
Pd		[96]
Ag		[97], [98]
Pt		[99]–[101]
Au		[100], [102], [103]
	Transition metals	
Cu		[104], [105]
V		[88]

Table 3. Non exhaustive list of TiO₂ dopants.

[106]	Fe
[107]	Co
[108], [109]	Ni
[110], [111]	Zn
[112]	Sn
[113], [114]	W

2.4. Other photocatalysts

2.4.1. ZnO

Zinc oxide resembles titanium oxide in many regards, with its comparable electrical, optical and mechanical properties. Likewise, ZnO is a wide bandgap semiconductor with an energy of \sim 3.37 eV, and thus, as a photocatalyst, it is only active under UV light. In recent years, zinc oxide based photocatalysts have been investigated as potential replacements for TiO₂. Studies have shown that this semiconductor not only displayed photocatalytic activity, but it also possesses antifouling and antibacterial properties [115].

Compared to titanium dioxide, zinc oxide uses a narrower fraction of the solar spectrum, but this weakness can be offset by its up to 1000 times higher electron mobility [116]. Additionally, S. Liang *et al.* estimated that zinc oxide manufacturing could be up to 75 % more affordable than titanium dioxide [117]. Unfortunately, this photocatalyst also exhibits similar weaknesses to TiO₂, with a high charge-carrier recombination rate and poor visible light absorption. Likewise, efforts have been made to improve the capabilities of this photocatalyst by doping it or coupling it with other semiconductors [118].

2.4.2. SnO₂

Tin oxide, has a high transparency, high infrared light reflectivity, good thermal and chemical stability, and is relatively inexpensive [119]. Like TiO₂ and ZnO, it has a large bandgap of \sim 3.6 eV, and thus, requires UV light to generate mobile carriers. SnO₂ crystallises in a rutile structure, analogous to TiO₂, with an arrangement of SnO₆ octahedron[120]. As a large bandgap semiconductor, SnO₂ suffers from the same drawbacks as TiO₂ or ZnO and the same means are used to cover these weaknesses.

2.4.3. Bismuth based photocatalysts

Bismuth (Bi) is a post-transition metal, 70th most abundant element, characterised by its poor mechanical properties, low toxicity and low melting point. Being considerably less toxic and having properties similar to lead, it is often used as a replacement in alloys. As an oxide, Bi₂O₃ is a semiconductor exhibiting good photocatalytic activity, whilst displaying chemical stability, non-toxicity and relative inexpensiveness. It can crystallise into 4 main polymorphs α , β , γ , and δ , corresponding to the monoclinic, tetragonal, body-centred cubic, and face-centred cubic crystal systems, respectively [121]. Out of all possible polymorphs, α and δ are the only stables phases (low and high temperature, respectively), whilst the other ones are metastable. Although all four polymorphs exhibit photocatalytic activity, the α and β phases have captured most of the attention for their high activity, and most importantly low band gap energies, varying from ~2.1 to ~2.8 eV [121]–[124].

Bismuth vanadate is another interesting material, known for its ferro-elasticity and ionic conductivity, recently introduced to the field of photocatalysis [123]. There are three crystalline phases: monoclinic, tetragonal zircon, and tetragonal scheelite [125], [126].

Of the three, the monoclinic has shown the most potential, with its efficient photocatalytic activity, low band gap of ~2.4 eV, stability, inexpensiveness and non-toxicity [123], [127], [128]. Although it can utilise a larger part of the solar spectrum than titania, it is still held back by poor adsorption and high charge-carrier recombination rate [129]. These limitation were mitigated by doping and/or photocatalyst association, which have shown encouraging results [123], [130].

In recent studies, bismuth has been used as a dopant in TiO_2 for its ability to redshift the bandgap and to favour charge separation [131]–[134]. Bismuth and titanium's ionic radius are respectively 0.96 [134] and 0.64 Å [134], which forbids bismuth from being substituted with titanium in the titanium dioxide scaffold. Instead, when bismuth is introduced, a new bismuth titanate phase $Bi_xTi_yO_z$ arises from bismuth oxide (Bi_2O_3) by substitution of Bi^{3+} by Ti^{4+} ions [131]. Bismuth titanate (BT) refers to a family of semiconductors, mainly comprised of $Bi_{12}TiO_{20}$, $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$, characterised by their high Curie temperature, high dielectric constant and low dielectric energy loss. Hence, BT is mainly used as a replacement for lead based ceramics in capacitors, sensors and actuators [135]. Recently, BT received attention for its photocatalytic activity. $Bi_4Ti_3O_{12}$ belongs to the Aurivillius family and is formed by pseudo-perovskite units ($Bi_2Ti_3O_{10}$)²⁻ sandwiched by fluorite-like (Bi_2O_2)²⁺ layers [136], [137]. $Bi_{12}TiO_{20}$ belongs to the Sillenite family, formed by a network Bi-O polyhedrons connected to TiO₄ tetrahedrons [138], [139]. Finally, $Bi_2Ti_2O_7$ is a pyrochlore, with a cubic structure comprising of Ti_2O_6 octahedron and Bi_2O tetrahedron [140].

2.5. Photocatalytic reactors

To use photocatalysis outside of the boundaries of a laboratory, it must be performed in a so-called photocatalytic reactor. Although there is a wide variety of different looking photocatalytic reactors, they usually share common features such as the presence of a chemical reactor, a light source, a catalyst, a support and a form of solution agitator. Photocatalytic reactor aimed toward wastewater treatment can generally be classified in two categories: the slurry and immobilised ones.

Regardless of their classification, the main characteristics of an efficient photocatalytic should be the following:

- High scalability
- High quantum efficiency
- Low pressure drops
- High catalyst specific surface area
- High mass transfer
- Low cost

Scalability is generally regarded as the main obstacle, in the development of efficient photocatalytic reactors, for industrial and commercial applications. Hence, one must consider reactor geometry, photocatalyst type, form, and irradiation, to overcome such a challenge. On its own, photocatalysis is already hindered by poor visible light absorption and high charge carrier recombination rate. When integrated into a water treatment reactor, these weaknesses are compounded with poor light transmission, due to light scattering and medium absorption.

Although some of the physics and chemistry involved in photocatalysis are relatively well understood, reactor design and engineering still require consideration [141].

2.5.1.Slurry reactor

Slurry reactors are the most commonly used type of reactors in the field of photocatalysis for waste water treatment [142]–[146]. In this configuration, the reactor contains a suspension of supported or unsupported catalyst in a liquid phase with a mechanical or gaseous agitation. Examples of different configurations of slurry reactors are given in Table 4. Generally, slurry reactors outperform their immobilised counterpart because of their inherent higher catalyst specific surface area in contact with the liquid phase and light. The price to pay for this higher efficiency is an added retrieval step, necessary to prevent potentially hazardous catalyst particles from reaching the biosphere. Particles are usually separated from the treated wastewater by porous membranes, integrated into slurry reactors. Although efficient, membrane are susceptible to fouling, light scattering, UV light damage, difficult maintenance and high operational cost [147].

The strength and weaknesses of the slurry reactor configuration are generally the following:

Advantages:

- Uniform catalyst distribution
- High catalyst surface area to water ratio
- Limited mass transfer
- Low pressure drops

Disadvantages:

- Post treatment catalyst filtration step required
- Light scattering and adsorption by suspended particles

Configuration	onfiguration Description	
Slurry annular reactor	Closed annular cylinder reactor filled with the photocatalyst slurry. The light source is positioned at the centre. The inner walls are usually made of quartz to allow the UV to pass through.	[18], [22]–[24]
Open Upflow Reactor	Open or closed reactor design containing the photocatalyst slurry. A micro bubbler provides agitation to the system and improves the photocatalytic reaction by enriching the system in dissolved O ₂ .	[151]–[153]
Integrated Flow Reactor – Membrane Filtration	Combination of a slurry annular reactor with a second membrane filtration reactor. The slurry annular reactor is used to treat the wastewater while the membrane filtration reactor retrieves the photocatalyst to latter be reinjected in the slurry.	[154], [155]
Swirl Flow Reactor	Reactor comprised of two circular Pyrex glass plates separated by soft paddings. The slurry is injected tangentially to create a swirl flow which improves the mass transfer.	[156]–[159]
Taylor Vortex Reactor	Tubular reactor with a rotating cylinder at its centre containing the light source. The rotation creates Taylor-Couette vortices which improves the mass transfer.	[160], [161]
Turbulent Slurry Reactor	Ceramic filters prevent the turbulent slurry from being mixed with the treated water. Those filters are periodically exposed to shockwaves to prevent any clogging.	[162], [163]

Table 4. List of different slurry reactor configurations.

2.5.2. Immobilised catalyst reactors

In typical immobilised configuration, the photocatalyst is chemically or physically bonded to the reactor walls, light source or a substrate. Examples of different configurations of slurry reactors are given in Table 5. As the catalyst is bonded to a substrate, there is no need for a separation and retrieval step to safely discard the treated water. However, the pollutant/water/light contact area is reduced, which hinders the performances of such photocatalytic reactor configurations [142]. The strength and weaknesses of the immobilised reactor configuration are generally the following:

Advantages:

- Continuous operation
- No catalyst filtration step

Disadvantages:

- Low light efficiency
- Possible mass transfer limitation
- Possible catalyst leaching

Table 5. List of immobilised reactor configurations.

Configuration	Description	Reference
Falling Film Reactor	The inner part of a tubular reactor is coated with TiO ₂ . A lamp is centrally placed in the reactor to activate the catalyst, while a descending flow of water runs down Reactor on the inner walls. There is a good amount of contact between the water and the catalyst, but the total volume of treated water is limited.	
Fibre Optical Cable Reactor	Silica optical fibres are coated with TiO_2 and illuminated by an external light source, inside a water filled reactor. The photocatalyst is activated by refraction of the light travelling through the optical fibre. High cost	[165], [166]

and light attenuation are the main drawbacks to this method.

 Cylindrical vessel containing numerous hollows,

 Multiple Tube
 U-shaped quartz tubes (coated with TiO₂), immersed in

 Reactor
 water. The light travels inside the hollow quartz tube,

 activating the photocatalyst.
 [167]

	Annular reactor, irradiated by a central lamp, and	
Packed Bed	packed with mesh, glass or beads coated with titanium	[1/1]
Reactor	dioxide. Light attenuation and pressure loss are the main	
	drawbacks encountered in these types of reactors.	

	Titanium dioxide is immobilised at the surface of	
Rotating Disk	a disk, illuminated by a light source and rotating at a rate	
Reactor with controlled	ranging from 20 to 100 rpm. There is a good amount of	
	contact between the water, the catalyst and the photon.	[168]
periodic	However, the system can be complex, and the amount of	
illumination	treated water can be limited.	

	Rectangular vessel with an inner rectangular	
Tube Light	welded plate, containing U-shaped light sources coated	[1/1]
Reactor	with TiO ₂ . High catalyst-water contact, but complex	[141]
	hydrodynamics involved.	

Chapter 3. Thin film deposition

This chapter introduces thin films and existing deposition processes. The chapter provides an overview on vacuum, various sputtering techniques, the plasma state and discusses several thin film growth models.

The chapter is structured as follows. Section 3.1 gives an overview of the different existing thin film deposition methods, Section 3.2 gives an overview of vacuum and pumps, and Section 3.3 provides an introduction to the plasma state. Finally, Section 3.5 gives an overview of recent advances in sputtering technologies while Section 3.6 discusses various thin films growth.

A thin film is defined as a low-dimensional material with a thickness ranging from a few nanometres to a few micrometres [169]. Historically, they have been used since the 1960s in a wide variety of fields, such as electronic, superconductors, batteries, optic, aeronautic, military and decorative [169], [170]. Thin films can be employed on their own, but are generally used to improve a solid bulk material and/or surface properties, be it, its transmission, reflection, mechanical resistance, chemical resistance, electrical and magnetic properties [171]. By nature, to be produced, thin films require a low amount of material and energy, which makes it an environment-benign material technology [169]

3.1. Deposition methods

Generally, thin film deposition methods can be separated into three main categories: chemical solution deposition (CSD) chemical vapour deposition (CVD) and physical vapour deposition (PVD), as illustrated in Figure 9.



Figure 9. Deposition techniques

3.1.1. CSD

Chemical solution deposition is a broad term, referring to any method involving chemical precursor-based solutions used to produce coatings, ranging from sol-gel to metalorganic decomposition. To obtain the desired coating, precursors are either suspended or dissolved in a solvent and deposited on a substrate [172]. They are then heated to high temperatures, to evaporate the solvent, decompose organic components, and most importantly, form the material of interest. Precursor can be produced by a plethora of soft chemistry methods such as: sol-gel [44], [173]–[175], polymer derived ceramics [176], hydrothermal/solvothermal synthesis [175], [177]–[179], metal-organic decomposition [180]. Likewise, precursors can be immobilised via dip-coating [181], [182], spin coating [181], [183], screen printing [184]– [186] and spray pyrolysis [187], [188]. Unlike other deposition methods, CSD has a lower investment and operational cost, as it takes place at atmospheric pressure and does not require any type of vacuum chamber. However, chemicals involved in these deposition methods can be environmentally harmful, while the produced films can be subject to significant amounts of internal stress, as a result of the organic component and solvent removal [172].

3.1.2.CVD

In a typical chemical vapour deposition (CVD) process, gas phase precursors are transported to the surface of a heated substrate by an inert gas carrier, such as argon. Heterogeneous surface reactions occur, leading to the conversion of the precursor into a material of interest, forming high purity, homogeneous films. Depending on the deposition conditions, these films can be amorphous, polycrystalline, epitaxial or uniaxially oriented polycrystalline films. CVD is a versatile deposition technique, with a large variety of usable precursors; operating temperature and pressure vary from 100 to 2200 °C and atmospheric pressure to <10⁻⁵ Pa, respectively [171]. Additionally, unlike PVD, which is a directional deposition process, complicated forms or porous substrates can be coated on all surfaces, as the precursors are transported by carrier gases. However, to enable these chemical reactions, energy is usually provided in the form of heat, which is associated with high operational cost and substrate limitations.

To address these issues, plasma enhanced CVD (PECVD) was developed, to deposit thin films at lower temperatures than conventional CVD, by reducing the activation energy of the chemical reactions. A plasma is incorporated into the process, usually ignited and sustained by applying microwave, ultrahigh or radio frequencies to a plasma forming gas. As precursor gas molecules are ionised by inelastic collisions with electron, they form reactive species, such as radicals, ions and secondary electrons [171]. Although chemical vapour deposition has many advantages, it suffers from drawback similar to CSD as it is limited by the availability of precursors, and it produces hazardous chemicals.

A notable sub-category of CVD is atomic layer deposition (ALD). The main difference is that in ALD, two gaseous precursors are introduced and each account for half of the synthesised thin film material. These precursors are introduced sequentially for gas-surface reactions termed 'half-reactions' to occur. These 'half-reactions' are self-limiting, which provides a better coating thickness control and conformality than any other deposition technique. However, it suffers from the same drawbacks as CVD and from low deposition rate due to the sequential nature of the process [189].

3.1.3.PVD

Physical vapour deposition (PVD) refers to the thermal vaporisation or sputtering of atomic or molecular material from a solid source, under a vacuum, onto a substrate. These processes are used to deposit films of elemental, alloy, compound and polymeric materials, with thickness ranging from nanometres to microns [190]. Contrary to chemical vapour deposition, PVD strictly requires low pressures to operate, ranging from high (0.1 - 10^{-5} Pa) to ultra-high vacuum (< 10^{-5} Pa). Low pressures are essential to allow the vaporised or sputtered material, to reach the substrate without collision with gas phase molecules [190]. Consequently, it is a directional deposition process, *i.e.*, the trajectory of the source material is line-of-sight. This vacuum requirement implies a high initial investment, but it also guaranties the production of thin films free of atmospheric contamination. A wide variety of materials can be deposited via physical vapour deposition, but unlike CVD and CSD processes, it doesn't require nor produce hazardous materials. PVD processes can be categorised into 4 main categories: thermal evaporation, cathodic arc vapour evaporation, ion plating and sputter deposition. As one of the focus of this work, the latter one will be detailed in its dedicated section 3.5.

- Thermal evaporation: a material is heated under vacuum to a temperature high enough to be evaporated (e.g., Al, Pb, Sn, Mo, W) or sublimed (e.g., Cr, Mg). The vapour then condenses at the surface of a substrate, to form a film [190]. Equilibrium vapour pressure above 1 Pa is generally required to obtain reasonable deposition rates.
- Cathodic arc evaporation: vaporisation of a molten spot on a cathode or of a molten anode by applying a low-voltage high-current DC arc, in a low-pressure gaseous atmosphere [191]. Vaporised atoms are ionised as they pass through a high-density electron cloud and can be accelerated by an electric field [190]. If a reactive gas is introduced, it can be ionised to form compound materials such as ceramics (oxides, nitrides etc.).

- Ion plating: the source material can be deposited by sputtering or evaporation combined with concurrent or periodic bombardment of the substrate, by atomic-sized energetic particles [192]. Prior to deposition, the bombardment is used to sputter clean the surface, improving substrate adhesion and the nucleation of the deposited material. During the deposition, the bombardment, increases the surface temperature which enhances surface diffusion and facilitate chemical reactions. It is a versatile technique, as during the deposition process, the bombardment can be adjusted to tailor the coating's properties [190].
- Sputtering: a negative voltage is applied to a target (source material) in a vacuumed chamber. Positively charged gas ions bombard the target, which results in the ejection, also known as sputtering, of surface target atoms. These atoms are sputtered toward a substrate and form a thin film composed of the source material [193].

3.2. Vacuum

The word "vacuum" originates from the Latin *vacuus*, which translates to "empty" or "unoccupied". A perfect vacuum can be interpreted as space completely devoid of matter, *i.e.*, molecules, particles, which can only exist in the depths of space. When we commonly talk about vacuum, we refer to "partial vacuum", which is defined as a space with a lower pressure than the atmosphere. Vacuums are generally achieved by mechanically removing gaseous species, from a given volume, using pumps. Depending on the amount of extracted gaseous species, different types of vacuum can be achieved, with different properties; these are given and summarised in Table 6 [194].

Characteristics	Unit	Low vacuum	Medium	High vacuum	Ultrahigh
Characteristics			vacuum		vacuum
Pressure	Pa	$100 - 10^5$	0.1 - 100	$10^{-5} - 0.1$	< 10 ⁻⁵
Particle number	cm ⁻³	$10^{16} - 10^{19}$	$10^{13} - 10^{16}$	$10^9 - 10^{13}$	$< 10^{-9}$
density	CIII	10 - 10	10 10	10 10	< 10
Mean free path	m	$10^{-4} - 10^{-7}$	$0.1 - 10^{-4}$	$10^3 - 0.1$	< 10 ³
Collision rate	cm ⁻² .s ⁻¹	$10^{20} - 10^{23}$	$10^9 - 10^{13}$	$10^{13} - 10^{17}$	< 10 ¹³
Volume collision rate	cm ⁻³ .s ⁻¹	$10^{23} - 10^{29}$	$10^{17} - 10^{23}$	$10^9 - 10^{17}$	< 10 ⁻⁹
Flow regimes	-	Viscous	Knudsen	Molecular	Molecular

Table 6. Vacuum types and their characteristics (for gases similar to air at 300 K).

3.2.1. Flow regimes

An important concept in gas kinetic theory is the "mean free path". A gas can be considered as a set of particles with given directions and kinetic energies. As particles collide, they change direction without losing energy, resulting in random travel patterns called Brownian motion. The distance travelled by a gas particle between two successive collision is known as the mean free path. The higher the pressure, the higher the gas particle density, the lower the mean free path and vice-versa. The mean free path of gas particles plays a key role in chemical and physical vapour deposition processes and mainly depends on the type of vacuum used.

When pumping a system through an aperture, as the pressure decreases, gases behave differently depending on the vacuum type; these different flow regimes are characterised by the Knudsen number. As shown in equation (23), the Knudsen number Kn is a ratio between the mean free path \bar{l} of gas particles and the dimension, d, of the aperture; these different flow regimes are illustrated in Figure 10 [194].

- In a low vacuum, the mean free path of all gas particles is lower than the diameter of the aperture. The gas particles experience quasi-constant mutual collisions and behave as a cohesive fluid or a viscous flow.
- In a medium vacuum, two populations of gas particles co-exist, with mean free path higher and lower than the diameter of the aperture. Collisions of gas particles with the walls are as likely as mutual gas particles collisions. This marks a transition region between the viscous and molecular flow, known as Knudsen flow.

• In a high or ultrahigh vacuum, the mean free path of all gas particles is higher than the diameter of the aperture. The gas particles rarely collide with each over and only collide with the walls in a random pattern. When the behaviour of all individual particles is averaged, they exhibit a macroscopic flow behaviour known as molecular flow.

$$Kn = \frac{l}{d} \tag{23}$$



Figure 10. Schematic representation of different flow regimes.

3.2.2.Pumps

Vacuum deposition processes are usually carried out under high or ultrahigh vacuum and require different pumping methods. In practice, pump dedicated to different flow regimes are used conjointly, in a sequential manner, following the pressure changes. Positive displacement pumps are used for viscous regime flows while diffusion pumps or turbomolecular pumps can be used for molecular flows.

3.2.3. Positive displacement pumps

This type of pump is the most important and commonly used technology for low vacuum. These systems aspirate, compress and discharge a gas pumped with valves, pistons, rotors or sliders. When paired with a high vacuum pumps, positive displacement pumps are named roughing or backing pumps. Although there is a wide range of available systems (piston pump, diaphragm pump, rotary plunger pumps etc.), rotary vane pumps remain the most popular choice [194]. According to the ISO 3529-2:2020, a rotary vane pump comprises of a cylindrical housing, in which an eccentric placed rotor revolves tangentially, to the fixed surface a stator [195]. This arrangement creates a space division between the inlet (1) and outlet (2), while the centrifugal force draws in and compresses the gas, respectively. As illustrated in Figure 11, as the vane rotates, the gas is aspirated through the inlet into an expanding space (1). On the other side, the gas is compressed by the contracting space (2) and exhausted. This cycle repeats over and over and results in the pressure dropping in the vacuumed chamber. This system is fast and efficient to reach low vacuum pressures, but as particle density decreases, the gas enters a molecular regime flow and prevents the pump from extracting additional gas particles.



Figure 11. Schematic representation of a rotary vane pump; (1) gas being sucked in expanding space; (2) gas being compressed and exhausted in contracting space.

3.2.4. High vacuum and ultra-high vacuum pumps

Positive displacement pumps reach their limits when the gas behaviour changes from a viscous fluid to a molecular regime flow. Gas particles collide almost exclusively with the chamber walls, their random motion is driven by the system's temperature. Hence, different types of pumps, based on momentum transfer, are required to achieve high and ultra-high vacuum pressures. The two most popular systems are diffusion and turbomolecular pumps [194]. In the former, described in Figure 12, oil is heated up and vaporised in a boiling chamber. Vapour is ejected at high velocity, in a downward motion, toward cooled pump walls and condensed, to be vaporised again. Gas particles diffuse in the vapour and are accelerated downward, toward the bottom of the diffusion pump which is connected to a roughing pump [194]. In the latter, described in Figure 13, gas particles are accelerated downward by fast rotating rotor blades paired with symmetrical stator disks in between. The angled rotor blades rotate at velocities ranging from 20×10^3 to 90×10^3 rpm, drag down gas particles through channels between the blades, toward the roughing pump [194]. In both systems, as gas particles accumulate at the bottom of high vacuum pumps, a viscous flow is established, which enables the connected positive displacement pumps to exhaust the gas. The pros and cons of diffusion and turbomolecular pumps can be summarised as follow:

Diffusion pumps

Advantages

- Simple maintenance
- Low running cost
- Robust

Turbomolecular pump

Advantages

- Easy to operate
- Low maintenance
- Robust
- No sample contamination

- Disadvantages
- More fragile due to mechanical moving parts
- Intolerant to particle contamination

Disadvantages

• Sample contamination by oil

Requires cooling water



Figure 12. Schematic representation of a diffusion pump.



Figure 13. Schematic representation of a turbomolecular pump.

3.4. Plasma "the 4th state of matter"

Eons ago, matter was scattered in the most violent explosion to ever happen, known as "Big Bang". Matter, which composes the Universe, was so hot that everything was in a plasma state, until it cooled down, over billions of years to gas, liquid and solid states. Therefore, chronologically, plasma was the first state of matter. However, since "plasma" was identified and named in the 20th century by I. Langmuir, it is referred to as the "fourth state of matter" [196].

Matter exists in four states, solid, liquid, gas and plasma, illustrated in Figure 14. In a solid state, the constituents are closely bonded together, the particles cannot move freely and can only vibrate. They have a finite shape and volume. A liquid is a nearly incompressible fluid that takes the shape of its container, its components are closely bonded, but can move freely, relative to each other. A gas is a non-conductive compressible fluid that not only takes the shape of its container, but also expands to fill it. Atoms and molecules are distant from each other and move freely.



Figure 14. Schematic representation of (a) solid state; (b) liquid state; (c) gas state; (d) plasma state.

A plasma can be described as an ionised gas, consisting of free moving electrons, ions, atoms and molecules; they approximately have an equal number of positively and negatively charged species. Although it is considered as an overall neutral medium, it is conductive due to the mobility of the charge carriers (free electrons and ions). Hence, plasmas can be influenced by external electrical and magnetic fields.

They can be classified, according to their "temperature", either as thermal (hot) or nonthermal (cold) plasmas. In thermal plasmas, the temperature of the electrons is roughly equal to the temperature of the ions and the gas. In cold plasmas, the temperature of the electrons is far greater than the temperature of the ions and of the gas [171]. Hot plasmas require gargantuan amounts of energy to exist, although they are common in the universe (stars), they are pretty rare on earth (thermonuclear fusion). Most terrestrial plasmas are non-thermal, such as neon signs, fluorescent lamps, plasma processing and lightning. Figure 15 illustrates various types of plasmas, characterized by their electron densities and energies [192]. Plasma density, also referred to as "electron density", is defined as a number of electrons for a given volume (cm⁻³), while electron energy, also referred to as "electron temperature", is expressed in eV.



Figure 15. Average electron density and energy of various plasma types [192].

Plasmas play an important role in material processing due to their unique properties, *i.e.*, ionisation, global neutrality, electrical conductivity and response to electromagnetic fields. It is especially true in deposition processes such as physical and chemical vapour deposition, which require high degrees of ionisation to be efficient. The degree of ionisation α can be calculated with equation (24), where n_i represents the ions density and n_n the neutral atoms density.

$$\alpha = \frac{n_e}{n_e + n_n} \tag{24}$$

Most man-made cold plasmas are generated in a vacuum environment, with an electric field applied between a cathode and an anode and in the presence of a plasma forming gas (Ar, N_2 , O_2 , etc.). As the electric field is applied, free electrons, from already ionised gas atoms, are accelerated toward the negatively charged cathode [192]. Elastic collisions between electrons and the nucleus of gas atoms occur, but due to the mass difference, only result in electron scattering. However, if these free electrons acquire enough kinetic energy, they may ionise gas atoms by inelastic collision with their orbital electrons.

Hence, pressure plays an important role in the ionisation process. If the pressure is too high, too many inelastic collisions occur, and the free electrons do not accumulate sufficient energy to trigger ionisation events. On the contrary, if the pressure is too low, there are too few gas atoms and electrons reach the cathode without triggering any ionisation events.

3.5. Sputtering

"Sputtering" refers to the ejection of atoms, from the surface of a target material (metallic or ceramic), due to collisions of accelerated gas particles with said atoms [169]. This phenomenon was first reported by and named by W. R. Grove, in 1852 [191]. Of all the PVD processes, sputtering is often preferred to evaporation as [171]:

- High melting point material or dielectrics materials can be readily deposited from a solid target (source material).
- The source material remains relatively cold during the deposition process, compared to other PVD processes.
- Ceramic films with a defined stoichiometry can be produced from elementary target material by introducing a reactive gas (O₂, N₂ etc.) or directly from ceramic targets.
- Large areas can be coated with high lateral homogeneity.
- Unlike thermal evaporation, the sputtering source can be positioned in any direction.

In practice, the process is carried out in a vacuumed chamber, backfilled with a noble gas, to a low working pressure. Argon is often used as a noble gas, for its relative abundance and elevated mass. A negative voltage is applied to a target (cathode), that causes a portion of an insulator, in this case the Ar filled chamber, to become electrically conductive due to the presence of background electrons and Ar^+ ions. This minimum voltage required to ionise the Ar atoms into Ar^+ ions is called the "breakdown voltage". As a result, a glow discharge is produced and the Ar^+ ions are drawn toward the negatively charged cathode, these accelerated ions transfer their kinetic energy to the target's surface atoms, knocking them off toward the substrate, and forming a thin film. Additionally, secondary electrons essential to plasma stability, are generated from these collisions. The principles of the sputtering process are illustrated in Figure 16. An illustration of different target geometries is given in Figure 17.





Figure 17. Picture of different types of targets used in sputtering. (Source: Gencoa)

3.5.1.DC diode sputtering

This process is arguably the simplest form of sputter deposition. As illustrated by the schematic representation in Figure 18, in a vacuum chamber, two plate-electrodes, a cathode and an anode, are placed parallel to one another [171]. The former is composed of the source material and is referred to as the target, while the latter is the substrate to be coated. With a DC power supply, a negative potential of a few kV is applied to the cathode, in a plasma forming gas atmosphere, at pressures ranging from 10 to 0.1 Pa. A glowing plasma is formed between the two-parallel plate-electrodes, separated from each other by a dark space. The glowing is a result of a high enough number of energetic electrons, exciting the gas molecules and generating visible light. Generated electrons are accelerated away from the cathode and collide with gas atoms, ionise them and are eventually lost to ground, while positively charged ions are drawn to the cathode, causing sputtering. As the source material is sputtered, secondary electrons are also ejected and collide with neutral gas atoms, ionising them [171].

These ions then strike the target to produce even more electrons and so on; this property it is essential to ensure plasma stability. Prior to thin film deposition, shutters are usually positioned in front of the substrate to allow the target to be cleaned by pre-sputtering. Additionally, metallic targets are naturally covered by an oxide layer that needs to be removed prior to deposition, to produce high purity and defect-free coatings.



Figure 18. Schematic representation of a DC diode sputtering setup.

DC diode sputtering is a simple PVD deposition method adapted to the production of metallic coatings. However, dielectric materials, oxides in particular, are very difficult to produce by reactive sputtering [197]. Traditionally, in reactive PVD, a reactive gas such as O_2 or N_2 is introduced in the deposition chamber and reacts with the evaporated or sputtered source material, to coat the substrate with a ceramic thin film.

In the case of DC diode sputtering, the introduction of O_2 "poisons" the target, *i.e.* the target itself is coated with a dielectric layer. This non-conductive layer not only reduces the sputtering rate by covering the target, it also acts as a capacitor, charging up until breakdown occurs, in the form of electric arcs [197]. Each arcing event is accompanied by the ejection of droplets of source material, resulting in defects in the deposited films; these arcs can also damage the power supply.
Arcs are detrimental to the structure, properties and composition of the coating. Nitrides are an exception though, as many can be conductors or semi-conductors. Overall, the pros and cons of DC diode sputtering can be summarised as follow:

Advantages

- Simple and inexpensive setup.
- Large areas can be uniformly sputtered over long periods of time.
- The target material is well utilised.

Disadvantages

- Low deposition rate.
- Target poisoning when using reactive gases.
- Substrate heating due to the accelerated electrons.
- Requires high voltage, due to low ionisation efficiency.

In practice, this technique is only used with unreactive metal targets such as gold, copper, silver etc. Even then, DC diode sputtering is outperformed by most PVD deposition techniques and is rarely used; in particular, it lost its appeal with the development of magnetron sputtering. Nowadays, it still finds its place next to Scanning Electron Miscopy (SEM) setups and other analytical techniques, which require inexpensive and simple deposition of non-reactive, conductive material.

3.5.2. Magnetron sputtering

One of the biggest limitations of DC diode sputtering is its deposition rate. As secondary electrons are generated, instead of triggering ionisation events, an important portion is lost to the chamber's walls. This design flaw was actively and passively addressed with the development of triode DC and magnetron sputtering. In triode DC sputtering, the plasma's ionisation level is increased by incorporating a hot cathode and an auxiliary anode to the process [171]. The former, generally a tungsten filament heated to 2500 °C, generates electrons. The latter, generally a biased disk or tube, accelerates them by producing an electric field.

Although this setup solves the poor ionisation levels of DC diode sputtering, it is considerably more costly and complex.

Hence, magnetron sputtering, a passive solution, is usually preferred for its relative simplicity and low-cost. A magnetron has a permanent magnet structure located behind a target, which is used to confine a plasma to the target's surface. The magnets, usually made of a neodymium alloy, are arranged in such a way that one pole is positioned at the central axis of the target, while the other one forms a ring around the outer edge of the target, as illustrated in Figure 19.



Figure 19. Picture of a magnetron; (×) north pole, (•) south pole. (Source: Gencoa)

Whilst ions are too massive to be influenced by the strength magnetic fields typically used in these devices, electrons are governed by the Lorentz force (25); with q the electronic charge, v the electron's velocity and B the strength of the magnetic field [198]. The electron's velocity can be described by its perpendicular and parallel components v_{\perp} and v_{\parallel} , respectively. In practice, when subjected to a uniform magnetic field, an electron will drift parallel to the field line at a velocity v_{\parallel} , orbiting around it at a velocity v_{\perp} , in a helical motion. When an electric field E, perpendicular to the magnetic field B, is added to the equation (26), it exercises a constant force on the charged particle. As a result, the charged particle drifts in a helical motion, known as " $E \times B$ drift", perpendicular to both the magnetic and electrical fields, at a v_e velocity.

$$\vec{F} = q(\vec{\nu} \times \vec{B}) \tag{25}$$

$$\vec{F} = q \times \vec{E} + q(\vec{\nu} \times \vec{B}) \tag{26}$$

Hence, crossed electric and magnetic fields can be employed in a sputtering chamber, to improve the ionisation yield, by trapping free electrons in an "electromagnetic tunnel", instead of losing them to the chamber's walls (Figure 20). It effectively increases their probability of encountering an Ar atom and ionising it into an Ar^+ ion. Additionally, generated secondary electrons are repulsed by the negatively charged target, toward the electromagnetic trap, further increasing the probability of ionisation events. Compared to DC diode sputtering, which requires elevated Ar pressure to ensure sufficient levels of ionisation, magnetron sputtering can produce denser plasmas at reduced Ar pressures. Consequently, as the mean free path of sputtered atoms increases, higher deposition rates can be achieved, while retaining more energy. Unlike triode DC sputtering, a magnetron does not need an additional type of power input to increase the plasma's ionisation levels, it acts as both a plasma and vapour source, which makes it a more elegant and attractive solution.

The combined electric and magnetic field can provide high deposition rate $(1-5 \mu m/h)$ and plasma stability to the sputtering process; thus, their configuration should be considered carefully [169]. The permanent magnet's arrangement greatly influences the shape of the confined plasma and different configurations are possible; although in practice, only one is used [193].

- When the permanent magnets' poles are of equal strength, then it is referred to as "conventional" or "balanced" magnetron, as illustrated in Figure 20(a). The magnetic field lines close on themselves. The plasma is strongly confined, with high ionisation levels, but typically only extending a few cm from the target's surface.
- When the central pole is stronger than the outer poles, it is referred to as a "type-1 unbalanced" magnetron, as illustrated in Figure 20(b). Similarly, the plasma is confined near the target's vicinity and the plasma is directed to the wall. The electromagnetic field lines do not all close in on themselves, instead, some of them are directed towards the chamber's walls.

• When the outer poles are stronger than the central pole, it is referred to as a "type-2 unbalanced" magnetron, as illustrated in Figure 20(c). Contrary to previous configurations, the plasma is not only confined to the target's vicinity, it also extends toward the substrate. The magnetic field lines do not all close in on themselves, instead, some of them are directed towards the substrate and a significant ion current can be transported to the growing film [199].



Figure 20. Schematic representation of the plasma confinement observed in (a) conventional balanced magnetrons, (b) type-1 unbalanced magnetrons and (c) type-2 unbalanced magnetrons.

3.5.3. Pulsed DC magnetron sputtering

When using DC sputtering in reactive mode, especially for oxides, insulating layers form on the cathode, this phenomenon is known as "target poisoning". These insulating layers act as capacitors, and accumulate electric charges, until they discharge in the form of electric arcs. These arcs slow down the deposition rate as the power supply switches off until the arc is quenched and can potentially damage it. Moreover, these arcing events produce anarchic ejection of insulating materials on the substrate, resulting in defects in the thin film [200]. These problems were overcome in the early 1990s by the introduction of pulsed DC magnetron sputtering. Figure 21 is an example of a typical voltage sequence used in pulsed dc-reactive sputtering with a single magnetron. A high negative voltage is applied (unipolar) periodically applied during the "pulse on" period, followed by a "pulse off" where no voltage is applied, or, more commonly, switched to a small positive voltage, usually about 20 V (asymmetric bipolar).

It is nominally set to 10% of the "pulse on" voltage to take advantage of the high mobility of electrons compared to ions, due to their size difference. The insulating layers charging up during the "pulse on" are discharged during the "pulse off". Ideally, the "pulse on" should be short enough to avoid charge build-up while the "pulse off" should be long enough to fully discharge the insulating layers.



Figure 21. Voltage waveform of a power supply operating in asymmetric bipolar pulsed DC mode.

In the field of pulsed DC magnetron sputtering, the duty cycle is often used to characterise the voltage waveform of the power supply, in lieu of the "pulse on" and "pulse off" periods. The duty cycle can easily be calculated by dividing the duration of the "pulse on" by the full cycle duration. The magnetron discharge is usually pulsed with frequencies ranging from 10 to 350 kHz and duty cycles ranging from 50 to 90% [200]. P. Kelly *et al.* reported that magnetron discharge pulsed in the medium frequency range, *i.e.* 10 to 200 kHz, significantly reduced the formation of arcs, providing the correct duty setting was selected [193]. Consequently, defect-free thin ceramic films could be produced by reactive magnetron sputtering, with deposition rates close to those obtained for the deposition of pure metallic films.

3.6. Thin film growth

In the field of vacuum deposition, thin film growth is a complex process involving the condensation of ions, atoms or molecules on a bare substrate. These condensed particles accumulate and come together to give birth to two- or three-dimensional structures. The growth process is influenced by several factors (substrate properties, deposition conditions, source material etc.), which determine the physical and chemical properties of the thin film.

3.6.1. Nucleation-growth

In the early stages, source material particles, adatoms, condensate on the substrate, forming small dispersed stable domains, called nuclei. In this context, domain stability refers to a higher probability of growth rather than dissociation. Depending on the energies of interaction between the substrate and source material atoms, three solid thin growth modes can occur, as illustrated in Figure 22 [169], [201].

- Island: In the Volmer–Weber growth mode, source material adatom bond more strongly to each over than to substrate atoms. There is a high interfacial energy density resulting in weak interaction between the substrate and the thin film. As a result, source material adatoms cluster together to form islands, which eventually coalesce to form a continuous film.
- 2D layer growth: In the Frank–van der Merwe growth mode, the interfacial energy density is low, adatoms-to-adatom binding energy is similar to adatom-to-substrate atoms. As a result, layers of source material grow one on top of another.
- 2D layer growth + island: the Stranski–Krastanov growth mode is a combination of the Volmer–Weber and Frank–van der Merwe models. At first, the interfacial energy density is low, adatoms-to-adatom binding energy is similar to adatom-to-substrate atoms. 2D layers grow on top of another, but after a while, further layer growth becomes energetically unfavourable and instead islands grow on top of the 2D layers.



Figure 22. Schematic representation of three possible thin film growth modes.

Figure 23 details the processes involved in the nucleation and growth of a thin film. As nuclei collect adatoms, either by diffusion or direct capture, they grow following one of the previously mentioned solid thin growth modes. It has to be noted that adatoms condensing on a substrate must possess a sufficient amount of energy to diffuse and interact with other adatom to form metastable clusters or re-evaporate [192]. If the clusters reach a critical size, they will continue to grow to form 2D layers or 3D islands, coalescing, until a continuous film is formed. In an infinite 3D crystal, surfaces or interfaces, *i.e.*, atoms not bound to other atoms, are considered defects and come with an energy cost. The system's free energy ΔG associated with the formation of a solid cluster, considered a spherical solid in a homogeneous fluid, can be calculated with equation (27), where r is the cluster radius, γ is the interfacial energy per unit area and ΔG_V the change in free energy per unit volume. As illustrated in Figure 24, the difference between the decrease in ΔG_V and increase in interfacial energy varies as a cubic and square function of the radius r, respectively [169]. As a result, there is a free energy activation barrier for nucleation, also known as cluster critical size.

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_V \tag{27}$$



Figure 23. Schematic representation of processes involved in nucleation, 3D and 2D growth.



Figure 24. Schematic diagram with total system free energy as a function of the radius r of a spherical nucleus in a homogeneous fluid [192].

The resulting thin film can either be amorphous, crystalline or a combination of both. The crystalline state exhibits long and short-range order while the amorphous state exhibits short range disorder and long-range order. When adatoms do not have sufficient energy and/or time to diffuse to low energy sites, they cannot form a highly order structure, hence, the amorphous state has a higher occurrence rate. Consequently, high adatom mobility is key to obtaining a well crystallised structure, which in sputtering can be achieved by adjusting several deposition parameters such as:

- Substrate temperature
- Mean free path (depends on distance substrate-target and pressure)
- Sputtering voltage
- Biasing the substrate
- Ion-to-atom ratio at the substrate

Alternatively, crystallisation can be achieved post-deposition, by annealing the thin film at high temperatures. However, this is achieved with high energy and financial costs, additional steps and possible loss of surface area. Above a certain temperature threshold, a phenomenon known as Oswald ripening occurs, where small grains are consumed by bigger grains through diffusion processes, resulting in an increased grain size. In catalysis, active site surface area plays a determining role in reaction kinetic; thus, it is generally preferable to avoid annealing, when possible.

3.6.2. Microstructure evolution

Although the nucleation-growth mechanisms of thin films in vacuum deposition processes are well understood, there are still gaps regarding the evolution of the microstructure, with further source material condensation.

The final structure seems to be determined by the following processes [202]:

Shadowing: low substrate temperature (T) process with interaction between the condensing adatoms and the substrate morphology (roughness).

- Surface diffusion: medium (*T*) process with diffusion of adatoms at grain boundaries.
- Bulk diffusion: high (*T*) process with diffusion of bulk atoms.

Recrystallisation: high (T) process with phase transition and change in crystal orientation.

Although important, the substrate temperature is not the only factor that determines the properties of the final structure. For most dielectrics and metal materials, diffusion processes are also governed by the melting temperature (T_m) of the source material. Hence, in 1969 Movchan and Demchishin (MD) proposed a structure zone model (SZM) [203], which predicts the morphology of vacuum deposited thin films as a function of homologous temperature (T/T_m) , *i.e.* the ratio between the substrate's temperature and the source material's melting temperature. As illustrated in Figure 25, the films microstructure can be divided into three distinct zones depending on the (T/T_m) ratio:

Zone I: the homologous temperature is inferior to 0.3, adatom mobility is low and virtually no diffusion occurs, resulting in the formation of a porous and fine-grained microstructure.

Zone II: the homologous temperature ranges from 0.3 to 0.5, interfacial diffusion occurs with activation energies ranging from 0.1 to 0.3 eV, resulting in the formation of a columnar structure.

Zone III: the homologous temperature is superior to 0.5, bulk diffusion occurs with activation energies above 0.3 eV, resulting dense films with large grains, similar to bulk source material.



Figure 25. First structure zone model proposed by Movchan and Demchishin [203].

In 1974, Thornton *et al.* extended the SZM initially proposed by MD to also account for argon gas pressure, in sputtered metal films [204]. As shown in Figure 26, contrary to MD's SZM, zone I persisted for homologous temperatures above 0.3 with increased argon pressure. This effect was attributed to sputtered atom scattering and reduced mean free path at higher pressure, which decreased the adatoms' energy and increased the shadowing effect. Thornton also reported the presence of an additional zone between zone I and zone II, believed to be a transition zone between the two zones. In this transition zone, termed zone T, adatoms have sufficient mobility to diffuse and compensate for shadowing effect, producing a densely packed fibrous microstructure.



Figure 26. Structure zone model developed by Thornton [204].

Compared to DC diode sputtering, magnetron sputtering produces denser plasma, with a higher degree of ionisation, as explained in 3.5.2. Furthermore, electrons trapped by the magnetic field not only have a probability of ionising argon atoms, but also sputtered ones. Hence, the population of sputtered species reaching the substrate is composed of atoms and ions, which can be described as atom (j_a) and ion (j_i) fluxes. Magnetron sputtering produces significantly more sputtered ions than DC diode sputtering. This distinction is of importance, as energetic sputtered ions interact with the growing thin film and produce collision cascades, resulting in adatom displacement, vacancies, phonons and electronic excitations. Therefore, ion species, their energy, and their proportion to atom species (j_i/j_a) , play an important role in the thin film's microstructure and overall properties [201]. Their impact on film growth was indirectly taken into account in Thornton's SZM; high pressures decrease ion energy and flux due to lower mean free path and higher scattering, respectively. However, this model drew an incomplete picture, as the effect of ion energy and flux couldn't be discriminated.

In 1998, Kelly and Arnell (KA) refined the Thornton SZM, by investigating the properties of thin films deposited by closed-field unbalanced magnetron sputtering (CFUBMS) [205]. In CFUBMS systems, multiple magnetrons of opposite polarity are used to sputter using multiple targets simultaneously. This arrangement allows the magnetic field lines to close in on themselves across the chamber, to increase the trapping of electrons and the ion current [193].

As illustrated in Figure 27, Kelly *et al.* developed a 3-axis SZM which describes the thin films microstructure as a function of homologous temperature (T/T_m) , ion flux (J_i/J_a) and ion energy (bias voltage). Interestingly, KA reported dense and columnar microstructures (zone II and III) for films deposited at low T/T_m , which according to previous SZM, should be porous (zone I), demonstrating the capabilities of the closed field system. Energy was provided in the form of ion bombardment, enabling adatom mobility, surface and bulk diffusion. These findings demonstrate that combining energy parameters in SZM can be misleading. Instead, homologous temperature, ion energy and ion flux should be considered separately as microstructure predictors, to avoid cofounding effects [205]. Additionally, these findings have shown that it was possible to obtain dense microstructure at relatively low temperatures, which opens up the possibility of coating temperature sensitive substrates such as polymers.



Figure 27. Kelly and Arnell SZM [205].

Chapter 4. Design of experiment

This chapter introduces the basics principles of Design of experiment (DoE) in Section 4.1, while Section 4.2 presents the different designs and their characteristics. More details on the statistical and analytical tools used in this work are provided in Annexe B.

A design of experiment or DoE defines the process of planning, designing and analysing an experiment with a precise methodology, allowing objective and accurate conclusions to be drawn efficiently. To this day, the most employed method to conduct an experiment is the OVAT or One-Variable-At-a-Time approach. While conducting an OVAT experiment, one parameter at a time is varied while the other ones are kept constant. Not only does this approach rely on guesswork, experience and intuition but it is also time and resource consuming. For example, if a researcher wanted to optimise a catalytic reaction by studying 3 parameters (catalyst load, pH and temperature), along 3 levels (high, medium and low), he would have to conduct 27 experiments. In contract, the equivalent DoE array would only require 9 experiments, but would still return 90% of the information generated by the OVAT approach. In addition, the DoE approach provides answers on the importance of each parameter, their interactions and sources of variations. The statistical thinking present at the heart of any DoE abides by the three following rules [206], [207]:

- Any work occurring in a system is comprised of interconnected processes.
- Variations exist in all processes.
- Understanding and reducing variations are the key to success.

Although inevitable, variations should be kept to a minimum to ensure the quality and reliability of a product or process. What constitutes a process? As illustrated in Figure 28, a process can be defined by its input(s), output(s) and variables.

For example, in the case a photocatalytic reactor, the input would be the pollutant and the output the degradation of the pollutant. The controllable variables can be parameters such as catalyst load, light intensity and flowrate while the uncontrollable variables would be pH, temperature and oxygen concentration. In that case, the goal is to find the optimum parameters to maximise the degradation rate while minimising its variability to make the process more efficient and robust. Usually, the controllable parameters are varied from low (-1) to high (+1) levels in a 2-level experiment, or low (-1), medium (0) and high (+1) in the case of 3-level one. In a real-world experiment, that would translate into varying the temperature at 25 (-1) and 50 (+1) degrees Celsius in the case of a catalytic reaction for example. Every statistical analysis and plotting related to DoE were made using the software JMP 14 SW from SAS Institute.



Figure 28. Schematic representation of a process

4.1. Basic principles

Processes are always subject to uncontrollable variations, bias and noise. To negate these effects and improve the efficiency of an experiment, the following three principle should be applied [206], [208]:

- Randomisation
- Replication
- Blocking

Randomisation of the experiment allows to reduce the effect of experimental bias as it removes sources of variation which are not controllable in a real-life [206], [209]. Randomisation ensures that all varied parameters have an equal chance of being affected by noise, thus averaging its effect.

Replication gives an estimate of the experimental error and provides more precise information on the factors/interaction effects [206]. A high number of replications may reduce the experimental errors and increase the precision of the experiment. However, it can be time and resource consuming, and thus should be used appropriately.

Blocking is a method used to negate sources of variability in an experiment such as batch-to-batch, day-to-day, operator-to-operator etc. A block is considered as a set of homogeneous experimental conditions [206], [210]. Analysis conducted on the same day, with the same operator, using the same batch of material would be considered as one block.

4.2. Design

To perform a design of experiment, one must first choose a design adapted to the number of factors and levels one choses to study. The designs used to perform such experiments are called array and are by convention named $L_a(b^c)$, where *a* is the number of experimental runs, *b* the number of levels for each studied factor and *c* the number of columns in the array. For example, as illustrated in Table 7, an $L_9(3^4)$ has 9 experimental runs, 3 levels and 4 columns.

Experiment No.	Factor A	Factor B	Factor C	Factor D
1	-1	-1	-1	-1
2	-1	0	0	0
3	-1	+1	+1	+1
4	0	-1	0	+1
5	0	0	+1	-1
6	0	+1	-1	0
7	+1	-1	+1	0
8	+1	0	-1	+1
9	+1	+1	0	-1

Table 7. Structure of an $L_9(3^4)$ orthogonal array

A wide range of arrays are available in the literature with different properties and applications for virtually any experiment [211], [212]. Although important, the number of factors and levels are not the only parameters to take into account when choosing an array. Each design has a resolution which summarises its confounding patterns or the extent to which the main effects are aliased with the interaction effects [206]. Therefore, depending on the strength of the interactions with the main effect, the experimenter will be restricted to specific design resolutions as described in Table 8. If a process is suspected not to have strong interactions between the main effects and themselves, an array with a resolution III design can be used. Otherwise, or if unknown, resolution IV or V designs can be considered.

Design resolution	III	IV	V
Main effects \times Main effects	\checkmark	\checkmark	\checkmark
Main effects \times 2 nd order interactions	×	×	\checkmark
Main effects \times 3 rd order interactions	-	-	\checkmark
2^{nd} order interactions $\times 2^{nd}$ order interactions	×	×	\checkmark
2^{nd} order interactions $\times 3^{rd}$ order interactions	-	-	×

Table 8. Summary of different design resolution's properties

 \checkmark No cofounding effect, \times Cofounding effect

Part 2. Analytical and experimental techniques

Chapter 5. Analytical techniques and deposition process.

The chapter presents the analytical techniques used to analyse the photocatalytic coatings discussed in this thesis. Background information is provided for each technique and their advantages and disadvantages are discussed; a summary of these information is given in Table 10.

The chapter is structured as follows. The Nordiko sputtering rig, used to produce photocatalytic coatings, is presented in Section 5.1. Section 5.2 gives an overview of electron microscopy, Section 5.3 reviews the use of Raman spectroscopy and Section 5.4 described the UV-Vis spectroscopy. X-ray diffraction, XPS spectroscopy and Time-Resolved Photoluminescence are discussed in Sections 5.5, 5.6 and 5.7, respectively. Roughness measurements were carried out using AFM and White Light Interferometry, which are discussed in Sections 5.8 and 5.9, respectively. An extensive overview of the photocatalytic testing technique used in this work is given in Section 5.10. Finally, a summary of information obtained using different characterisation techniques and tests, along with their drawbacks and advantages, is given in Section 5.11.

5.1. Thin film deposition

5.1.1.Nordiko sputtering rig

Photocatalytic thin films were all deposited with a Nordiko sputtering rig (Figure 29), under a high vacuum, with a base pressure of 0.0025 Pa achieved through a combination of rotary (BOC Edwards 80) and turbo molecular (Leybold TMP1000) pumps [213]. Rectangular metallic targets ($300 \times 100 \text{ mm}^2$) were vertically mounted in closed field configuration on unbalanced type II magnetrons from Teer Coatings Ltd. The substrates were placed on a rotatable drum-shaped substrate holder.

For all deposition runs, the distance between the target and the substrate was maintained at 50 mm and the argon flow rate was kept constant at 50 sccm. The pressure was monitored with Penning, Pirani and Baratron gauges (capacitance manometer). Despite of the fixed argon flowrate, the working pressure of the system could be adjusted, from 0.44 to 3.10 Pa, by changing the aperture size of the gate valve, between the turbomolecular pump and the chamber. The magnetron was powered by an Advanced Energy Pinnacle Plus power supply, in pulsed DC mode, operating in dual channels at a frequency of 100 kHz and 60% duty.



Figure 29. Schematic representation of the Nordiko sputtering rig.

Photocatalyst thin films were deposited on the following substrates:

- Square sheets (3 × 3 cm²) of stainless-steel 304L mesh, purchased from The Mesh Company Ltd.
- Fisherbrand[™] Microscopic Slides, purchased from Fisher.
- BRAND[™] AR-Glas[™] Stirring Rods, purchased from Fisher.

All substrates were ultrasonically pre-cleaned in acetone. They were mounted on a drum-shaped electrically floating substrate holder, in static mode for single target sputtering and in rotating mode when co-sputtering. All chemicals used were purchased from Sigma Aldrich, unless stated otherwise. When producing titanium dioxide coatings, a single $300 \times 100 \text{ mm}^2$ titanium target (99.5% purity) was used. When producing bismuth titanate coatings, a $300 \times 100 \text{ mm}^2$ titanium target (99.5% purity) and a $300 \times 100 \text{ mm}^2$ bismuth target (99.5% purity) bonded to a copper backing plate) were used simultaneously.

5.1.2.Speedflo[™] PEM

Speeflo is an advance reactive feedback control system used in sputtering to improve the quality of the coatings, the process reliability and the deposition rate. The system is composed of an optic fibre looking directly at the plasma on one end and connected to the Speedflo with a filter on the other end. The filter choice depends on the target composition, in the case of a titanium target, for TiO₂ sputtering, a 400 nm filter was used, which correspond to Ti's emission wavelength. The Speedflo regulates the flowrate of each individual gas through actuators controlling the mass flow controllers (MFC) on the Ar and O₂ gas lines. There are three main operating modes of gas flow control: constant, sensor, layers and slave. The latter two were not used during this work and thus, won't be described. In "constant mode", the gas flowrate is set to a fixed value, this is typically used for non-reactive gases such as argon, which was always set to 50 sccm.

In "sensor mode" the reactive gas flowrate is adjusted dynamically depending on the strength of the plasma emission signal and maintained to a constant setpoint value (%) throughout the deposition process. To do so, each run is preceded by a calibration step, in which the target is sputtered in metallic and poisoned mode, by blocking and flowing an excess amount of reactive gas, respectively. As shown in Figure 31, there is a negative correlation between the signal (red line) and the actuator (blue line), as more reactive gas in introduced in the process, the target is progressively poisoned. The maximum and minimum signal values are used to scale the sensor from 0 % (poisoned) to 100 % (metallic). This ensures that for a given sensor setpoint, regardless of the deposition conditions (pressure, power, frequency etc.), the coating stoichiometry will remain consistent across all samples.

The signal is kept constant during the deposition process, thanks to the control algorithm, which reacts to the sensor feedback.

It is governed by coefficients called K1 and K2, which affect the controller's response characteristics, speed of response and dampening/stability, respectively. These coefficients are determined automatically during the "tuning phase", as the reactive gas flowrate is periodically increased and decreased to gauge the system's behaviour, as shown in Figure 31. The coefficients can also be adjusted manually, whenever the "tuning phase" is unable to find appropriate values due to non-standard system behaviours. Tweaking the speed of response and dampening/stability is an important part of the feedback control system, as it can make the difference between a stable and instable deposition process (Figure 30). A sensor oscillating with great amplitude around the setpoint not only makes the process unreliable, but it can also produce metallic coatings due to the lack of supplied reactive gas.

In the case of TiO₂, a setpoint value of 15 % was shown to produced stoichiometric titanium dioxide coatings, as demonstrated by Ratova et al., for a similar deposition system [214].



Figure 31. Speedflo calibration step prior to sputtering.





5.2. Electron microscopy

A normal human eye can only see objects as small as 0.1 millimetres, anything below that requires some sort of magnification to be observed. To this end, microscopes were invented to observe and characterise a wide range of infinitesimal materials. All microscopes rely on the same principle and can be classified in two categories, optical and electron ones. Optical microscopes are rather simple and inexpensive, but their resolution is limited by light diffraction. Electron microscope offer superior resolutions compared to their optical counterpart but are considerably more complex and expensive.

5.2.1.SEM

A scanning electron microscope (SEM) is a non-destructive multipurpose instrument commonly used to observe and characterise the surface of different materials, with a spatial resolution as low as 1 nm. In practice, an electron gun is used to generate primary electrons, focused into an electron beam by a set of electromagnetic lenses, toward the sample's surface. The acceleration voltage can be up to 30 kV and the operation is carried out under vacuum to prevent collisions between primary electrons and gas particles. Ideally, samples should be electrically conductive to avoid electrostatic charging effects, otherwise, they can be coated via diode DC sputtering with a thin conductive layer (Au, Pt etc.). As illustrated in Figure 32, primary electrons spread through the sample by inelastic and elastic collisions in a small volume, known as an interaction pear, resulting in secondary electrons (SE2), backscattered electrons (BSE), x-rays and cathodoluminescence emissions [215]. These different signals are collected and processed by a computer, to produce an image of the sample or extract information.

• SE2 are generated when inelastic collisions occur between primary electrons and electrons from the sample's surface. Steep surfaces and edges allow more secondary electrons to escape than than flat surfaces, producing a so-called edge effect. This results in detailed images, ideal to study the morphology and topography of a sample.

- BSE are the result of inelastic collisions between primary electrons and the nucleus of the sample's surface. They are atomic number dependant, as inelastic collisions are far more likely to occur with heavy elements than with light ones. Hence, in BSE imaging, areas composed of heavy elements appear brighter than the one composed of lighter elements, it is a quick way to distinguish multiple phases or obtain high resolution compositional maps.
- When an electron is knocked off by a primary electron it leaves a positively charged hole. This hole is filled by an electron from a higher energy shell, which releases excess energy in the process, in the form of an X-ray. The X-ray's energy is atomic number dependant and thus can be used to identify the type of elements present in the analysed sample.

In this work, the morphology and composition of the produced thin film was evaluated by scanning electron microscopy (SEM) using a Zeiss Supra 40 VP-FEG-SEM. The composition was determined by energy-dispersive X-ray spectroscopy (EDX), with an EDAX Trident system installed on the FEG-SEM.



Figure 32. Emitted signal resulting from the interaction between primary electron beam and analysed sample.

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5.2.2.TEM

Transmission electron microscopy (TEM) is one of the most advanced and versatile non-destructive technique, used for in depth characterisation of almost any material. As the name suggests, contrary to SEM, this technique does not rely on deflected or knocked-off electrons, but on the ones passing through the sample. The acceleration voltage varies from 60 to 300 kV and the analysis is carried out under ultra-high vacuum to avoid electron beam interference with gas particles. TEM images are 2D projection of the sample's inner structure, which can be visualised with a spatial resolution as low as 50 pm [215]. As it relies on transmitted electrons, sample thickness should usually be lower than ~150 nm. Otherwise, regions of interest in thick samples can be ablated and extracted by mechanical polishing, electropolishing, ion-beam thinning, focused ion beam (FIB) etc. The components of a TEM are similar to the one found on an SEM with at its core an electron source (thermionic emission, field Emission, electron gun) and various electromagnetic lenses used to either focus the electron beam or project images. As electrons are invisible to the naked eye, to obtain an image, their signal must be converted to light intensity using a scintillator, usually with an yttrium aluminium garnet (YAG) crystal. Photons are then transferred to a charge coupled device (CCD) camera for high-resolution images acquisition and X-rays detection. Transmission emission microscopes not only provide unparalleled high-resolution images, they provide crystalline structure, morphology, defects and stress state information. In this work, coatings were analysed by HRTEM using a FEI Titan Themis FEG STEM. Samples were prepared with a FEI Helios G4CX FIBSEM, for lamellae extraction.

5.3. Raman spectroscopy

Raman spectroscopy analysis is a versatile and non-destructive vibrational spectroscopy characterisation technique. Molecular vibrations are dependent on the composition and structure of molecules, they can be considered as their "fingerprint". Hence, Raman spectroscopy is perfectly fitted to identify the chemical composition and structure of different materials. This technique relies on an inelastic light diffusion phenomenon, known as Raman scattering, occurring when a monochromatic light source (UV-Vis-IR) transfers its energy to a sample's molecular vibrations. This phenomenon was discovered in 1928 by physicist C.V. Raman, who reported a light frequency shift when a monochromatic light passed through organic liquids.

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As illustrated in Figure 33, when incident photons interact with the molecular bonds of electron clouds, they may excite electrons, for a brief instant, from a ground energy state to a virtual excited one, until relaxation occurs by photon emission. The vast majority of interactions are elastic and known as Rayleigh scattering, i.e. the scattered photons have the same frequency v_0 as the incident ones. By comparison, inelastic scattering is rare and only occurs in 1 out of 10^7 emitted photons. Raman scattered photons have a frequency of $v_0 \pm v_R$, with v_R the molecular vibration frequency. Scattered photons with a frequency of $v_0 + v_R$ and $v_0 - v_R$ are known as anti-Stokes and Stokes Raman scattering, respectively. The frequencies and relative intensities of these Raman scattered photons depend on the composition and structure arrangement of the analysed molecule. Hence, Raman spectroscopy consist in measuring the Raman shift or frequency shift between the molecular vibration v_R and incident light v_0 . A Raman spectrum is usually plotted with the event count rate in ordinate and the Raman shift, typically expressed in wavelength (cm⁻¹), in abscissa.

A typical modern Raman spectroscopy set-up uses a laser as monochromatic light source, a high-pass filter to separate Rayleigh scattered photons from Raman scattered ones and a very sensitive signal detector such as a charge coupled device (CCD). Herein, coatings were analysed by Raman spectroscopy with a Renishaw Invia (514 mm laser) and a DXR Raman microscope from Thermo Scientific. When performing Raman mapping analysis, the latter was used with the laser operated at a wavelength of 532 nm, with a power of 10 mW, 900 lines per mm grating, a long working distance microscope objective with magnification of 50, an estimated spot size of 1.1 µm and a 25 µm pinhole.



Figure 33. Energy-level diagram with different possible states in Raman spectrum.

5.4. UV-Vis spectroscopy

A UV-Vis spectrometer typically consists of a UV-Vis light source, a filter monochromator, a beam splitter a reference and a detector (photomultiplier), as shown in Figure 34. The UV spectrum ranges from 190 to 400 nm, while the visible ranges from 400 to 780 nm. As such, to produce a UV-Vis light, different sources are combined; typically, a deuterium lamp is used for the UV region, while tungsten or halogen source are used for the visible region. To analyse the extended or full range of the UV-Vis spectrum, filter monochromators with prisms or grating can be rotated.

When a sample is illuminated by an incident light source with an intensity (I_0) , the light/matter interaction may result in light reflection (I_R) , scattering (I_S) , absorption (I_A) and transmission (I_T) . According to the energy conservation law described in equation (1), individual components can be evaluated by measuring a couple of individual components and bringing the remaining ones to zero.

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$$I_0 = I_A + I_T + I_R + I_S (28)$$

UV-Vis spectroscopy is a simple and affordable characterisation technique, which can be employed to obtain qualitative and quantitative information from a wide range of materials: metals, organic compounds, polymers, macromolecules, microorganisms etc. During this project, UV-Vis measurements were performed using an Ocean Optics USB4000 UV–vis spectrometer and a Cary 300 UV–vis spectrophotometer.



Figure 34. UV-Vis spectrometer schematic.

5.4.1.Band gap measurement

The optical bandgap energy of semiconductors can be estimated using the Tauc plot method, [216]. For wide band gap semiconductors, the optical band gap value E_g may be obtained using the equation (29), where α is the absorbance coefficient, h is Plank's constant, v is the vibration frequency. The coefficient n is related to the nature of sample the material, for indirect bandgap materials, as is the case for titanium dioxide, n = 1/2 [175]. The absorbance coefficient α can be obtained using the equation (30), with T the sample's transmittance, R the sample's reflectance and d the coating's thickness. The value of the optical bandgap energy is estimated by plotting $(\alpha hv)^{1/2}$ as a function of hv and extrapolating the linear region to the abscissa.

$$\alpha h v = (h v - E_g)^n \tag{29}$$

$$\alpha = \left(\frac{1}{d}\right) \ln\left(\frac{1-R}{T}\right) \tag{30}$$

5.5. X-ray diffraction

Like visible light, X-rays are a form of electromagnetic radiations, which were discovered in 1895, by physicist Wilhelm Röntgen. They have a significantly higher ability to penetrate matter than visible light, due to their higher energy and shorter wavelength, in the Ångstrom (10⁻¹⁰ m) range. This property is exploited in the field of geology, medicine and materials science by various diagnostic and characterisation techniques.

X-ray diffraction (XRD) is a characterisation technique used to determine the crystalline phase(s) present in metallic, ceramic and mineral samples. The instrument used to characterise such materials is an X-ray diffractometer. It mainly consists of an X-ray tube producing a monochromatic source of X-rays and of an X-ray detector. Both components can be rotated at angles ranging from 0 to 120 degrees by a goniometer. To produce X-rays, a tungsten filament is heated to produce electrons. These electrons then are accelerated toward an anode by an electric field. Core electrons from the anode are excited from low energy levels to higher ones, through inelastic collisions. As a result, X-rays are generated by relaxation of these excited electrons, as they return to their lower energy level. The wavelength (lambda) of X-rays depends on the anode's nature, for example, copper's is 1,54 A while molybdenum's is 0.71A.

$$n\lambda = 2d\sin\theta$$

Crystals are characterised by their arrangement of atoms, ions or molecules periodically repeated along three directions (h, k, l). Diffraction occurs when the wavelength of incident radiation is of the same order of magnitude as interatomic distances.

5.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is an elemental analysis technique, it provides qualitative and semi-quantitative information about a sample's surface down to a 10 nm depth. It is based on the photoelectric effect discovered by Hertz in 1887 and applied to surface analysis by Siegbahn in the mid 1960s [192].

The main components of an X-ray spectrometer are an X-ray source, an ultrahigh vacuum chamber, an electron collection lens, an electron detector and an electron energy detector.

When a sample is irradiated with monoenergetic soft X-rays (0 to 1000 eV), it emits core electrons, as illustrated in Figure 35. According to the Einstein's "principle of the conservation of mass", an emitted core electron has the same energy (kE) as the incident Xray (hv), minus the core electron's binding energy (BE) and the spectrometer's work function (ϕ_s) , as described in equation (31). As the X-rays' incident energy and the spectrometer's work function are known, the core electron's binding energy, which is element specific, can be determined by measuring the kinetic energy of emitted photoelectrons. Hence, X-ray spectroscopy can be used to identify almost any element at the exception of hydrogen and helium, in part due to their small photoelectron cross-section [192]. Furthermore, since BE is environment sensitive, the chemical state of an element can be determined by measuring the shift of its corresponding XPS peak. Additionally, identified elements can be quantified as their photoemission is proportional to their concentration in the sample. However, this type of analysis is considered semi-quantitative due to the detection limit (0.01-0.1 at.%.) and relatively small, analysed area (1-10 um). Herein, the chemical state information of various coatings was obtained using X-ray photoelectron spectroscopy (XPS), performed with an AMICUS photoelectron spectrometer (Kratos Analytical Ltd.) equipped with Mg K X-rays as the primary excitation source.

The binding energy was referenced to the C 1s line at 284.8 eV for calibration. Curve fitting was performed applying a Gaussian function with a Shirley background.



 $kE = h\nu - BE - \phi_s \tag{31}$

Figure 35. Schematic representation of photoemission process used in X-ray spectroscopy analysis.

5.7. Time-resolved photoluminescence

Photoluminescence (PL) is a relaxation process characterised by light emission; it occurs after a substance is excited by photons absorption [192]. Photoluminescence spectroscopy consist in analysing the energies distribution and temporal characteristics of these photon absorptions and emissions processes. It is a versatile, contactless, non-destructive characterisation technique applicable to solids, suspensions, liquids and gaseous materials. The mechanisms involved in photoluminescence are described by the Jablonski diagram (Figure 36) [192]. Upon photon absorption, an electron from the ground electronic state S_0 may be promoted to a vibrational level (V = 0,1,2...) of a higher electronic state ($S_1, S_2...$). Excited electrons quickly relax, within picoseconds range, to the lowest vibrational level V = 0 through vibrational relaxation (VR), then return to lower excited state by internal conversion (IC), a form of non-radiative relaxation [192].

Electrons at the S_1 electronic state can further relax to the electronic ground state through non-radiative pathways internal conversion (IC) or collisional quenching (CQ), and through fluorescence (photon emission). Alternatively, electrons at the S_1 electronic state can relax to a lower energy triplet state (T_1) through intersystem crossing (ISC) and then relax to the ground state through IC or phosphorescence (photon emission). Both fluorescence and phosphorescence are forms of photoluminescence, differing in their lifetime, occurring within microsecond and millisecond ranges, respectively. Photoluminescence spectroscopy is of particular interest in semiconductor characterisation, as photon emitted through radiative electron-hole recombination usually have an energy equal to the bandgap. Hence, photoluminescence spectra can provide information such as direct bandgap energy measurement and dopant/impurities/defects identification. Additionally, time resolved photoluminescence spectroscopy (TRPL) allows one to study the decay rate of photoluminescent emission, which is directly linked to the charge carrier lifetime. A typical PL spectrometer typically include a monochromatic excitation light source (usually Xenon lamp), monochromators, a photomultiplier and CDD detectors. Time-resolved photoluminescence (PL) analysis was performed externally on samples of interest, with an Edinburgh Instruments FLS1000 Photoluminescence Spectrometer, using a Nd:YAG laser as the excitation source with an excitation wavelength of 355 nm. The PL decay profiles were normalised to maximum intensity value (based on material emission spectrum identified with PL mapping): 510 nm for titanium dioxide samples and 540 nm for bismuth titanate samples. The PL decay profiles were fitted using Fluoracle software package.



Figure 36. Jablonski diagram

5.8. Atomic force microscopy

Atomic force miscopy (AFM) is a scanning probe technique used to produce topographic images, down to the atomic level. It is based on the interaction between a proximal probe and a sample's surface. The probe mechanically scans the sample, displaced in a raster pattern by a piezoelectric scanner, whilst the force between its tip and the surface is recorded to produce an image [192]. The probe's tip is a cantilevered force sensor that deflects upward or downward if the net force is repulsive or attractive, respectively. The magnitude of the deflection is proportional to the force applied to the sensor as described by Hooke's law, shown in equation (32), with F the force applied on the cantilever, k its spring constant and x the deflection length. As illustrated in Figure 37, a laser light is reflected off the cantilever's back to a position sensitive photodiode detector [192].

This detector tracks the laser spot movements, due to topographical changes in the sample, and relay the information to a feedback control system to generate an image of the sample. An AFM instrument can be operated in three imaging modes: contact, tapping and non-contact.

- Contact: The cantilevered force sensor is kept in constant physical contact with the sample, as the probe raster scans the surface, the deflection induced by topographic change is used to produce an image [192]. Alternatively, the AFM cantilever's deflection can be fixed by maintaining a feedback loop between the photodiode and the piezoelectric; the scanner's height change is used to produce an image. Contact mode is the simplest way to produce atomic scale topographic images, but it is prone to sample damaging, probe tip wear and scan induced artefacts.
- Tapping: The cantilevered force sensor is oscillated close to resonance frequency the sample's above surface [192]. The oscillating probe is brought into contact with the sample surface, altering its original amplitude. Deviation from this reduced amplitude is used as a feedback, to produce a topographic image. Since the probe only "taps" the surface, there is minimal wear to the tip and the sample. This mode is particularly useful when analysing soft sample such as polymers.
- Non-contact: Similarly to the tapping mode, the cantilevered force sensor is oscillated close the sample's surface, but is never brought into contact. A change in topography causes a frequency shift of the cantilever, due to the attractive Van der Waals force. The frequency shift is used a feedback to produce a topographic image of the sample.

$$F = kx \tag{32}$$

In this project, AFM analysis were performed on a Horiba XPlora Plus atomic force microscopy (AFM) system, in tapping mode.



Figure 37. Schematic representation of a typical AFM instrument setup.

5.9. Optical profilometry

White light interferometry (WLI) is a non-contact optical 3-D profilometry method, based on Michelson's interferometer and used to extract topographic information for rough and smooth surfaces [217]. As shown in Figure 38, white light is directed toward a beam splitter, one (measurement) beam is directed toward the sample and the other (reference) toward a mirror. Both beams are reflected by the beam splitter to a CCD image sensor to form an interference pattern.

The surface morphology and average roughness (Ra) of the various coatings were measured using a white light interferometer Profilm3D from Filmetrics, with a magnification of 50. Three images were obtained on random areas of the mesh and were averaged to find the Ra (ISO 4287).


Figure 38. White light interferometer schematic.

5.10. Photocatalytic testing for wastewater treatment

Photocatalytic tests are performed to estimate the performance and stability of different photocatalysts. When synthesizing a photocatalyst or designing a photocatalytic reactor, the synthesis conditions and reactor designs are tailored to maximise the photocatalytic activity. The most common methods used to assess said activity are usually based on the degradation of a model pollutant in contact with the surface of the photocatalyst, when irradiated over a certain period of time. A non-exhaustive list of photocatalytic tests is provided in Table 9, and describes the different types of pollutant that can be tested, as models for photocatalytic wastewater treatments application.

Pollutant	Examples	References	Characterisation techniques
Dyes	Methylene Blue, Orange II, Rhodamine B, Congo red, Methyl Orange	[11], [57], [96], [121], [149]	
Pharmaceuticals	Ciprofloxacin, Norfloxacin, Levofloxacin, Acetaminophen, Sulfamethazine, Carbamazepine	[218]–[223]	UV-Vis spectroscopy, GC-
Phenolic compounds	Phenol, Bisphenol A, 4 Chlorophenol, 2,4- Dinitrophenol	[99], [157], [158], [166]	MS, HPLC, LC-MS, TOC
Pesticides	Diazinon, Astrazine, Azoxystrobin, Flutriafol, Triadimenol	[59], [224], [225]	
Micro- organisms	Escherichia coli, Enterococci, Klebsiella pneumoniae, Escherichia virus MS2, Microcystis Aeruginosa	[223], [226]– [229]	Spread-plate method, Membrane filtration method, Double layer agar method, UV-Vis spectroscopy

Table 9. Non exhaustive summary of existing photocatalytic tests for wastewater treatment application

5.10.1. Dye testing

UV-Vis spectroscopy was used to assess the dye degradation abilities of various photocatalyst under irradiation. Transmittance (T) and absorbance (A) spectra are of particular interest in analytical chemistry. The former refers to the quantity of light passed through a sample and is defined as a ratio between the transmitted (I_T) and the incident light (I_0) intensity (33). The latter refers to the quantity of light absorbed by the sample and has a logarithmic relationship with transmittance (34). When a material is irradiated by visible or ultraviolet light, electrons from the outer shell are excited from their ground electronic state to a higher vibrational level or electronic state. The energy range required for photon absorption is not only compound specific, but it is also sensitive, as it is influenced by ion type, conjugation, ligand, solvent etc. The resulting absorption peaks obtain in UV-Vis absorbance spectrum can be considered as the fingerprints of different molecules/ions. For example, methylene blue, a dye commonly used for photocatalytic testing, presents a main absorption peak between 660 and 670 nm (Figure 39). This absorption peak corresponds to the $n - \pi^*$ transition where n is a free doublet in the C = N and S = C bonds of the nitrogen and sulphur atoms, respectively [230]. The shoulder peak at 605 nm corresponds to the vibronic transition from the ground to the level 1 excited state. UV-Vis absorbance spectra can be used for compound identification, but it can also be used for quantitative purposes, notably by using the Beer-Lambert law. This law states that there is a linear relationship with the absorbance and the concentration of a solution, as shown in equation (35) with A the absorbance, ϵ the molar attenuation coefficient, c the concentration and l the light path length. Hence, by measuring the main absorbance peak of a compound over time, it is possible to estimate the evolution of its concentration overtime (36).

The photocatalytic degradation of a dye typically follows a pseudo-first order kinetic reaction model (37). The pseudo-first order reaction constant k_{α} can be extracted by plotting $ln \frac{c_t}{c_0}$ or $ln \frac{A_t}{A_0}$ against the time (38). This constant is usually expressed in s^{-1} , min^{-1} or h^{-1} . For example, when exposed to UV light and in the presence of a photocatalyst, the main absorbance peak of a dye solution, such as methylene blue, decreases in intensity and broadens over time Figure 40(a). As shown Figure 40(b) there is good agreement between the photocatalytic degradation rate and the pseudo-first order reaction model with a $R^2 > 0.99$. The reaction constant k_{α} can be used as a metric to compare different photocatalysts during dye degradation experiment; the goal is always to maximise k_{α} . One could just measure the photocatalytic degradation percentage achieved by different photocatalysts and compare them after a given amount time, but it is important to make sure that the reaction follows a pseudo-first order reaction model. In photocatalytic dye degradation tests, low R^2 values should be treated as suspicious as they are usually indicative of flaws in an experiment such as dye adsorption, catalyst inactivation, catalyst instability, mass transfer limitation etc.

$$T = \frac{I_T}{I_0} \tag{33}$$

$$A = -\log_{10} T \tag{34}$$

$$A = \epsilon c l \tag{35}$$

$$\frac{A_t}{A_0} = \frac{c_t}{c_0} \tag{36}$$

$$c = c_0 e^{-k_\alpha t} \tag{37}$$

$$\ln\frac{c_t}{c_0} = \ln\frac{A_t}{A_0} = -k_{\alpha}t \tag{38}$$



Figure 39. UV-Vis absorption spectrum of methylene blue solution.



Figure 40. Methylene blue solution exposed to UV light in the presence of TiO_2 (a) absorbance spectra; (b) absorbance peak (665 nm).

The photocatalytic properties of different photocatalysts were assessed using the testing bench described in Figure 41. Samples are placed on top of a sample holder, in a quartz cuvette filled with 50 mL of dye solution, typically methylene blue. The samples are left in the dark for 60 minutes under continuous stirring, to reach adsorption-desorption equilibrium. Then, they are irradiated by a UV-A source (2x15 W Sankyo Denki BLB lamps, peaked at 365 nm) for a given amount of time. The UV-A source's spectral radiant flux is given for the test bench in Figure 42 and the bespoke water treatment reactor in Figure 43. The methylene blue main absorption peak (664 nm) was monitored with an Ocean Optics USB4000 UV-Visible spectrometer.



Figure 41. Schematic of the photocatalytic dye degradation test setup.



Figure 42. Spectral radiant flux of the UV light source used in the photocatalytic testing bench.



Figure 43. Spectral radiant flux of the UV light source used in the bespoke water treatment reactor.

5.10.2. Microbiological testing

Wastewaters do not only contain organic pollutant and pharmaceuticals, but they are also the perfect breeding ground for all sorts of microorganisms, of which some can be highly toxic to humans. Trace amounts of antibiotics can be found in municipal, hospital and industrial wastewaters This constant exposition to antibiotics may result in the development and transfer of antibiotic resistant genes between microorganisms. Hence, it is important to develop water treatment techniques which are efficient against both pharmaceuticals and microorganisms. To evaluate the antimicrobial activity of the produced photocatalysts, test were carried out using a modified version of the BS ISO 27447 methodology used for antibacterial activity assessment of semiconducting photocatalytic materials [231]. *Escherichia coli* (*E. coli*) NCTC 9001 was stored in glycerol stock at -80 °C and maintained on tryptone soya agar (TSA) (Oxoid, Basingstoke) at 4 C°.

For testing antimicrobial photocatalytic activity, 2-4 colonies of E. coli were inoculated into 10 mL of Tryptone Soya broth (TSB, Oxoid, Basingstoke) and grown for 22 ± 1 hour at 37 °C with agitation (180 rpm). Cells were harvested by centrifugation (4000 rpm, 10 min) and resuspended in sterile saline water to an optical density of 1.0 at 540 nm (Jenway 6305 Spectrophotometer, UK) resulting in an average "standardised cell suspension" of 1.21x108 CFU.mL⁻¹. Neutralizer media was prepared by mixing sodium thiosulphate 3 g/L, Polysorbate 80 30g/L, Lecithin 3 g/L and distilled water up to 1L and sterilized by autoclave for 15 minutes at 121°C.

Uncoated and photocatalyst coated glass coupons ($2 \text{ cm} \times 2.5 \text{ cm}$) were sterilized by autoclaving for 15 minutes at 121°C. Each coupon was inoculated with 10 µl of standardised cell suspension and covered with a sterile piece of polypropylene film of the same size. Coupons, in duplicate, were placed in sterile plastic petri plates, which in turn was placed in a larger petri plate containing moistened paper towel to retain humidity. The coupons were placed at a distance of 30 cm from a UVA lamp (15 W Sankyo Denki BLB lamps, peaked at 365 nm). The irradiance received by the coupons, through the petri plates was measured at 0.25 mW cm⁻², by a UVP UVX radiometer. To verify the presence of photocatalytic activity, dark control experiments (no irradiation) were performed, following the same experimental protocol but with the petri plates wrapped in aluminium foil. Coupons were incubated under these conditions for the required experimental time (24 or 48 hours), and then were recovered into neutralizer media and serially diluted ten-fold in sterile saline to a dilution on 10⁻⁷. 100 µl of each dilution was spread on to Tryptone Soya Agar (TSA), in duplicate and incubated overnight at 37°C. Colonies were counted and the number of colonies forming units (CFU) per mL of the original suspension were calculated. The whole experiment was repeated three times to ensure reproducibility.



Figure 44. Schematic representation of the photocatalytic E.coli inactivation test.



Figure 45. Flow chart of the *E.coli* photocatalytic inactivation testing methodology.

5.12. Summary of information provided by various analytical techniques

Method	Information	Comments
Scanning electron microscopy (SEM)	Topographical, morphological and compositional (EDX).	Resolution as low as 1 nm, require small amount of sample preparation.
Transmission electron microscopy (TEM)	Topographical, morphological, compositional and crystalline information.	Resolution as low as 50 pm, requires a significant amount of sample preparation.
Raman spectroscopy	Phase identification in crystalline structures.	Quick analysis, limited information on crystallographic planes.
X-ray diffraction	Phase identification in crystalline structures.	Relatively slow analysis, extensive information on crystallographic planes.
X-ray photoelectron spectroscopy	Surface composition and chemical state.	Spatial resolution of 10 nm.
Atomic force microscopy	Surface roughness and surface area.	High resolution but cannot be operated on sample with macro- scale roughness.
Optical profilometry	Surface texture and coating thickness.	Resolution limited to micro and macro-scale roughness
Time resolved photoluminescence spectroscopy	Charge carrier lifetime.	Only considers radiative recombination events.
UV-vis spectroscopy	Estimate optical bandgap, monitor pollutant absorption	Range limitation (200-800 nm)
UV-vis dye degradation	Reaction kinetic	No monitoring of reaction by- products
Microorganism inactivation	Effectiveness against microorganisms	Inactivation pathways unclear.

Table 10. Summary of information obtained using different characterisation techniques and tests.

Part 3. Results

Chapter 6. Crystalline TiO₂ deposited in a one-step process by magnetron sputtering.

This chapter presents the results obtained in a study of titanium dioxide thin films coated onto stainless steel mesh substrate for wastewater treatment application. The findings of this work were published in the Journal of Materials Research and Technology [232]. Passages and figures were reproduced verbatim in accordance with Elsevier's Journal Author Rights guidelines.

This chapter discusses such aspects as choice of photocatalyst-substrate combination (Section 6.1), thin film morphology (Section 6.2), photocatalyst crystallinity (Section 6.3), photocatalytic activity (Section 6.4), crystallisation process (Section 6.5) and the effect of high power applied to the magnetron (Section 6.6). A summary of this part of the project is given in Section 6.7.

6.1. Work overview

TiO₂ and other photocatalysts are often produced and tested in powder form [66], [93], [233]. They generally possess higher activity than thin films and are convenient for laboratory scale testing, but they require post-treatment separation to safely discharge the treated water. This limits the scalability and widespread adoption of powder-based photocatalytic water treatment systems. An alternative is to produce TiO₂ as a thin film, via chemical vapor deposition, sol-gel, pulsed laser deposition, solvothermal synthesis, etc [175], [178], [234], [235]. Reactive magnetron sputtering, the chosen deposition method for this work, has the advantage of directly immobilising the catalyst on the substrate, which facilitates the catalyst recovery. This deposition process is reproducible, scalable, produces uniform films and provides great control over chemical and morphological properties [193].

Unfortunately, TiO₂ thin films deposited by reactive magnetron sputtering are often amorphous, and thus non photocatalytic, when produced without substrate bias [236], radio frequency power supplies [236], [237], substrate heating [238] or post-annealing [239]–[241].

Ratova *et al.*, successfully deposited anatase on glass using reactive magnetron sputtering without any of these, using relatively elevated working pressures (2 to 5 Pa) to drive the sputtering process [242]. Herein, a similar set of conditions were used to not only investigate the influence of pressure, but also power, on the crystallisation process. Instead of soda lime glass, stainless steel 304L woven mesh was chosen as a substrate, for its high surface area, low cost, flexibility, porosity to light and tolerance for high temperatures [243]. Stainless steel mesh can be used as a photocatalyst support and integrated in a photocatalytic reactor, for efficient waste water treatment [244], [245]. As the substrate allows light to pass through, several layers of mesh can be stacked inside a photoreactor, to increase the catalyst load whilst maintaining light permeability. This work aims at finding deposition conditions to produce photocatalytic TiO₂ on stainless steel mesh in a one-step process via reactive magnetron sputtering. Optimising the catalyst deposition process will help reduce the upfront cost of a photocatalytic reactor and improve the scalability and widespread adoption of such water treatment systems.

In this work, the oxygen flowrate in the Nordiko sputtering chamber was regulated by a Speedflo®TM controller from Gencoa Ltd, to produce stoichiometric films whilst minimising target poisoning. A single 300x100 mm (99.5% purity) titanium target, was fitted on a Teer Coatings Ltd. unbalanced type II magnetron [193]. Stainless steel mesh squares $(3 \times 3 \text{ cm}^2)$, with an aperture of 0.41 mm and a wire diameter of 0.22 mm, were used as substrates and coated with TiO₂ by reactive magnetron sputtering. 9 samples termed No. 1 to No. 9 were produced with varying levels of applied power (250 to 750 W) and working pressure (0.44 to 3.10 Pa). Sample morphology was evaluated by SEM and WLI analysis, while the crystallinity was assessed by X-ray diffraction and Raman spectroscopy analysis. The photocatalytic activity of each sample was assessed by MB degradation tests under UV-A. Based on these results, additional high-power samples, termed No. 10 and No. 11, were produced at 1000 and 1500 W, respectively. The deposition conditions and characteristics of each sample is given in Table 11. The best performing sample (No. 10) was used for dye degradation mechanism investigation and durability tests. JMP 14 SW statistical software from SAS was used to assess the effect of power and pressure on different coating characteristics such as thickness, roughness and photocatalytic activity.

Sample No.	Pressure (Pa)	Power (W)	Thickness (µm)	Ra (µm)
0*	-	0	-	0.34
1	0.44	250	0.23	0.46
2	0.44	500	0.26	0.29
3	0.44	750	0.83	0.14
4	1.77	250	0.18	0.40
5	1.77	500	0.15	0.41
6	1.77	750	0.54	0.28
7	3.10	250	0.31	0.18
8	3.10	500	0.51	0.22
9	3.10	750	0.60	0.24
10	0.44	1000	1.40	0.31
11	0.44	1500	1.79	0.26
*Uncoated mesh sample	Frequency: 10	0 kHz Duty cyc	cle: 60 % Deposition	time: 2 hours

Table 11. List of samples with deposition conditions with corresponding thickness and roughness measurement.

6.2. Coating morphology

The morphology of TiO_2 coated stainless steel mesh was evaluated by SEM and WLI. The appearance of the mesh samples wasn't altered by the deposition process, the only difference being a slight colour change (Figure 46 (a) & (b)). Likewise, low magnification SEM (Figure 46 (c) & (d)) and WLI (Figure 46 (e) & (f)) analysis didn't reveal any significant morphologic change between the uncoated and TiO₂ coated samples.



Figure 46. Photography of stainless-steel mesh (a) uncoated, (b) TiO₂ coated; SEM micrographs of stainless steel-mesh (c) uncoated, (d) TiO₂ coated; WLI images of stainless steel-mesh (a) uncoated, (b) TiO₂ coated.

WLI analysis was performed on samples No. 1 through No. 9 to investigate the effect of working pressure and applied power on the morphology of the coatings. As shown in Figure 47, no significant difference was observed, regardless of the deposition conditions. *Ra* values of the same order of magnitude, varying from 0.14 to 0.46 μ m, were estimated by WLI for the 9 coated samples (Table 11). The ANOVA, for power and pressure, presented in Table 12 shows that both variables have a low F-ratio and a high p-values and confirms the lack of statistically significant of their effects. There is a possibility that the absence of correlation is a result of the measurement method, as WLI has a limited resolution. Different results may have been obtained by AFM analysis, but the flexible nature of the substrate made the analysis difficult to perform reliably and was not included in this work.



Figure 47. WLI images of TiO₂ coated stainless-steel mesh with varying levels of working pressure and power.

Source	Degree of Freedom	Sum of Squares	Mean Square	F-ratio	p-value
D	2	0.02220(5(0.011020	1 5700	0 2011
Pressure	2	0.03320656	0.011830	1.5/98	0.2811
Error	6	0.06305949	0.012101		
C. Total	8	0.09626605			
Power	2	0.02366027	0.016603	0.9776	0.4290
Error	6	0.07260578	0.010510		
C. Total	8	0.09626605			

Table 12.	One-way	ANOVA	table	for	roughness	(Ra).
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SEM analysis was performed on samples No. 1 through No. 9 to investigate the effect of working pressure and applied power on the morphology of the coatings. The samples were mechanically fractured to reveal their cross-sections and measure the coatings' thicknesses. Micrographs of both the surface (Figure 48) and the cross-section (Figure 49) of the samples were obtained and revealed the presence of two distinct coating morphologies.

The first one, observed for samples No.1, 2, 4, 5, 6, 7, 8 and 9 is a dense cauliflowerlike structure, while the second one which was only observed in sample No. 3 is a dense mixture of cauliflower-like and crystal-like features. In all cases, a columnar structure was observed for all deposition conditions. It has to be noted that crystal-like features were sporadically observed in samples No. 2 and No. 6, as shown in Figure 48 and Figure 49. Regardless of the deposition condition, all sample show evidence of conformality with the coating conforming to the shape and roughness of the stainless-steel mesh substrate. This will later be confirmed by a Raman mapping analysis.



Figure 48. SEM micrographs (surface) of sample No. 1 to No. 9, produced with varying levels of power and pressure.



Figure 49. SEM micrographs (cross-section) of sample No. 1 to No. 9, produced with varying levels of power and pressure.

ANOVA shows that power is the only parameter having a statistically significant effect on coating thickness, with a large F-ratio (7.9854) and small p-value (0.0204). This outcome was expected as an increase in sputtering power is known to result in higher sputtering rate [246]. Contrary to our results, Wu et al. found that not only power, but also pressure had an effect on coating thickness, when studying the deposition of titanium coatings [247]. The thickness was found to increase between 0.6 and 0.8 Pa and to decrease between 0.8 and 1.0 Pa. This discrepancy can be explained by the different studied pressure windows.

Source	Degree of Freedom	Sum of Squares	Mean Square	F-ratio	p-value
Pressure	2	58192.49	29096.2	0.5336	0.6119
Error	6	327165.93	54527.7		
C. Total	8	385358.42			
Power	2	280121.40	140061	7.9854	0.0204
Error	6	105237.02	17540		
C. Total	8	385358.42			

Table 13. One-way ANOVA table for thickness (µm).

6.3. X-ray diffraction & Raman spectroscopy results.

X-ray diffraction was performed to characterise samples No. 1 through No. 9 to investigate the effect of working pressure and applied power on crystallinity of the coatings. Diffraction peaks at 44.42° (111) and 51.58° (200) were identified as austenite stainless steel using the JCPDS card 00-003-0397, arising from the stainless-steel mesh substrate (Figure 50). Crystalline TiO₂ diffraction peaks were only identified in sample No.3 (Figure 50). Anatase peaks at 25.4° (101), 37.9° (004), 53.9° (105) and 55.3° (211) were identified with the JCPDS card 96-720-6076, while a rutile peak was identified at 27.4° (110) with the JCPDS card 96-900-4145. The other samples did not show any detectable peaks, which may indicate that they are amorphous or nanocrystalline, with crystallites below the detection limit of the XRD instrument, such as the ones identified in samples No. 6 and No. 2. The only crystalline sample was produced at the highest power and lowest pressure levels, which indicates that at 0.44 Pa, a power threshold of about 750 W is required to trigger the crystallisation process.



Figure 50. XRD patterns of TiO₂ thin films deposited onto stainless steel mesh.

To maximise the performance and improve the reliability of coated stainless-steel mesh based photocatalytic reactor, the TiO₂ coating should fully cover the substrate and be uniform. Hence, Raman mapping was performed on the array's only crystallised sample, No. 3 (750 W – 0.44 Pa), to assess the coating's integrity. Under these deposition conditions, anatase was observed on every thread of the coated stainless-steel mesh (Figure 51), with Raman bands identified at 144 cm⁻¹ (E_g), 197 cm⁻¹ (E_g), 399 cm⁻¹ (B_{1g}), 516 cm⁻¹ (A_{1g} , B_{1g}) and 639 cm⁻¹ (E_g) [248]. The intensity of the anatase phase main Raman band (144 cm⁻¹) was used as a reference to produce the Raman maps (Figure 51). 1677 Raman spectra were acquired using a step size of 100 µm along the Y and X axes to obtain them. The coating seems to be homogeneously distributed, despite of the substrate's complex geometry.



Figure 51. Raman mapping of sample No. 3 a) Raman map, b) 3D rendered Raman map, c) analysed area of TiO₂ coated mesh, d) corresponding Raman spectrum.

200

300

400

500

600

700

800

900

1,000

6.4. Photocatalytic activity assessment

The photocatalytic activity of the samples produced under varying levels of power and pressure were assessed via MB degradation tests under UV-A. All 9 samples outperformed the uncoated mesh, which reduced by about 4.5 % the initial MB solution concentration, after 1 h of UV-A irradiation (Table 14). When considering the 9 deposition conditions, sample No. 3 stands out with a significantly higher MB degradation rate, with a pseudo first order constant k_{α} of $4.5 \times 10^{-5} s^{-1}$ (Figure 52). This result is to be expected, as this sample is the only crystalline TiO₂ coating.

Although no XRD peaks were observed for all runs except sample No. 3, the fact that photocatalytic activity was measured for the other samples does suggest that they may possess nano crystallites, such as the ones identified by SEM in samples No. 2 and No. 6. As previously shown in Table 11, the measured thickness of the coated mesh varied from < 200 nm to > 800 nm. The measured roughness of the samples was of the same magnitude as the uncoated mesh. Therefore, the photocatalytic performances of the coatings were compared directly with no additional factor required for the effect of surface area. The results seem to suggest that increasing the target power and reducing the operating pressure tend to favour the crystallisation of TiO₂, with an associated increase in photocatalytic activity. However, the ANOVA results (Table 15) didn't find any statistically significant correlation between any of the deposition parameters and photocatalytic activity. This is due to the presence of confounding effects, as applied power influences the crystallinity which affects the photocatalytic activity.



Figure 52. Results of MB photocatalytic tests under UV-A a) absorbance b) kinetic.

Sample No.	Degradation after 1 h (%)	Pseudo first-order constant $(10^{-5}s^{-1})$	R ²
0*	4.5	1.3	0.93
1	5.9	1.9	0.97
2	5.2	1.5	0.85
3	15.2	4.5	0.94
4	7.7	2.4	0.96
5	7.5	2.3	0.96
6	7.6	2.3	0.99
7	6.4	1.4	0.96
8	10.5	1.8	0.86
9	7.7	2.5	0.95
	*Uncoated	l mesh sample	

Table 14. Summary of the results of the MB photocatalytic tests under UV-A.

Table 15. One-way ANOVA table for MB degradation (%) under UV-A.

Source	Degree of Freedom	Sum of Squares	Mean Square	F-ratio	p-value
Pressure	2	0.00019384	0.000097	0.0811	0.9231
Error	6	0.00716734	0.001195		
C. Total	8	0.00736118			
Power	2	0.00190586	0.000953	1.0481	0.4070
Error	6	0.00545533	0.000909		
C. Total	8	0.00736118			

6.5. Crystallisation process

It is widely known that amorphous titanium dioxide thin films can be converted into anatase when annealed at temperatures above 673 K [249]–[253]. To ensure that during the deposition process, crystallisation didn't occur by direct annealing through substrate heating, the substrate's temperature was measured at equilibrium, using a PicoSens probe from Opsens, with two sets of conditions. In the first set, the pressure was set to 0.44 Pa and power varied from 250 to 750 W (Figure 53a) while in the second one, power fixed to 750 W and pressure varied from 0.44 to 3.10 Pa (Figure 53b). In both cases increasing the applied power and the working pressure did increase the temperature, but not to the same extent, as power seemed to have a greater impact. Regardless of the conditions, the temperature stayed well below the 673 K mark, which suggests that crystallisation occurred mainly because of the ion bombardment and not by direct substrate annealing.

During deposition process, the growing film is bombarded with energetic ions from the plasma and substrate bombardment by high energy ions can provide sufficient mobility to the sputtered adatoms, to produce crystalline thin films without additional substrate heating [254], [255]. Alfonso *et al.* studied the crystallinity of ZrN_xO_y thin films sputtered at different powers and, similarly to our results, found out that a power threshold had to be reached to obtain a crystallised structure. This effect was attributed to the increased ion bombardment [255]. To investigate this effect, the current drawn at the substrate holder during selected run conditions was estimated using a biased probe. For each set of conditions, the bias voltage applied to the probe was increased progressively using an Advanced Energy MDX power supply. The current drawn at the substrate was recorded from the power supply. Two sets of conditions were tested; pressure fixed at 0.44 Pa and power varied from 250 to 750 W (Figure 53c) and power fixed at 750 W and pressure varied from 0.44 to 3.10 Pa (Figure 53d). According to probe theory [256], without any potential applied to an electrically isolated probe facing a plasma, the net measured current should be null and a floating potential ranging from -20 to -30 V should be measured. The null current is due to an equal number of ions and electrons reaching the probe. The negative potential, also called floating potential V_f, is a result of the self-biasing of the probe, which arises due to the greater e⁻ mobility, compared to ions. By applying an increasing negative potential to the probe, the electrons are increasingly repelled, which is observed by a greater current drawn by the probe and marks a transition region (II).

If the applied potential is sufficiently large, all the electrons are repelled from the probe and only ions are collected in the ion saturation region (I). The current drawn in this region gives an estimate of the ion current incident, at the substrate. The I-V characteristics of the probe revealed an increased ion current with higher target power (Figure 53a), while an inverse effect was found for higher pressure (Figure 53b).

At high power, the greater ion flux density bombarding the substrate is likely providing enough mobility to the adatoms to form a crystalline structure. On the other hand, at high pressure, the greater amount of gas phase collisions is probably responsible for the loss in ion energy, which may hinder the crystallisation process.

Contrary to other studies, increasing the pressure did not increase the photocatalytic activity but had the opposite effect [242], [257]. This disparity could be explained by the arrangement of each deposition chamber with different power supply, magnetron, target-substrate distance and deposition time. As for the power, a similar study by Wang *et al.* found that it was possible to obtain crystalline TiO₂, in a one step process on an aluminium alloy substrate, by increasing the magnetron power and substrate bias voltage [258]. This is in accordance with our results, although in this case, crystallised TiO₂ was obtained without substrate bias.

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Figure 53. Substrate measured temperature with a) increased power (250 to 750 W) at 0.44 Pa and b) increased pressure (0.44 to 3.10 Pa) at 750 W; Plasma I-V characteristics c) with increasing power (250 to 750 W) at 0.44 Pa, d) increasing pressure (0.44 to 3.10 Pa) at 750 W. (I_p: probe current, V_p: probe voltage, V_f: floating potential, I: ion saturation, II: transition region).

6.6. High power sample

It appears that power applied to the target plays an important role in the formation of crystalline structures. To confirm this, an additional "high-power" sample, termed No. 10, was produced at 1000 W. Further power increase (up to 1.5 kW) was investigated but resulted in films with photocatalytic activity like sample No. 10, and thus were not included in the dataset. The pressure was maintained to the lowest achievable value of 0.44 Pa, for which a stable plasma can be obtained (with an argon flowrate of 50 sccm and the gate valve fully opened). The scanning electron microscopy analysis of the high-power samples revealed the complete disappearance of the cauliflower-like features found in sample No. 3 (Figure 54). The coating's columnar profile became more prominent, as revealed by the cross-section shown in Figure 54.

"Zone III" in the SZM model [204]. At such elevated power, the greater ion flux density bombarding the substrate may be enough for recrystallisation of existing structures to occur.



Figure 54. SEM micrograph of TiO₂ sample produced at 750 W (No. 3), 1000 W (No. 10).

The XRD patterns of samples No. 3 and No. 10 are presented in Figure 55. Just like sample No. 3, sample No. 10 has the same anatase peaks at 25.4° (101), 37.9° (004), 53.9° (105) and 55.3° (211) (JCPDS card 96-720-6076) and rutile peak identified at 27.4° (110) (JCPDS card 96-900-4145). Not only did these diffraction peak become shaper and more prominent, new anatase peaks were identified for at 37° (103), 38.6° (112), 48.1° (200) and 62.7° (204) (JCPDS card 96-720-6076).

These results confirm that power plays an important role, as the higher ion flux density enables crystallisation to occurs during the deposition process.



Figure 55. XRD analysis of TiO_2 sample produced at 750 W (No. 3), 1000 W (No. 10) and 1500 W (No. 11).

Sample No. 10 was tested for MB degradation under UV-A, the summary of the results is presented in Table 16 and illustrated in Figure 56. Compared sample No. 3, sample No. 10 (1000 W) degraded MB 18% faster. As can be expected, there seem to be a direct correlation between the crystallinity of the samples and the photocatalytic activity. As sample No. 10 was the best performing sample, it was selected for further investigation of the degradation pathways and cyclability.



Figure 56. Results of MB photocatalytic tests for high power samples under UV-A a) absorbance b) kinetic.

Sample No.	Degradation after 1 h (%)	Pseudo first-order constant k_{α} (10 ⁻⁵ s ⁻¹)	\mathbb{R}^2
0*	4.5	1.3	0.93
3	15.2	4.5	0.94
10	17.2	5.3	0.98
	*Uncoate	d mesh sample	

Table 16. Summary of the results of the MB photocatalytic tests for high power samples under UV-A.

Sample No. 10 was used to decompose methyl orange (MO) under UV-A in the presence of different trapping agents. The following trapping agents wre employed at a concentration of 7 mmol.L⁻¹ each: isopropanol (IPA) for 'OH [259]–[261], 4-hydroxy TEMPO (TMP) for O₂⁻⁻ [259], [262], sodium oxalate (SO) for h⁺ [263], [264] and sodium nitrate (SN) for e⁻ [265]. Methylene blue having a complementary colour to 4-hydroxy TEMPO, it formed a green solution when mixed. To prevent possible self-photosensitization effects due to coloured substance interactions [266], methyl orange was chosen instead. The same testing conditions used for methylene blue tests were used with MO instead, at a concentration of 1.5 μ mol.L⁻¹. The main absorption peak of methyl orange (465 nm) was monitored with an Ocean Optics USB4000 UV-Visible spectrometer. The results of the experiments are given in Figure 57. When isopropanol (Figure 57d) and 4 hydroxy-TEMPO (Figure 57b) were used, no dye

degradation was observed, suggesting that 'OH and O^{2-•} are the main active species generated on the photocatalysts' surface.

In the presence of sodium oxalate (Figure 57a) and sodium nitrate (Figure 57c) no degradation rate change was observed. Electrons and holes do not seem to directly participate in the degradation of the dye. Therefore, the oxidation pathway may be designated as indirect oxidation [267]. The 'OH radicals produced by oxidation of surface hydroxyl or adsorbed water, are known to play an important role in initiating oxidation reactions. It is especially true when the adsorption is negligible, as it is the case in thin films [267].



Figure 57. MO degradation test under UV-A by sample No. 10 (1000 W) in the presence of scavengers for a) h^+ , b) e⁻, c) O^{2-,}, d) 'OH scavengers.

Finally, the reusability of sample No. 10 was evaluated for its ability to degrade rhodamine B, over 10 consecutive cycles. This particular dye was chosen its known resilience to photocatalytic degradation, which would make any loss of activity more apparent than with methylene blue [268]. The same testing conditions used for methylene blue test were used with rhodamine B instead, at a concentration of 2 μ mol/L.

The main absorption peak of rhodamine B at 554 nm was measured before and after 1 h of UV-A exposition with a Cary 300 UV-Vis spectrophotometer. Afterwards, each test the sample was washed with distilled water, dried with compressed air and the operation was repeated with the same sample 9 more times; each test and washing step constitute 1 cycle termed C1 to C10. The sample's ability to degrade rhodamine B did not decrease significantly after multiple uses (Figure 58). These results confirm this substrate/catalyst combination's potential, for future integration into a photocatalytic reactor.



Figure 58. Cycling RhB degradation tests under UV-A by sample No. 10 (1000 W)

6.7. Summary

This work demonstrates that crystalline, photocatalytic, TiO₂ thin films can be deposited in a one-step process, on woven stainless-steel mesh substrates. A combination of low working pressure (0.44 Pa) and high applied power (>750 W) tend to produce the best results in terms of both crystallinity and photocatalytic activity. Ion current measurements suggest that a high ion current is required for crystallisation to occur. Raising the power resulted in an increased ion current drawn at the substrate, while pressure had an opposite outcome. High ion current is believed to improve adatom mobility, facilitating the crystallisation process [255]. However, these results contradict the findings of several authors, who reported previously that using high pressure improved the crystallinity of thin TiO₂ films [242], [257], [269]–[271]. These divergent outcomes could be explained by the arrangement of each deposition chamber with different power supply, magnetron, target-substrate distance and deposition time. To fully understand the mechanisms behind the crystallisation process of TiO₂, those previously mentioned parameters should also be varied to grasp the significance of their effect and the nature of their interactions.

In multiple recent publications, TiO_2 was produced by magnetron sputtering using small (4 to 8 cm diameter) metallic target [258], [272]–[274]. These target sizes are not fit for high-volume industrial processes. In this case, 300x100 mm metallic targets were used, in a large chamber without substrate bias [236], radio frequency power supplies [236], [237], substrate heating [238] or post-annealing [239]–[241], keeping the deposition process simple and reproducible. This methodology could easily be replicated and scaled up for high-volume production of photocatalytic TiO_2 supported on stainless steel mesh.

To summarise, crystallised titanium dioxide was successfully grown onto stainless-steel mesh in a one-step process by pulsed DC magnetron sputtering without annealing, substrate heating, substrate bias or additional energy sources. A High power applied to the target was identified as essential, to obtain photocatalytic crystalline TiO₂, on stainless steel mesh. On the other hand, increasing the pressure seemed to hinder the crystallisation process and was kept to a minimum (0.44 Pa). Methylene blue, methyl orange and rhodamine B, the three most common types of dye used in the photocatalysis field, were successfully degraded under UV-A, by this catalyst/substrate combination. The scavenger test revealed that the degradation mechanism seemed to be driven mainly by superoxide and hydroxide radicals.

Finally, the reusability of the coated mesh was demonstrated with little to no activity loss after 10 consecutive cycles. This substrate/coating combination seems to be a good fit for the high scale production of affordable stainless-steel mesh-based photocatalytic reactors, which will be explored in Chapter 7.

Chapter 7. Photocatalytic water treatment reactor based on TiO₂ coated stainless steel mesh.

This chapter presents the results obtained in a study of a bespoke photocatalytic reactor based on titanium dioxide coated stainless steel mesh. This reactor was developed as a continuation of the work presented in Chapter 6 and its finding were published in the Journal of Cleaner Production [275]. Passages and figures were reproduced verbatim in accordance with Elsevier's Journal Author Right guidelines.

This chapter discusses such aspects as reactor and experiment design (Section 7.1), coating morphology and crystallinity (Section 7.2), statistical analysis and model building (Section 7.3) and coating durability (Section 7.4). A summary of this part of the project is given in Section 7.5.

7.1. Photocatalytic reactor design

To address the limited scalability of powder-based systems, efforts were made to use immobilised photocatalysts, as they do not require any post-treatment separation, but their effectiveness can be limited by mass and photon transfer. These limitations can be mitigated when catalyst thickness, reactant proximity, catalyst surface area and light permeability are considered carefully [147]. In his critical review, Juan José Rueda-Marquez identified several barriers, which hinder the development of real world photocatalytic water treatment applications [52]:

- Most studies are performed on a laboratory scale.
- There is a lack of attention given to photocatalyst reusability.
- More than 60% of studies are performed on powders.
- Upfront and operational water treatment cost are rarely included.
This work aims at addressing some of the points raised by Rueda-Marquez et al., by building and optimising a photocatalytic reactor, made with inexpensive components and loaded with stainless steel mesh coated with TiO_2 thin films. The upfront and operating cost of this proof of concept are included in Table 17, while the reusability was assessed for 360 h of consecutive use.

Component	Material		Price ¹				
Component		£	€	\$			
Reactor	PMMA	15.5	17.4	19.2			
Tubing	PVC	12.7	14.2	15.7			
Flowmeter	Aluminium alloy + POM	36.9	41.3	45.8			
Temperature probe	Aluminium alloy	19.0	21.3	23.6			
Sampling cell	Acrylic	5.7	6.4	7.1			
Mesh	Stainless steel 304	0.8	0.9	1.0			
Pump	Acrylic	31.8	35.6	39.4			
Miscellaneous	-	30.0	33.6	37.2			
UVP XX-15 Series UV Bench Lamp	Aluminium	229.5	257.0	284.6			
Total (without light source)		152.4	152.4	170			
Total (with light source)		381.9	381.9	427.7			
¹ as of 15th September 2020.							

Table 17. Upfront and operating cost estimation of the LCPR-I.

Practical use of photocatalytic materials for water and wastewater treatment can be facilitated through their integration into so-called photocatalytic reactors. Although there is a wide variety of reactor types (fluidized bed, optical fibre monolith, micro-channel, annular etc.), they usually share common features, such as the presence of a reactor vessel, a light source, a photocatalyst and a form of solution agitator. Photocatalytic reactors aimed towards wastewater treatment can generally be classified in two categories: slurry type and immobilised type. Regardless of the chosen type, the main attributes of an ideal photocatalytic reactor should be the following [142]: high quantum efficiency, high catalyst specific surface area, efficient mass transfer, low cost and low toxicity.

To enable efficient transfer from a laboratory environment to real-world applications, the photocatalyst manufacturing process should be scalable and the reactor components should be inexpensive. The work done in Chapter 6 demonstrated that photocatalytic TiO₂ could be coated in a one-step process on 304 stainless steel and shown high activity against a wide range of model pollutants. The photocatalyst was deposited by reactive magnetron sputtering, which represents a significant time and economic gain, especially for high volume manufacturing, compared to multi-step chemical techniques. TiO₂ coated stainless steel mesh was integrated in a bespoke photocatalytic reactor, LCPR-I (Low-Cost Photocatalytic Reactor-I) and key parameters were optimised to maximise the reactor's efficiency, based on its ability to degrade a model pollutant; methylene blue (MB). Five parameters were varied along an augmented screening design template to identify the most important parameters and optimise the water treatment process: UV-A light intensity, number of TiO₂-coated mesh layers, coating thickness, water flowrate and initial dye concentration.

This reactor fabrication process didn't involve any expensive components (glass, quartz, membranes, air injector etc.) and it was almost exclusively built from components available in an everyday computer store, making this system easily accessible and affordable. The combined affordability, simplicity and efficiency of this proof of concept represents a sustainable option to treat wastewater and help bridge the gap between materials research and real-world applications.

Deposition parameters	Condition 1	Condition 2	Units
Deposition time	1	2	h
Power	2	2	kW
Frequency	100	100	kHz
Base pressure	0.3	0.3	(10 ⁻²) Pa
Working pressure	44	44	(10 ⁻²) Pa
Gas	Ar/O ₂	Ar/O ₂	-
Distance target-substrate	5	5	cm
Crystalline phase(s)	Anatase	Anatase + Rutile	-
Thickness	1.1	1.6	μm

Table 18. Summary of deposition conditions and coating characteristics.

The LCPR-I design inspiration can be traced to the Photo-CREC-Water I, developed at the Chemical Reactor Engineering Centre (CREC) of the University of Western Ontario, by Lasa et al. (2005). Likewise, the catalyst was immobilised on stainless steel mesh, albeit using another immobilisation technique, and the reactor was operated in batch mode. Unlike Photo-CREC-Water I, this bespoke reactor utilises an external light source and doesn't involve quartz or glass components, significantly reducing the system's cost and increasing its durability. Except for the UV-A lamps, the set-up was built exclusively from affordable and readily available components, purchased from the computer enthusiast market. Figure 59 provides a schematic representation of the bespoke water treatment photocatalytic reactor loaded with TiO₂-coated stainless-steel mesh photocatalyst.



Figure 59. Schematic representation of LCPR-I utilising TiO2-coated stainless-steel mesh.

In brief, the system is comprised of a cylindrical reactor made from PMMA (OD: 5 cm, h: 24 cm), transparent PVC tubing (OD: 16 mm, ID: 10 mm), a 12 V pump, a flowmeter, a temperature probe and an acrylic analysis cell. The reactor was placed in an aluminium enclosure with a UV-A irradiation source, detailed in Section 2.3.

Depending on the design matrix experiment, either 1×15 W or 2×15 W light bulbs were used, the pump's voltage was varied between 6 and 12 V to adjust the flowrate. The reactor was loaded with either 15×12.5 cm² or $15 \times 12.5 + 15 \times 9$ cm² cylinder(s) of stainless steel 304 sheets of mesh rolled into cylinders, coated on both sides with TiO₂ with varying thickness levels. To evaluate the impact of coating thickness on the reactor's photocatalytic capabilities, two deposition times were used, 1 and 2 h. The woven mesh was coated with TiO₂ by pulsed DC reactive magnetron sputtering in conditions similar to the one laid out in Chapter 6, with power and pressure kept at 2000 W and 0.44 Pa, respectively. Power was increased compared to the earlier work to reduce the deposition time required to produce each sample given the high number of samples presented in this dataset.

Variables	Symbol	Unit	Range and levels		
variables	Symbol	Unit	-1	+1	
UV light	X1	W	15	30	
Number of TiO ₂ -coated mesh layers	X2	-	1	2	
Coating thickness	X3	μm	1.1	1.6	
Flowrate	X4	L.min ⁻¹	5.14	9.54	
Initial dye concentration	X5	µmol.L⁻¹	1	5	

Table 19. Experimental ranges and levels of the independent operating variables.

7.2. Coating morphology and crystallinity.

The coatings obtained at the two deposition times were examined by FEG-SEM and their top view and cross-sectional micrographs are given in Figure 60. The top view of the two conditions revealed a dense microstructure with crystal-like features, as shown in Figure 61b, d. An analysis of the samples' cross-section, in Figure 61 a, c, highlighted the columnar aspects of the coatings. As expected, the coatings have the same morphology as the high-power ones shown in Chapter 6. Average thicknesses of 1.1 and 1.6 μ m were measured for the 1 and 2 h depositions, respectively.



Figure 60. SEM micrographs of TiO₂ coating on stainless steel mesh after 1 h deposition a) crosssection b) surface; 2 h deposition c) cross-section, d) surface.

The XRD analysis of the TiO₂ coated mesh revealed the presence of well-defined diffraction peaks, corresponding to crystalline TiO₂ for both deposition times (Figure 61). Diffraction peaks at 44.42° (111) and 51.58° (200) were identified as austenite stainless steel using the JCPDS card 00-003-0397, arising from the substrate material. The diffraction pattern of the 1 h deposition revealed anatase diffraction peaks at 25.35° (101), 37.93° (004) and 38.61° (112) identified with the JCPDS card 96-720-6076. After 2 h of deposition anatase 25.35° (101), 37.93° (004), 38.61° (112), 48.10° (200), 53.89° (105), 55.29° (211) and rutile diffraction peaks at 54.32° (211), 62.74° (002) were identified with the JCPDS cards 96-720-6076 and 96-900-4145, respectively.

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Figure 61. XRD analysis of the TiO₂-coated mesh samples; (A) 1 h deposition; (B) 2 h deposition

For both deposition times, crystalline titanium dioxide structures were obtained in a one-step process without any thermal treatment. Increasing the coating's thickness gave rise to new anatase diffraction peaks and to the appearance of an additional rutile phase. Anatase and rutile mixtures are known to have an enhanced photocatalytic activity compared to each polymorph on its own [72]. This rutile and anatase mixture could result in an increase photocatalytic activity for the 2 h deposition samples.

7.3. Design of experiment

The independent variables used for this design of experiments array are presented in Table 19, including corresponding levels and coding. The augmented screening design was constructed and analysed using the JMP 14 SW statistical software from SAS. The studied variables were UV light intensity (W) (X_1) , number of TiO₂-coated mesh layers (X_2) , coating thickness (μ m) (X₃), flow rate (L min⁻¹) (X₄), and initial dye concentration (μ mol.L-1) (X₅); these variables were varied along two levels; low (-1) and high (+1); all variable parameters were chosen to be within operational range of the proposed reactor and therefore, no design modifications were required. MB degradation % after 5 hours was chosen as a response to optimise the photocatalytic degradation process. Noise factors, namely, temperature (K) and power consumption (W) were also recorded during each experiment. Although temperature is known to positively influence photocatalytic reactions [276]–[278]; the measured variations were considered too low to have a significant impact (Table 20). Z. Shams-Ghahfarokhi et al. reported an increased decolorization efficiency at higher temperatures, with significant improvements only occurring above 333K [279]. The power drawn by the system was measured directly at the wall with a wattmeter. Power consumption varied from 37 to 67 W, depending on the levels of the independent operating variables (Table 20). The pH values of the media were measured before and after each experiment; this value was 6, regardless of variable experimental parameters, therefore, was not discussed further in work progression.

Run	ın			MB removal (%)		Uncontrollable variables			
No.	X_1	X_2	X ₃	X_4	X_5	Experimental	Dradiated	Temperature	Power drawn
					Experimentai	riculted	(K)	(W)	
1	+1	+1	-1	-1	+1	64.8	60.8	300	54
2	-1	-1	+1	+1	+1	45.2	43.8	300	50
3	-1	+1	-1	+1	+1	36.4	44.0	300	49
4	+1	-1	-1	-1	+1	37.6	44.3	300	53
5	-1	+1	+1	-1	-1	61.3	70.8	298	37
6	+1	-1	-1	+1	-1	72.4	72.6	303	67
7	-1	-1	-1	+1	-1	54.9	55.8	299	50
8	+1	+1	+1	+1	-1	82.5	87.6	303	67
9	+1	+1	+1	+1	+1	58.4	59.3	306	66
10	-1	+1	-1	-1	-1	73.2	72.3	300	37
11	+1	-1	+1	-1	-1	88.7	89.0	300	54
12	-1	-1	+1	-1	+1	37.0	43.8	298	38
13	+1	+1	-1	+1	+1	60.1	60.8	303	66
14	+1	-1	+1	-1	+1	70.3	60.6	300	53
15	-1	+1	+1	+1	-1	77.6	70.8	300	49
16	+1	+1	-1	-1	-1	93.0	89.2	300	54
17	-1	-1	-1	+1	+1	26.8	27.4	300	37
18	+1	-1	+1	+1	-1	85.2	89.0	302	67
19	-1	-1	-1	-1	-1	64.1	55.8	297	37
20	-1	+1	+1	-1	+1	52.1	42.4	296	38

Table 20. Design matrix for the 5 tested independent variables with the experimental and predicted responses.

The two-levels design matrix with the corresponding experimental and predicted results for each statistical combination of independent variables are displayed in Table 20. The predicted values were obtained by fitting a regression model to the experimental data, to determine the optimal operating conditions. Regression coefficients were determined to develop a regression model, based on significant main or interaction effects. In the case of a 2levels experiment, the regression coefficients are calculated by dividing the estimates of effects E_f by 2. A regression model (39) can then be designed, with \hat{y} as the predicted response, β_0 as the intercept, β_i as a regression coefficient, β_{ij} as the interaction between the process parameters X_i and X_j , and ' ϵ ' as the random error component.

(39)
$$\hat{y} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_{12} X_1 X_2 + \beta_{12} X_1 X_2 + \dots + \varepsilon$$

Using a backward selection method, a regression model was generated with all factors and 2^{nd} order interactions [280]. Statistically significant independent variables and 2^{nd} order interactions were identified using a parameter estimate and half-normal plots. The parameter estimates report the size of contribution and direction of each predictor and, for each, gives a t-test for the hypothesis that it equals zero. A near-zero estimate indicates that a factor or interaction has no statistically significant influence on the response and should be removed from the model. Half-normal plots are a graphical tool used to estimate the effects and assess the significance of factor(s) and interaction(s) [281]. Insignificant factors or interactions should fall along a straight line, while significant one's should form outliers. As displayed in Table 21 and Figure 62, initial dye concentration (X₅), UV light intensity (X₁), number of TiO₂-coated mesh layers (X₂), coating thickness (X₃) and the interaction between coating thickness and number of TiO₂-coated mesh layers (X₂X₃) seem to stand out as significant. Flowrate doesn't seem to play any significant role in the MB removal, suggesting that the lowest selected level is appropriate, and that mass transfer doesn't bottleneck the reaction.

Term	Estimate (%)	Std Error (%)	t-ratio	p-value
Intercept	0.620843	0.021166	29.33	<.0001
X1	0.083893	0.024944	3.36	0.0282
X2	0.046956	0.024944	1.88	0.1329
X3	0.045544	0.024944	1.83	0.1419
X4	-0.009629	0.024944	-0.39	0.7191
X5	-0.14264	0.024944	-5.72	0.0046
X1X2	-0.000706	0.024944	-0.03	0.9788
X1X3	0.0004	0.024944	0.02	0.988
X1X4	-0.022608	0.024944	-0.91	0.416
X1X5	0.005883	0.024944	0.24	0.8251
X2X3	-0.040546	0.024944	-1.63	0.1794
X2X4	-0.001093	0.024944	-0.04	0.9672
X2X5	0.016643	0.024944	0.67	0.5412
X3X4	0.008455	0.024944	0.34	0.7517
X3X5	0.02844	0.024944	1.14	0.3179
X4X5	-0.00515	0.024944	-0.21	0.8465

Table 21. Parameter estimates for all independent variables and 2nd order interactions.



Figure 62. Half-normal plot for all independent variables and 2nd order interactions.

After having removed statistically non-significant predictors using the parameter estimates (Table 21) and half-normal plot (Figure 62), the following regression model (40), was designed to predict MB removal percentage, after 5 h, by the TiO₂-coated mesh reactor.

$$\hat{y} = 62 + 8.4 \times X_1 + 3.8 \times X_2 + 3.7 \times X_3 - 14.2 \times X_5 - 4.4 \times X_2 X_3 \tag{40}$$

According to the new parameters estimates (Table 22), all selected predictors have an absolute t-ratio greater than 1.96 and p-values smaller than 0.05, confirming the statistically significance of their effects.

Term	Estimate (%)	Std Error (%)	t-ratio	p-value			
Intercept	62.0	1.5	42.3	<0.0001			
X1	8.4	1.5	5.6	<0.0001			
X2	3.8	1.5	2.6	0.0212			
X3	3.7	1.5	2.5	0.0242			
X5	-14.2	1.5	-9.5	<0.0001			
X2X3	-4.4	1.5	-2.9	0.0112			
(X1) UV light; (X2) number of TiO ₂ -coated mesh layers; (X3) Coating thickness; (X4) Flowrate;							
(X5) Initial dye concentration							

Table 22. Parameter estimates for significant independent variables and 2nd order interactions.

The quality of the fit for this model was assessed using an analysis of variance (ANOVA), presented in Table 23. The F-ratio was used to assess whether the designed model differed significantly from a model where all predicted values are equal to the response mean. If the null hypothesis is true, the F-ratio should be close to 1, *i.e.* the chosen parameters do not describe accurately the actual data variations [113], [282]. The associated p-values measured the probability of obtaining a F-ratio as large as the one observed with all parameters set to zero except the intercept. Small p-values (<0.05) would indicate that the observed large F-ratio is unlikely to be obtained by pure chance alone and that the null hypothesis can be rejected. The large F-ratio (28.895) and small p-value (<0.0000) obtained with the ANOVA confirm that the model describes accurately the data variations and that the chosen parameters are significant.

In addition, the accuracy of fit between the experimental values and the model was assessed by analysing the lack-of-fit (LOF) [113]. The regression model fits the experimental data well, as the mean square of the lack-of-fit error (0.004) was close to the pure error (0.005). The lack-of-fit for this model was statistically insignificant with a large p-value (0.610) and a F-ratio close to 1 (0.850), confirming that this model can be used for both prediction and optimisation.

The model's goodness-of-fit was confirmed by the R^2 (0.91) and $R^2_{adjusted}$ (0.88) for experimental data points plotted against the predicted values [283]. The $R^2_{adjusted}$ is a modified version of R^2 which takes into account the model's number of predictors. The small gap between R^2 (0.91) and $R^2_{adjusted}$ (0.88) indicates that the experimental data variations are in accordance with the model and that the predicted responses are trustworthy (Table 23). Plotting the data against the predicted responses (Figure 63a) highlighted the agreement of the model with the experimental values. The normal probability plot of the residuals, shown in Figure 63b, approximately forms a straight line, supporting the assumptions that the error terms are normally distributed, while the studentized residuals plot didn't reveal the presence of any outlier Figure 63c.

Overall, the analysis of variance, lack of fit, and R^2 results all confirmed that the model was statistically significant and could be used to predict and optimise the % removal of MB after 5 h using the TiO₂-coated mesh photocatalytic reactor.

Source	DF	Sum of Squares	Mean Square	F-Ratio	p-value		
Model	5	0.620	0.124	28.895	<0.0000		
Error	14	0.060	0.004				
C. Total	19	0.680					
Lack of fit	9	0.036	0.004	0.850	0.610		
Pure error	5	0.024	0.005				
Total error	14	0.060					
$R^2 = 0.9117, R^2_{adjusted} = 0.8801$							

Table 23. Analysis of variance (ANOVA) and Lack-of-fit (LOF) for MB removal efficiency of the TiO₂-coated stainless-steel mesh-based photoreactor.



Figure 63. Diagnostic plots for the photocatalytic MB removal % after 5 h a) experimental by predicted plot; b) normal probability plot of residuals; c) studentized probability plot of residuals.

7.4. Durability assessment

The best performing set of conditions (sample No. 16), predicted by the model and verified experimentally, was used to assess the reusability potential of the TiO₂-coated stainless-steel mesh. As displayed in Figure 64, no apparent reduction in photocatalytic activity was observed after 10 consecutive cycles equivalent to 360 h of testing. In Figure 65, the Raman mapping confirmed this trend, with no obvious change in the coating's integrity being observed between the first analysis and after 180 and 360 h of testing. The visual differences observed in Figure 65 (d) are due to the bending of the sample in certain areas (mainly lower left) after multiple handlings, while performing repeated analysis. This bending of the mesh resulted in out of focus analysis, which is why some threads appear bare whilst other apertures appear coated.



Figure 64. Reusability assessment of the TiO₂-coated mesh; MB removal percentage after 5h for 10 consecutive cycles.



Figure 65. Raman maps with integrated intensities of (A) the main anatase peak at 144 cm⁻¹ of the same area after the (B) 1st, (C) 5th and (D) 10th MB degradation cycle.

The influence of five parameters was investigated for their role in the removal of methylene blue after 5 h, in this bespoke photocatalytic reactor. Using a linear regression model, UV light intensity (X_1) , number of TiO₂-coated mesh layers (X_2) , coating thickness (X_3) and initial dye concentration (X_5) were identified as the most important and influential parameters. Flowrate (X₄) had no effect on the MB removal rate, at the minimum (5.14 L min⁻ ¹) and maximum (9.54 L min⁻¹) operating conditions of the 12 V pump. This is consistent with the findings of de Lasa et.al, who concluded that mass transfer was not limiting the removal of MB in their photocatalytic reactor, for flowrates equal or higher than 1.7 L.min⁻¹ [141]. Decreasing the initial dye concentration (X_5) resulted in an increased MB removal rate, which could be the result of a lower consumption of radical species by intermediary products [284], [285]. Increasing the UV light intensity (X_1) improved the MB removal, as it is known to increase the photogeneration of excitons and of radical species [285]-[287]. Increasing the coating thickness (X₃) and the number of TiO₂-coated mesh layers (X₂) also improved the MB removal rate. The former has been reported as having a positive effect on photocatalytic activity, with significant improvements occurring between 100 and 500 nm, and to a lesser extent between 500 nm and 2 µm [238]. Increasing the latter comes down to increasing the catalyst load, which is known to improve the reaction rate [288]. Interestingly, a significant negative interaction between the coating thickness (X₃) and the number of TiO₂-coated mesh layers (X₂) seemed to play a role in the MB removal efficiency. Overlapping two sets of mesh coated with TiO₂ for 2 h could hinder light permeability, in turn decreasing the efficiency of the system. It was confirmed experimentally, by measuring the UV light intensity (at 365 nm) received by a UVP UVX Radiometer detector, after passing through the reactor loaded with different mesh configurations (Figure 66). Decreases of 12.7 and 13.8 % were observed, respectively, for one and two sets of coated stainless-steel mesh, when the coating thickness increased from 1.1 to 1.6 µm. These values are only indicative, as the measurements were performed without the reflective surfaces.



Figure 66. UV light intensity measured for different mesh configurations;(a) 1 set of mesh, 1 h deposition; (b) 1 set of mesh, 2 h deposition; (c) 2 sets of mesh, 1 h deposition; (d) 2 sets of mesh, 2 h deposition.

To scale the performance of the reactor with other system designed by various authors the figure of merit (FOM) was calculated. It is a performance indicator which takes into account the volume of treated solution, the amount of catalyst, the treatment time and the energy consumption of the system. FOM was calculated using equation (41) and graded between 0 and 100 using a conversion factor used to index 85 different photocatalytic systems [289].

$$FOM = \frac{Product \ obtained \ (L)}{Catalyst \ dosage(g.L^{-1}) \times Time(h) \times Energy \ consumption(Wh. \mu mol^{-1})}$$
(41)

Parameters	Unit	LCPR-I			
Catalyst	-	TiO ₂			
Optical bandgap	eV	3.2			
		Pulsed DC Reactive			
Synthesis method	-	Magnetron sputtering			
Coating thickness	μm	1.6			
Pollutant	-	Methylene blue			
Catalyst loading	g.L ⁻¹	0.34			
Initial concentration	µmol.L ⁻¹	1			
Light power (peaked at 365 nm)	mW/cm ²	6.2			
Degradation efficiency after 5 h of	0/	02			
UV-A irradiation	%0	93			
Power consumption	Wh.µmol ⁻¹	627			
Reaction rate (r)	10 ⁻⁵ μmol.s ⁻¹	8.01			
*Figure of merit (FOM)	$\mu mol.Wh^{-1}.h^{-1}.g^{-1}$	1.14			
*FOM classification: best (100) $good (30 - 10)$ average (10 - 1) and below average (<1)					

Table 24 Summar	v of reactor	r characteristics	and performar	nce for co	ondition N	No 1	6
1 abic 24. Summar	y of reactor	characteristics	and performat		manuon	10.1	. 0

M classification: best (100), good (30 10), average (10 1) and below average (<1)

w

The characteristics and performance metrics of this bespoke reactor are summarised in Table 24. The LCPR-I displayed rather average FOM level, which can be explained by the composition of the reactor walls (PMMA), which absorbed >80 % of incident UV-A light, as shown in Figure 67. This is the result of the trade-off between choosing affordable parts available in the consumer market and custom-made expensive components. Despite the limited UV-A transmittance, LCPR-I still managed to achieve a FOM of 1.14, achieving better performance than >40 % of the 85 systems reviewed by Anwer et al. (2019). It should be noted though, that as a metric, the FOM parameter tends to favour powder-form photocatalysts, due to the "catalyst dosage" component used in equation (41). Specific surface area is known to be positively correlated with photocatalytic activity [290], which is negligible when comparing powder-form photocatalysts of similar specific surface area. This is not the case for immobilised photocatalysts, as photocatalytic reactions only occur on the film's exposed surface, which is orders of magnitude smaller than their powder counterpart.

This is especially true for thin films produced by reactive magnetron sputtering, which tend to form dense columnar structures [193]. Whilst the results of the current study are encouraging, there is still room for improvement for this proof of concept. The interaction between coating thickness and the number of TiO₂-coated mesh layers was identified as having a negative impact on the MB removal efficiency. To increase the catalyst load whilst maintaining light permeability, different strategies can be implemented, such as simultaneously irradiating the reactor from different angles and/or using different mesh aperture sizes.

Future work will be aimed at coating the LCPR-I mesh, using reactive magnetron sputtering, with a novel and more efficient photocatalyst, instead of TiO₂, and evaluating its effectiveness against micro-organisms, pharmaceuticals and real-world wastewater samples. Fouling was not investigated in this study due to the use of deionised water, as microbial presence in wastewater would produce biofouling and affect the photoreactor's performance.



Figure 67. Absolute irradiance measurements for different reactor configurations.

To summarise, a bespoke photocatalytic reactor (LCPR-I) was built from low-cost consumer market parts and used to degrade a model pollutant, methylene blue. The reactor utilises crystalline TiO₂-coated woven stainless-steel mesh photocatalyst, produced in a one-step process by reactive pulsed DC magnetron sputtering. This deposition process is sustainable and addresses the technical viability and economic feasibility challenges faced by photocatalytic waste treatment.

The methylene blue removal percentage after 5 h was optimised by investigating the influence of UV light intensity, number of TiO₂-coated mesh layers, coating thickness and water flowrate. All factors, except for flowrate, were found to have an influence on the removal process efficiency. 30 W UV-A, 2 layers of mesh coated with 1.1 µm of TiO₂ and a flowrate of at least 5.14 L.min⁻¹ were found to be the optimum conditions, leading to the removal of more than 90 % of the model pollutant under 5 h. The coated stainless-steel woven mesh has proven to be durable as the photocatalytic activity of the material remained unchanged after 360 h of consecutive use. The findings of this study, as well as the proposed reactor design, may be of considerable interest for those involved in practical implementation of sustainable and efficient photocatalytic water treatment processes.

Chapter 8. Bismuth titanate, an efficient and novel photocatalyst produced by magnetron sputtering.

This chapter presents the results obtained in a study of a bismuth titanate composite coating produced by magnetron reactive co-sputtering for wastewater treatment applications. The findings of this work were published in Applied Surface Science [291]. Passages and figures were reproduced verbatim in accordance with Elsevier's Journal Author Rights guidelines. This chapter discusses such aspects as choice of photocatalyst (Section 8.1), the current methods used to produce such photocatalyst (Section 8.2), crystalline phases investigation (Section 8.3), coating morphology (Section 8.4), photocatalytic activity (Section 8.5) and an investigation of the improved photocatalytic activity (Section 8.6). A summary of this part of the project is given in Section 8.7.

8.1. Bismuth titanate background

Wide bandgap and rapid electron-hole recombination makes practical exploitation of titanium dioxide photocatalysis a rather challenging task for real-world high-throughput processes [243]. Various attempts have been made to address these issues by either modifying TiO₂ [94], [292] or using alternative photocatalysts [293]–[295]. Lately, bismuth oxide-based materials have captured researchers' attentions, as possible viable alternatives to titanium dioxide. Bismuth oxide [121], vanadate [259], tungstate [296] and titanate [297] consistently displayed high photocatalytic activity and lower band gap, compared to conventionally used titania. Despite initially promising results, the overall number of studies of bismuth (complex) oxide-based materials is rather limited.

Bismuth titanate (BT) is a complex oxide semiconductor characterised by a high curie temperature, high dielectric constant and low dielectric energy loss. Hence, this ferroelectric material is mainly used as a replacement for lead-based ceramics in capacitors, sensors and actuators [297]. However, in recent years, it was also investigated for its photocatalytic properties; with two polymorphs namely, $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$, having shown promising results [139], [298]. The former belongs to the Sillenite family and is formed by a network of Bi–O polyhedra connected to TiO₄ tetrahedra [299]. The latter belongs to the Aurivillius family and composed of pseudo-perovskite units (Bi₂Ti₃O₁₀)²⁻, sandwiched by fluorite-like (Bi₂O₂)²⁺ layers [136]. Lardhi. S et al. The crystal structure of Bi₁₂TiO₂₀ and Bi₄Ti₃O₁₂ semiconductors is represented in Figure 68 [300].



Figure 68. DFT/PBE crystal structures of (a) Bi₁₂TiO₂₀ and (b) Bi₄Ti₃O₁₂. Colour legend: Bi in purple, Ti in gray, and O in red [300].

In 2003, Yao *et al.* were the first to report the remarkable photocatalytic activity of $Bi_{12}TiO_{20}$, which is believed to be the most active of the two studied polymorphs [139]. The Bi–O polyhedra are suggested to act as active donor sites, which can enhance O₂ electron transfer and reduce electron-hole pair recombination. $Bi_{12}TiO_{20}$ has a low bandgap, estimated at 2.4 eV, and therefore can be photoactivated with a broader range of wavelengths, compared to titanium dioxide.

Recent studies focused on producing a new generation of bismuth titanate-based composites, to improve light harvesting and extend charge carrier lifetime. Du *et al.* synthesized an efficient $Bi_{12}TiO_{20}/Bi_4Ti_3O_{12}$ photocatalyst composite using a low-energy solid-state reaction [301]. Single phase samples were all outperformed by mixed phases ones, with the highest activity being achieved for a Bi:Ti molar ratio of 12:6. Similarly, Meng *et al.* synthesized porous $Bi_{12}TiO_{20}/Bi_4Ti_3O_{12}$ composite nanofibers using electrospinning [302]. The best performing sample had a $Bi_{12}TiO_{20}:Bi_4Ti_3O_{12}$ molar ratio of 11.5:1 and showed excellent photocatalytic activity, cycling stability, and regeneration ability. Photogenerated electrons with low reduction potential in the $Bi_{12}TiO_{20}$ conduction band migrate to the $Bi_4Ti_3O_{12}$ valence band to recombine with low oxidation potential holes [301]. Consequently, electron and holes with high redox potential are less likely to recombine and more likely to diffuse to the surface.

8.2. Work overview

It should be noted that, to date, photocatalytic bismuth titanate photocatalysts were synthesised mainly via soft chemistry routes [138], [303] and solid-state reaction [298], potentially limiting their commercial exploitation. In contrast to chemical techniques, physical vapour deposition methods such as magnetron sputtering offer multiple advantages, such as lack of toxic / hazardous precursors and intermediates, precise control over material uniformity and composition and great up-scaling potential.

Bismuth titanate coatings were prepared by reactive pulsed DC (pDC) reactive magnetron co-sputtering onto soda-lime glass slides. This technique has the advantage of direct immobilisation of the catalyst which provides the added advantage of easy material recovery from treated media, unlike powdered photocatalysts, where membrane filtration is typically required, contributing to the overall cost of the treatment process [193]. Several studies have reported bismuth titanate production via magnetron sputter deposition [135], [304], [305], however these studies are based on the use of compound targets. In contrast to that, sputtering of metallic targets in a reactive oxygen containing atmosphere allows deposition at considerably lower cost (no sophisticated radio-frequency power sources required); enables higher deposition rates and therefore shorter deposition times; and is less prone to arcing / process failures.

This work presents the deposition of photocatalytic bismuth titanate films via pDC reactive magnetron co-sputtering; to the best of our knowledge, this technique has not been reported for the production of bismuth titanate to date for photocatalytic applications [306], [307]. Following the deposition process, the produced materials were thoroughly characterised by a variety of analytical techniques and the photocatalytic properties were studied via dye degradation and *E. coli* inactivation tests. Conventionally used photocatalytic titanium dioxide films were deposited using the same technique and compared to bismuth titanate. The results of the study confirmed the high efficiency of bismuth titanate compared to the titanium dioxide counterpart.

Soda-lime glass slides were coated with bismuth titanium oxide by reactive pulsed DC magnetron sputtering. Unlike in Chapter 6 and 7, stainless steel couldn't be used as a substrate due to iron diffusion occurring during the annealing process and resulting in photocatalyst inactivation. Bismuth titanium oxide samples were synthesized in an argon/oxygen reactive atmosphere for 4h by rotating the substrates between the two targets, whilst simultaneously sputtering both. Different coating compositions were obtained by varying the power applied to the Ti target from 0.5 to 1.5 kW with 0.25 kW increments, whilst keeping the power applied to the Bi fixed at 0.2 kW.

The power applied to the latter was maintained to a low value due to the high sputtering rate of metallic bismuth. TiO₂ samples were also deposited in an argon/oxygen reactive atmosphere, with 1 kW applied to the Ti target, without rotation for 1 hour (conditions were established in an earlier study for production of photocatalytically active titanium dioxide films) [232]. All depositions were operated with a pulse frequency of 100 kHz, a duty cycle of 60 %, while all samples were annealed in air at 600 °C post-deposition. BT samples were named according to the power applied to the titanium target. All the produced samples are presented in Table 25, with their respective deposition conditions. The oxygen was kept at a constant 25 sccm when sputtering multiple elements *i.e.*, bismuth and titanium.

Sample	Ti target power	Bi target power	Rotation	Deposition time
Sample _	kW	kW	Rpm	h
TiO ₂	1	-	-	1
BT500	0.5	0.2	2	4
BT750	0.75	0.2	2	4
BT1000	1	0.2	2	4
BT1250	1.25	0.2	2	4
BT1500	1.5	0.2	2	4

Table 25. Coating deposition parameters.

8.3. Crystallinity assessment

Initially, the bismuth titanate samples were analysed with Raman spectroscopy coupled with Raman mapping for identification of crystalline phases and assessment of their uniformity. According to the literature, $Bi_{12}TiO_{20}$ is the most active phase of bismuth titanate [139]. The results of Raman spectroscopy revealed the presence of $Bi_{12}TiO_{20}$ phase for all the prepared films. However, depending on deposition conditions, the intensity of the Raman peaks for $Bi_{12}TiO_{20}$ and homogeneity of their distribution varied significantly. Of the Raman peaks observed (Figure 69a), peaks identified at 720 and 664 cm⁻¹ are due to the stretching of TiO₄ tetrahedra, whilst the ones at 620, 320, 262, 224 and 206 cm⁻¹ are attributed to the vibration modes of the Bi-O [308].

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The 166 cm⁻¹ peak is attributed to the "breathing mode" of Bi and all O atoms, the 144 cm⁻¹ to the "breathing mode" of Bi and O2 atoms, and Bi and O2 to the vibrations elongating the cluster along the [100] or [010] [308]. The most intense Raman peak at 537 cm⁻¹ corresponds to the "breathing" of O1 atoms and was used as a reference to produce the Raman maps and assessment of Bi12TiO20 phase distribution and uniformity. As can be seen from Raman mapping results (Figure 69 (b, c)), application of lower levels of power to the titanium target resulted in deposition of samples with intense signals and an evenly distributed Bi₁₂TiO₂₀ phase. Increasing the power applied to the titanium target resulted in lower 537 cm⁻¹ Raman peak intensities and uneven distributions of the Bi₁₂TiO₂₀ phase, with clusters of crystallised Bi₁₂TiO₂₀ (red) surrounded by an amorphous structure (green), as shown in Figure 69d. Based on Raman mapping results, the deposition conditions used for the production of sample BT750 were selected for further studies. Additionally, cross-sections of samples TiO₂, BT1500, BT750 and BT500 samples were characterised by EDX analysis and k-factors were estimated using the Schriber-Wims fitting model for elemental quantification (data presented in the Table 26). As expected, increasing the power applied to the Ti target resulted in an increased proportion of titanium within the coatings, which hindered the crystallisation of the Bi₁₂TiO₂₀ phase, when the applied power was higher than 750 W.



Figure 69. Raman spectrum of (a) $Bi_{12}TiO_{20}$ phase and corresponding Raman mapping of samples (b) BT500, (c) BT750 and (d) BT1500.

Sample	Z	Element	Family	Atomic fraction (%)	Mass fraction (%)	Fit error (%)
TiO	8.00	0	K	50.90	27.90	0.05
1102	22.00	Ti	Κ	49.10	72.10	0.04
	8.00	0	Κ	35.90	6.57	0.13
BT1500	22.00	Ti	Κ	23.50	11.50	0.08
	83.00	Bi	L	40.70	81.90	0.04
	8.00	0	Κ	39.60	6.55	0.96
BT750	22.00	Ti	Κ	11.80	5.24	0.12
	83.00	Bi	L	48.50	88.20	0.04
	8.00	0	Κ	37.40	5.79	0.67
BT500	22.00	Ti	Κ	9.45	3.91	0.09
	83.00	Bi	L	53.10	90.30	0.05

Table 26. Results of elemental analysis (EDX)

Following phase analysis and mapping, optimum annealing temperatures and times were identified using XRD analysis. The crystallisation and phase transition processes were investigated by placing an as-deposited BT750 sample into an XRD hot stage chamber, for insitu X-ray diffraction study at varied temperatures. The sample was heated from room temperature to 600 °C with 100 °C increments, in an air atmosphere. As shown in Figure 70, no crystallisation occurs below 400 °C and samples annealed at lower temperatures are characterised by an amorphous structure. The crystallisation starts at 400 °C with formation of the δ -Bi₂O₃ phase (ICDD 96-101-0312), with rather broad diffraction peaks. Annealing at 500 °C results in disappearance of the δ -Bi₂O₃ phase and formation of bismuth titanate polymorphs, identified as Bi₁₂TiO₂₀ (ICDD 96-403-0657) and Bi₄Ti₃O₁₂ (ICDD 96-152-8446). Finally, at 600 °C, the Bi₄Ti₃O₁₂ phase (ICDD 96-152-8446) became more prominent with sharpened diffraction peaks and additional ones appearing. Higher annealing temperatures could not be investigated due to the nature of the substrate used. Therefore, an annealing temperature of 600 °C was identified as the preferential one for achieving BT750 sample crystallisation.

Titanium dioxide samples were annealed under identical conditions to enable direct comparison; all observed peaks can be indexed to anatase TiO₂ (ICDD 96-900-8215), as shown in Figure 70a. Additionally, different annealing times (up to 4h) were studied at 600 °C to monitor potential phase transitions depending on annealing duration. The results are presented in Figure 70b and reveal no changes in phase or texture of sample BT750, suggesting that the shortest thermal treatment time of 1h is adequate in this case. Overall, the findings on Bi₁₂TiO₂₀/Bi₄Ti₃O₁₂ phase transition temperatures were consistent with the results reported in earlier studies on the same material [138], [297], with annealing time for 1 hour at 600 °C being an adequate thermal treatment regime. The annealing temperatures above 600 °C were not considered, due to the softening temperatures of soda-lime glass (soda-lime glass reportedly softens at temperatures above 680 °C [309]). Additionally, the crystalline phases were quantified by extracting the weight fractions as percentages from a Pawley intensity refinement, given in Annex based on the areas of two non-overlapping peaks: Bi₁₂TiO₂₀ (020) and Bi₄Ti₃O₁₂ (600). The estimated phase composition of the BT750 sample is ~80% of the Bi₁₂TiO₂₀ phase and ~20% of the Bi₄Ti₃O₁₂ phase.



Figure 70. Results of XRD analysis; (a) XRD patterns of sample BT750 heated in an air from room temperature to 600 °C and pattern of TiO₂ annealed at 600 °C; (b) XRD patterns of BT750 sample heated in an air at 600 °C for up to 4 hours.

8.4. Coating morphology and band gap measurement

The surface morphology of the titanium dioxide and bismuth titanate coatings was studied with FEG-SEM; the micrographs are presented in Figure 71 (a, b), respectively. It is clear that there are some morphological differences between these two materials. TiO_2 has a homogeneous cauliflower-like structure, typical for thin films grown by magnetron sputtering [232], while the BT750 sample developed a rather heterogeneous structure, composed of angular crystallites, randomly distributed and embedded in a smooth matrix. Further studies of surface morphology were performed by AFM (results for TiO_2 and BT750 are shown in Figure 71 (c, d), respectively). It should be noted, that despite differences in morphology, similar surface roughness (R_a) values of 14.20 nm and 15.56 nm were obtained by AFM for TiO_2 and BT750, respectively, thus enabling direct comparison of photocatalytic properties in terms of sample surface area.



Figure 71. SEM micrographs: (a) TiO₂ sample; (b) BT750 sample; AFM micrographs of (c) TiO₂ sample; (d) BT750 sample.

The TEM micrograph (Figure 72a) of the BT750 sample's cross-section revealed a structure composed of interconnected grains with varying sizes (~50 to ~100 nm in diameter). EDX elemental mapping of the sample's cross-section revealed a heterogeneous distribution of the Bi and Ti elements, with distinct "bismuth rich" and "bismuth poor" areas (Figure 72b).

This is in accordance with the $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ phases identified by XRD analysis, which would correspond to the "bismuth rich" and "bismuth poor" areas, circled in purple and orange (Figure 72b), respectively. HRTEM micrographs were used to verify the crystalline phase(s) of the material's matrix and the presence of angular crystallites, previously discovered via XRD and FEG-SEM analysis, respectively. The d-spacing was estimated at ~3.2 and ~3.0 Å for the matrix (Figure 72c) and the crystallites (Figure 72d), respectively. These interplanar distances correspond to the (013) plane of the $Bi_{12}TiO_{20}$ phase for the matrix and to the (711) plane of the $Bi_4Ti_3O_{12}$ phase for the crystallites. The presence of the above-mentioned phases is in agreement with the XRD results.



Figure 72. Cross-sectional TEM micrographs of the BT750 thin film deposited on soda-lime glass slides: (a) Morphology of coating at low magnification, (b) EDX elemental mapping, (c) HRTEM micrograph of the Bi₁₂TiO₂₀ (013) phase, (d) HRTEM micrographs of the Bi₃Ti₄O₁₂ (711) phase.

The optical band gap energy of the crystalline semiconductors was estimated using the Tauc plot method [216], by plotting $(\alpha h v)^n$ as a function of hv and extrapolating the linear region to the abscissa (where α is the absorbance coefficient, h is Plank's constant, v is the frequency of vibration). Just like titanium dioxide, all bismuth titanate polymorphs are indirect bandgap materials, thus a coefficient n = 1/2 is used [310]. The BT750 and TiO₂ samples bandgap energy values were estimated at 2.82 and 3.20 eV, respectively (Figure). The bandgap of BT750 was significantly lower, compared to that of TiO₂, meaning it can be photoactivated with a broader range of wavelengths. Our estimated value for titanium dioxide is in accordance with published data, as its bandgap is typically reported as 3.20 eV [311].

The same applies for BT750, as Fang *et al.* estimated the band gap values of $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ at 3.03 and 2.59 eV, respectively [138]. Additionally, Du *et al.* studied a similar $Bi_{12}TiO_{20}/Bi_4Ti_3O_{12}$ composite produced by solid synthesis calcination and found band gap values ranging from 2.96 and 2.84 eV [301].



Figure . UV-Vis absorption spectra for TiO₂ and BT750 samples (a) and corresponding Tauc plots (b).

8.5. Photocatalytic activity evaluation

The photocatalytic activity of the prepared TiO₂ and BT750 samples was initially assessed by monitoring the removal of methylene blue (MB) over time under UV-A light irradiation. The test was performed for uncoated glass (used as reference sample), BT750 and TiO₂ coatings. As shown in Figure 73a, adsorption-desorption equilibrium was reached after 1 hour in the dark, with no significant variation across all samples. Under UV-A irradiation no significant MB degradation was observed for the uncoated glass sample, while for both TiO₂ and BT750, the MB concentration gradually decreased under irradiation. The photocatalytic performances of the two photocatalysts were compared by monitoring the main absorbance peak of MB under UV and over time. The pseudo-first order constant *k* was extracted using $Ln(A_0/A_t) = kt$, where *A* is the absorbance measured at 664 nm and *t* the time. Pseudo-first order constant *k* values of 0.18, 0.52 and 1.40 ($10^{-5}s^{-1}$) were obtained for uncoated glass, TiO₂ and BT750 samples, respectively. Although TiO₂ and BT750 coatings have a similar thickness and roughness, BT750 clearly outperformed TiO₂ with a photocatalytic activity around 3 times higher.

Since stability and reusability of photocatalysts are of extreme importance for practical application, the reusability of the photocatalysts was assessed during 15 consecutive cycles of MB degradation tests under UV-A. Surprisingly, as shown in Figure 73c, there was a clear trend of increased photocatalytic activity for BT750 with each consecutive cycle. The bismuth titanate composite pseudo-first order constant k_{α} rose to 7.76 ($10^{-5}s^{-1}$) after the 15^{th} cycle, which translates to a 6-folds increase when compared to the 1^{st} cycle. To put things into perspective, after its 15^{th} cycle, BT750 was 15 times more efficient at degrading MB under UV than TiO₂. When the same test was performed for the TiO₂ sample, there were no noticeable changes in activity over 15 cycles of consecutive use. In both cases, repeated usage did not affect the surface roughness value (R_a) of the samples, therefore, the increased photocatalytic activity of bismuth titanate cannot be attributed to increased area of contact with pollutant in this case.

Following the dye degradation tests, the photocatalytic properties of bismuth titanate and titanium dioxide samples were compared, based on their ability to inactivate *Escherichia coli* (*E.coli* – the model microorganism was selected based on recommendations of ISO 27447 [231], also being a significant indicator of poor water quality) under UV-A irradiation. The results are presented in Figure 73d. The intensity of UV light was adjusted (by keeping the

required distance between the light source and sample surface constant) to the level recommended in ISO 27447 standard of 0.25 mW cm⁻² to rule out photoinactivation of the microorganism by means of UV light itself. Similar to the MB degradation tests, antimicrobial properties of BT750 samples were compared to those of TiO₂ coatings, while uncoated glass was used as reference; the tests were performed both under UV-A irradiation, and in the dark. As evident in Figure 73d, BT750 samples were able to reduce the number of viable *E. coli* cells in suspension to below the level of detection within 48 hours of UV-A irradiation. When comparing irradiated vs non-irradiated samples, BT750 was the only material to demonstrate a statistically significant (p<0.05) antimicrobial effect after 24 hours, with 1.61×10^6 CFU/mL fewer cells recovered when compared to its corresponding dark control. No other irradiated vs non-irradiated a statistically significant antimicrobial effect. At the 48-hour mark, the number of cells recovered from the BT750 sample was nil, compared to the 2.9×10^5 CFU/mL recovered from the non-irradiated BT750 sample. The number of cells recovered from TiO₂ and uncoated glass, both irradiated and non-irradiated, as well as BT750 non-irradiated samples remained relatively consistent across the 48 hours.

These results clearly highlight the more efficient photocatalytic activity of BT750 against both model pollutants and microorganisms when compared to the well-established TiO₂.



Figure 73. Photocatalytic activity assessment; (a) MB concentration in the dark and under UV when exposed to BT750, TiO₂ and uncoated glass; (b) Pseudo-first-order reaction rate plotted for MB removal, calculated for BT750, TiO₂ and uncoated glass under UV light; (c) MB pseudo-first-order reaction rate calculated for TiO₂ and BT750 over 15 consecutive cycles; (d) E. coli CFU/mL after 24, 48 hours on different materials and under different irradiation conditions, * represents statistically significant difference (p<0.05).
8.6. Oxygen vacancies investigation

Along with a photocatalytic activity change, the colour of the coating changed from white to black at the end of the cycling experiment. Hence, the cycled sample was termed "BT750 – Black" to avoid confusion with the pristine sample which is termed BT750. XRD analysis at different grazing angles (from 0.3° to 5°) was performed to assess crystalline phases distribution through the bulk of the sample; it did not reveal significant difference between BT750 and BT750 – Black (Figure 74), which implies that there was no phase composition, crystal size nor orientation change after the cycling experiment (Figure 74). Additionally, the same 80:20 ratio of $Bi_{12}TiO_{20}$ to $Bi_4Ti_3O_{12}$ phases was estimated by direct derivation method at every grazing angle, suggesting a homogeneous phase distribution in the thin film (bulk and surface).



Figure 74. GIXRD analysis at different incident angle of (A) BT750 and (B) BT750 – Black.

Hence, to understand the origin of the increased photocatalytic activity observed during the reusability assessment, the chemical and electronic states of the BT750 and BT750 – Black coatings were investigated by XPS analysis. For reference, a pristine TiO_2 sample (TiO_2 -a) was analysed and compared to one that was cycled (TiO_2 -b). The results of the XPS analysis for TiO_2 and BT750 are presented in Figure 75 and Figure 76, respectively. Gaussian functions were used for deconvolution of individual peaks. The carbon 1s peak was observed on survey spectra of all samples (not shown here) at 284.8 eV and attributed to adventitious carbon; the binding energies were referenced to this peak.

High-resolution spectra of Ti 2p and O 1s peaks for the titanium dioxide coatings are presented in Figure 75 (a, b) for TiO₂-a and Figure 75 (c, d) for TiO₂-b, respectively. It is clear that the Ti 2p spectra of TiO₂-b (cycled) and TiO₂-a (pristine) samples showed no significant variation; with two peaks attributed to $Ti^{4+} 2p_{3/2}$ at 458.3 eV and $Ti^{4+} 2p_{1/2}$ at 464.1 eV clearly visible in each case. From the absence of Ti³⁺ 2p peaks (typically observed at 457.1 eV and 462.9 eV [92], [312]), it can be concluded that for both of the TiO₂ samples Ti was found in the Ti⁴⁺ oxidation state. The O 1s peak for TiO₂-a sample (Figure 75b) can be deconvoluted into two peaks at 529.6 and 531.5 eV, that are typically attributed in literature to lattice oxygen (O 1s L) and oxygen vacancies or defects (O 1s V) [313]. The same two peaks can be seen on the high-resolution O 1s XPS spectrum in TiO₂-b sample (Figure 75d), however the presence of a third peak at 532.4 eV is evident, corresponding to chemisorbed oxygen species O 1s C [313]. The oxygen vacancy peak, O 1s V, is indicative of the presence of oxygen vacancies (O⁻ , O_2^{-}) in the lattice of the metal oxide, while the chemisorbed oxygen peak, O 1s C, is indicative of the presence of loose oxygen species on the surface of the sample, from H₂O or M-OH. Therefore, the presence of a third peak on the high-resolution O 1s XPS spectrum of the TiO₂b sample is in good agreement with the fact that after 15 cycles in aqueous solution of MB dye there is a considerable amount of chemisorbed oxygen on the sample surface, compared to its unused counterpart. It is notable that for both TiO₂-a and TiO₂-b, the atomic percentage ratio of the lattice oxygen peak to oxygen vacancy peak was calculated (from relative areas of the peaks) as 2:1. The latter finding is in good agreement with MB degradation data, where the photocatalytic activity of the titanium dioxide sample, unlike BT750, remained stable over 15 consecutive testing cycles.



Figure 75. High-resolution XPS spectra of TiO₂-a (pristine) sample: (a) Ti 2p spectrum, (b) O 1s spectrum; and TiO₂-b (cycled) sample: (c) Ti 2p spectrum, (d) O 1s spectrum.

High-resolution XPS spectra of BT750 and BT750 – Black samples are shown in Figure 76. Thus, Figure 76 (a) and (d) depict the Bi 4f peak for BT750 and BT750 – Black samples, respectively. Clearly, no significant differences in peaks shape can be observed in this case. The spectrum of BT750 reveals two peaks at 158.9 and 164.3 eV that can be assigned to the binding energies of Bi 4f7/2 and Bi 4f5/2 states, which is in good agreement with the literature information [314]. However, for the Bi 4f spectrum on the BT750 – Black sample, there is a shift of the peaks of ca. 0.8 eV towards lower binding energies. For bismuth oxide-based photocatalysts the latter is typically attributed to the presence of additional oxygen vacancies [315]. The absence of additional shoulder peaks next to the main peaks is believed to be indicative of the presence of only the Bi³⁺ oxidation state for both BT750 and BT750 – Black, respectively) partially overlaps with Bi 4d, also in good agreement with the information found in the literature [306]. Deconvolution of the Ti 2p spectra in each case reveals three peaks, namely Ti⁴⁺ 2p3/2 at 458.3 eV and Ti⁴⁺ 2p1/2 at 464.1 eV, as well as Bi 4d3/2 at 466.1 eV.

In this case, due to strong peak overlapping, it is difficult to estimate the likelihood of the presence of $Ti^{3+} 2p$ peaks next to the $Ti^{4+} 2p$ peaks, though as the $Ti^{3+} 2p3/2$ peak is typically observed at a binding energy of 457.1 eV, it is rather likely that, similarly to TiO_2 , in the BT750 sample Ti was in the Ti^{4+} oxidation state. O 1s high-resolution spectra are shown in Figure 76 (c) and (f) for BT750 and BT750 - Black, respectively. Similarly, to the TiO_2 sample analysed earlier, O 1s peak of BT750 can be deconvoluted into two peaks, corresponding to lattice oxygen (O 1s L) and oxygen vacancies (O 1s V), while an additional peak attributed to chemisorbed oxygen can be clearly seen on the spectrum of BT750 - Black. However, in contrast to TiO_2 samples, the atomic percentage ratio of O 1s L to O 1s V (from relative areas of the peaks) changed from ca. 4:1 for the BT750 to ca. 1:0.7 for the BT750 - Black. The latter is clearly indicative of a significantly higher number of oxygen vacancies / defects being present in the BT750 – Black sample after cycling tests, and is good agreement with MB degradation test results, where a 6-fold increase in activity was observed after 15 cycles of use.



Figure 76. High-resolution XPS spectra of BT750 sample: (a) Bi 4f spectrum, (b) Bi 4d and Ti 2p spectrum, (c) O 1s spectrum; and BT750 – Black: (d) Bi 4f spectrum, (e) Bi 4d and Ti 2p, (f) O 1s spectrum.

For further insights into the increased photocatalytic activity of the Bi₁₂TiO₂₀/Bi₄Ti₃O₁₂ samples, time-resolved photoluminescence (TRPL) was used to evaluate the dynamics of photogenerated charge carriers of BT750, BT750 – Black and TiO₂ samples. As no variation in neither photocatalytic activity nor XPS results was observed after cycling, for the TiO₂ samples, the PL was only performed on an unused titanium dioxide coating. The PL decay graphs, as well as corresponding residuals are presented in Figure 77. All the decay curves obtained can be well described by simple multi-exponential decay model [317], [318] (Equation (42)), where τ is the electron lifetime, β is the shape factor and A is a baseline correction factor. The average lifetime of the photogenerated species, τ_{avg} was estimated using Equation (43).

$$\hat{Y} = \mathbf{A} + \sum_{i}^{n} \beta_{i} \times e^{(-t/\tau_{i})}$$
(42)

$$\tau_{avg} = \frac{\sum_{i}^{n} \beta_{i} \times \tau_{i}^{2}}{\sum_{i}^{n} \beta_{i} \times \tau_{i}}$$
(43)

The model accurately described the PL signal decay in all investigated samples, with χ^2 values close to 1 and residuals symmetrically distributed, clustering towards the middle of the plot (Figure 77 (b-d)). The parameters used to fit exponential decay curves are listed in Table 27. All the PL curves show charge carrier lifetimes in the microsecond range, while PL curves can be separated into three exponential decay components. The first component is related to the fast recombination of excitons, occuring around $\sim 10 \ \mu s$. While the two other components are related to slow recombinations of excitons, occuring around ~30 and ~90 µs, respectively. BT750 was fitted with only two components, which was attributed to its lower signal. Regardless, the photogenerated species' average lifetime was similar for both BT750 and TiO₂ at 40 \sim µs, while BT750 – Black had an average lifetime of \sim 52 µs. This significant increase is mainly due to the longest lasting photogenerated species identified in BT750 – Black, with a τ_3 of ~112 µs, which is double the lifetime of titania's τ_3 . The electron lifetime of the third exponential decay component is believed to favour the photocatalytic activity of semi-conductors, since it indicates an increased permanence of long living excited states [319]. Hence, these photogenerated species are the most likely to diffuse to the surface of a photocatalyst without recombining.

Thus, it is evident from the PL data after cycling the bismuth titanate composite, photogenerated charge carriers had longer lifetimes, that can be attributed to oxygen vacancymediated efficient charge separation and lower recombination rates of photogenerated electronhole pairs [315], [319]. These results are in accordance with the MB degradation cycling tests, as prolonged lifetime of charge carries results in higher degradation rates of the model pollutant.



Figure 77. Time-resolved photoluminescence spectra for: (a) TiO₂, BT750, BT750 – Black; (b) TiO₂ with fitted model and residuals; (c) BT750 – Black with fitted model and residuals; (c) BT750 – Black with fitted model and residuals.

Sample	Peak excitation wavelength	β_1	$ au_1$	β_2	$ au_2$	β_3	$ au_3$	$ au_{avg}$	χ²
_	nm	-	(µs)	-	(µs)	-	(µs)	(µs)	-
TiO ₂	510	148.0	7.0	123.0	22.2	48.0	66.6	40.3	0.99
BT750	540	222.2	11.6	8.3	56.8	-	-	40.8	1.09
BT750 – Black	540	1483.0	8.8	1153.0	30.3	239.8	112.1	52.2	1.06

Table 27. Curve-fitting results of the decay curves measured for BT750, BT750 - Black and TiO₂.

8.7. Summary

The synthesized bismuth titanate composite, $Bi_{12}TiO_{20}/Bi_4Ti_3O_{12}$, displayed high photocatalytic activity under UV light and consistently outperformed TiO₂ in every test. Interestingly, after repeated use, the sample changed colour from white (BT750) to black (BT750 – Black) and its photocatalytic activity increased 6-fold. The XPS analysis of the samples has shown an O 1s L to O 1s V ratio change from 4:1 to 1:0.7, for BT750 and BT750 – Black, respectively. This significant increase in the O 1s V peak is believed to be linked to a higher concentration of oxygen vacancies in the thin film.

This type of behaviour has previously been reported by several authors, for bismuthbased photocatalysts such as BiOCl [320]–[322]. Ye *et al.* prepared black BiOCl samples by exposing pristine BiOCl powders to UV light [320], [321]. The photocatalytic activity and visible light absorption of the UV treated BiOCl sample increased significantly compared to the pristine ones. UV-induced oxygen vacancies were identified by XPS, EPR and PL analysis and found to be responsible for the 20-fold increase in photocatalytic activity under visible light. Oxygen vacancies form mid gap states below the conduction band, acting as electron trapping sites, improving the electron-hole separation, and thus the photocatalytic activity [320].

This is consistent with the results of our TRPL analysis, as charger carriers photogenerated by BT750 – Black had a significantly longer lifetime than the ones photogenerated by BT750. The oxygen vacancies identified by XPS in BT750 – Black, may act as electron traps, increasing the lifetime of charge carriers and improving the photocatalytic activity, as shown during the cycling tests.

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The mechanism behind UV induced oxygen vacancy formation is still unclear, but *Ye et al.* attributed it to the low bond energy and long bond length of the Bi–O bond [321]. At this stage, it is not yet known if the Bi₄Ti₃O₁₂ phase plays a significant role in the photocatalytic degradation process and if a synergistic effect exists between $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$. While this study focused on the remarkable performance increase over repeated use of a specific composition, future work will be aimed at investigating the relationship between photocatalytic activity and the distribution of $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ phases. Producing thin films using metallic targets by reactive co-sputtering enables higher deposition rates, fewer arcs and lower cost when compared to using ceramic ones. However, this comes with an added layer of complexity as the phase composition and distribution in the thin film depends on multiple factors such as power applied to each individual target, working pressure, substrate-target distance, gas ratios etc.

To summarise, bismuth titanate photocatalytic coatings were successfully synthesised by means of pDC reactive magnetron co-sputtering, reportedly for the first time. Variation of power applied to the titanium target, as well as investigation of optimum annealing temperature and length of thermal treatment, allowed the synthesis of highly active Bi₁₂TiO₂₀/Bi₄Ti₃O₁₂ composite, significantly outperforming conventionally used titanium dioxide under UV-A irradiation in both dye degradation and bacterial inactivation tests. Thus, being characterised with comparable thickness and surface roughness values, bismuth titanate was found to be 3 times more efficient in MB degradation tests, as well as reducing the number of viable E. coli cells in suspension to below the limit of detection after 48 h of irradiation. Furthermore, unlike titanium dioxide, bismuth titanate was shown to be capable of developing additional oxygen vacancies over multiple use cycles, resulting in formation of longer-living photogenerated charge carriers and enhanced photocatalytic activity. Thus, in reusability assessments over 15 consecutive cycles of use, the photocatalytic activity of bismuth titanate increased 6-fold compared to the first use of the sample. Owing to the simplicity and excellent scalability of the deposition technique used, as well as the high photocatalytic efficiency of the studied material, we believe the findings of the present study are of high relevance to those working on enhancement of photocatalytic activity for water treatment applications, both in the laboratory and industrial environments.

Chapter 9. Photocatalytic reactor based on bismuth titanate coating.

This final chapter presents the results obtained in a study of a photocatalytic reactor based on bismuth titanate composite photocatalyst coated onto glass rods. This reactor was developed as a continuation of the work presented Chapter 8 and based on the finding presented in Chapter 7. As of the writing of this thesis, the findings of this work were submitted in The Journal of Applied Sciences. This chapter discusses such aspects as reactor design (Section 9.1), photocatalytic activity (Section 9.2) and tests against real world pollutants (9.4). A summary of this part of the project is given in Section 9.5.

9.1. Photocatalytic reactor design.

The design of the Low Cost Photocatalytic Reactor II (LCPR-II) is based on the LCPR-I presented previously in Chapter 7 [275]. Likewise, the bespoke reactor utilises an external light source and does not involve any costly components (quartz, membranes, air injector etc.); with the exception of the UV-A lamps, the set-up was built exclusively from affordable and readily available parts, purchased from the computer enthusiast market. Contrary to LCPR-I, the present photocatalytic reactor utilises coated glass rods as the photocatalyst. Additionally, TiO₂ was substituted with bismuth titanate, a more efficient and promising photocatalyst, as it was demonstrated in Chapter 8 [291]. Figure 78 provides a schematic representation of the bespoke water treatment photocatalytic reactor loaded with bismuth titanate coated glass stirring rods and a photograph of the separate components.

In brief, the system is comprised of a cylindrical reactor made from PMMA (OD: 5 cm, h: 24 cm), transparent PVC tubing (OD: 16 mm, ID: 10 mm), a 12 V pump, a flowmeter, a temperature probe and an acrylic analysis cell. The reactor was placed in an aluminium enclosure with a UV-A irradiation source. The pump was operated at minimum capacity, to minimise power consumption, without limiting mass transfer, resulting in a flowrate of 5.14 L.min⁻¹ [275].

Increasing the number of coated glass rods increases the catalyst load, and by extension the reaction rate, up to a certain point where light would be blocked, and performances would stop increasing. To find the best conditions, the reactor was loaded with 4 to 10 glass rods, with 2 rods increments, coated on two opposite sides with bismuth titanate, by reactive magnetron sputtering. A full breakdown of the upfront price of the LCPR-II is given in Table 28. The power drawn by the system was measured directly at the wall with a wattmeter and remained below 60 W.

Based on previous findings discussed in Chapter 8, bismuth titanate coatings were produced by applying 750 and 185 W of power to the titanium and bismuth target, respectively, to achieve the stoichiometry required to produce Bi₁₂TiO₂₀ thin films [291, p. 12]. The photocatalyst was deposited on two opposite sides of AR-Glas[™] Stirring Rods, for 4 h each, over a 250 mm length (purchased from the Fisher). Samples were annealed in air at 600 °C post-deposition for 1 h, to obtain crystalline coatings. In parallel, soda lime glass microscope slides were coated with bismuth titanate under the same conditions used for the stirring rods. Half of the coated microscope slide samples were cycled in the same manner as the rods for characterisation purposes and compared with pristine white samples (SEM, XRD, XPS, UV-Vis). The photocatalytic activity of the reactor was initially evaluated by assessing its ability to degrade methylene blue (MB) under UV-A with a varying number of coated rods. Then, the durability of the best-performing configuration was assessed through 25 consecutives cycling tests, which progressively turned the coated rods from white to black, as a result of UV induced oxygen vacancies, forming within the bismuth titanate photocatalyst. The reactor with the best configuration of black bismuth titanate coated rods was then used to decompose a solution of levofloxacin (LEVO). Levofloxacin is a broad-spectrum antibiotic belonging to the fluoroquinolone group, it is used to treat bacterial infections such as pneumonia, sinusitis, urinary tract infections and gastroenteritis [323]. It is considered an essential medicine by the World Health Organization (WHO) and a reserve antibiotic used to prevent drug resistance when resistant microorganisms are encountered [324].

Component	Matarial	Price ¹						
Component		£	€	\$				
Reactor	PMMA	15.5	18.1	21.6				
Tubing	PVC	12.7	14.9	17.7				
Flowmeter	Aluminium alloy + POM	36.9	43.2	51.4				
Temperature probe	Aluminium alloy	19.0	22.2	26.5				
Sampling cell	Acrylic	5.7	6.7	7.9				
AR-Glas [™] Stirring Rods (× 10)	Glass	5.3	6.1	7.3				
Pump	Acrylic	31.8	37.2	44.3				
Miscellaneous	-	30.0	35.1	41.8				
UVP XX-15 Series UV Bench	A.1 · · ·	220 5	2(0.5	319.5				
Lamp	Aluminium	229.5	268.5					
Total (without light source)		156.9	183.5	218.4				
Total (with light source)		386.4	452.0	537.9				
¹ as at 15 th of March 2021								

Table 28. Cost summary for LCPR-II.



Figure 78. LCPR-II a) schematic representation of LCPR-II, b) picture of disassembled LCPR-II.

9.2. Photocatalytic activity assessment

As displayed in Figure 79a, when the reactor was loaded with 4, 6, 8 and 10 rods, after 240 minutes of UV-A irradiation, it achieved MB removal percentages of 40, 59, 75 and 89 %, respectively. In the control experiment, residual adsorption and photolysis accounted for less than 10 % of the dye discoloration. This result was expected as increasing the number of rods, ultimately increased the photocatalyst loading. Even when using 10 rods, light blocking didn't impact negatively the reaction rate. Additional coated rods couldn't be added to the reactor in its current configuration, but future work will be aimed at further increasing the number of coated rods. The LCPR-II reusability was assessed with the best performing configuration (10 rods) by conducting 25 consecutive MB degradation test cycles with 240 min of UV-A irradiation (Figure 79b). The time required to decompose 90 % of the model pollutant ($\tau_{90\%}$) was estimated for each cycle. Between the first and last test, $\tau_{90\%}$ decreased from 4 to about 1 hour, while the colour of the BT coated rods changed from white to black. This behaviour was previously reported for bismuth titanate, as a result of oxygen vacancies forming when exposed to UV-A [291]. These vacancies act as trapping sites for electrons, prolonging their lifetime and improving the photocatalytic activity of the catalyst.



Figure 79. MB degradation tests results a) Varying number of BT-coated rods, b) cycling experiment with 10 coated rods.

9.3. Black bismuth titanate investigation

The optical band gap energy of the crystalline semiconductors was estimated using the Tauc plot method [216], by plotting $(\alpha hv)^{1/2}$ as a function of hv and extrapolating the linear region to the abscissa (where α is the absorbance coefficient, h is Plank's constant, v is the frequency of vibration). Although the cycling experiment resulted in a colour change, no significant change in the band gap was observed. Bandgap energy values were estimated at 2.69 ± 0.3 and 2.71 ± 0.2 eV for BT and B_BT, respectively (Figure 80).



Figure 80. UV-Vis absorption spectra for BT and B_BT samples a) and corresponding Tauc plots b).

XRD analysis didn't reveal any crystalline change between pristine bismuth titanate and black bismuth titanate (Figure 81), in both cases cubic (I23) $Bi_{12}TiO_{20}$ was identified (ICDD 96-403-0657). Crystalline peaks belonging to the cubic phase were identified at 21.3° (121), 24.7° (022), 27.6° (013), 30.3° (222), 32.8° (123), 35.2° (040), 37.4° (033), 39.5° (042), 41.5° (233), 43.4° (242), 45.3° (143), 48.9° (125), 52.2° (053), 53.9° (060), 55.5° (235) and 58.6° (145).



Figure 81. XRD analysis of a) pristine bismuth titanate and b) black bismuth titanate.

High-resolution O 1s XPS spectra of BT and B_BT samples are shown in Figure 82, both O 1s peaks can be deconvoluted into 5 peaks. The first two deconvoluted peaks at 529.4 and 530.9 eV were attributed to lattice and vacancy oxygen species, respectively [291]. The three following deconvoluted peaks at 533.6, 541.7 and 532.5 eV can be attributed to adsorbed organic species (C = 0, C - 0, 0 - C = 0). As expected, when compared to the pristine bismuth titanate sample (Figure 82a), black bismuth titanate (Figure 82b) has a higher proportion of adsorbed organic species as a result of the methylene blue degradation cycling tests. Interestingly, the black bismuth titanate sample also has a lower atomic percentage ratio of O 1s L to O 1s V species (from relative areas of the peaks), changed from ca. 4.4:1 to ca. 1.8:1 for the BT and B_BT samples, respectively.

Oxygen vacancies induced by UV light irradiation have already been reported for bismuth titanate coatings; these defects, have been shown to increase the lifetime of photogenerated species, leading to a significantly improved photocatalytic activity [291]. Depth profiling analysis didn't reveal any difference between the pristine and black bismuth titanate, in both cases only the lattice oxygen peak was present.



Figure 82. High-resolution O1s XPS spectra of a) BT and b) B_BT samples.

SEM micrographs of the samples didn't reveal any morphological difference between pristine (Figure 83a) and black bismuth titanate (Figure 83b). The surface of the black bismuth titanate sample appears a bit rougher, but this is most likely due to the cycling of the sample which was covered with organic contaminants that couldn't be washed off with distilled water. The EDX analysis didn't reveal any significant change, with a Bi, Ti and O atomic percentage content of 37.1 ± 0.4 , 3.5 ± 0.4 and 59.4 ± 0.1 % for pristine BT and 34.9 ± 0.5 , 3.1 ± 0.3 and 62.0 ± 0.2 % for B_BT, respectively. These bismuth titanate sample have a different atomic composition when compared to the one studied in Chapter 8, this difference can be explained by the lower power applied to the bismuth target (185 instead of 200W). The lower power was applied to produce a homogeneous bismuth titanate coating, containing only the Bi₁₂TiO₂₀ phase.



Figure 83. Surface SEM micrographs of samples a) BT, b) B_BT; EDX analysis of samples c) BT, d) B_BT.

To understand the mechanism behind the photocatalytic degradation of pollutants, BT and B_BT flat samples were used to decompose Orange II under UV-A, in the presence of different trapping agents. 4 hydroxy-TEMPO was used to scavenge superoxide radicals, isopropanol for hydroxyl radicals, sodium oxalate for holes and sodium nitrate for electrons. In the case of BT (Figure 84a), sodium oxalate and 4 hydroxy-TEMPO reduced significantly the photocatalyst's activity, with the latter having a greater effect, while sodium nitrate and isopropanol didn't slow down the reaction. Consequently, superoxide radicals ($O_2^{-\bullet}$) and, to a lesser extent, holes (h^+) appear to be the main driving force behind the photocatalytic activity of bismuth titanate. This is consistent with the findings of Guo et al. who reported that h^+ and $O_2^{-\bullet}$ are the main active species [325]. When testing B_BT (Figure 84b), not only did sodium oxalate and 4 hydroxy-TEMPO reduce significantly the photocatalytic activity of black bismuth titanate, but so did sodium nitrate. In ascending order of contribution, superoxide radicals ($O_2^{-\bullet}$), electrons (e^-) and holes (h^+) were the main driving force behind the photocatalytic degradation process. This is in accordance with the results of the XPS analysis, which revealed the presence of an increased amount of oxygen vacancies (V_o) in black bismuth titanate, when compared to the pristine one. These oxygen vacancies (V_o) are likely to act as trapping sites for electrons (e^-), increasing their lifetime and likelihood of reacting with the pollutant at the photocatalyst's surface. The proposed photocatalytic pollutant degradation mechanism in pristine and black bismuth titanate is illustrated in Figure 85.



Figure 84. Orange II degradation under UV-A irradiation by in the presence of h^+ , e^- , $O_2^{\bullet-}$ and OH^{\bullet} scavengers by a) BT and b) B BT.





Black bismuth titanate

Figure 85. Figure 8. Schematic of proposed photocatalysis mechanism in pristine and black bismuth titanate.

9.4. Contaminant of emerging concern degradation

The capabilities of LCPR-II were tested against levofloxacin (LEVO), an antibiotic commonly found in wastewater treatment plant effluents. The reactor was loaded with a 500 mL solution at a concentration of 10 mg.L⁻¹. After 24 h of UV light irradiation without the coated rods (Figure 86a), only a slight decrease in the LEVO main absorbance peak at 287.5 nm was observed by UV-Vis spectroscopy. Alternatively, when the black bismuth titanate coated rods were included (Figure 86b), the main absorbance peak was evidently not present. Broad absorbance peaks appeared between 200 and 280 nm, which may be attributed to the formation of different reaction intermediates during the photocatalytic degradation process. To assess the antimicrobial properties of the treated solutions, disk diffusions tests were performed with samples from the initial and treated LEVO solutions. Both the initial and the UV-only treated LEVO solutions demonstrated antibiotic activity, with a clear zone of inhibition forming around each corresponding disc (Figure 86c). On the other hand, no inhibition zone was identified when the solution was treated with UV in the presence of black bismuth titanate coated rods (Figure 86c). The same result was found for the distilled water control. In the UVonly treated solution, a 20 % reduction in inhibition zone diameter was observed for S. aureus and A. baumannii (Figure 86d). The UV was most likely able to degrade a small amount of LEVO. This effect was not observed in E. coli cultures, as they appear considerably more sensitive to the levofloxacin, with an inhibition zone diameter 30 % and 20 % larger, on average, than the ones measured for S. aureus and A. baumannii, respectively. These results confirm that the photocatalytic reactor was able to degrade the levofloxacin and that the reaction intermediates are innocuous to the tested microorganisms.



Figure 86. Levofloxacin (LEVO) degradation experiment a) UV-Vis spectrum of UV-A treated LEVO, b) UV-Vis spectrum of B-BT treated LEVO under UV-A, c) pictures of pathogens exposed to treated LEVO solutions (EC: E. coli, SA: S. aureus, AB: A. baumannii),

9.5. Summary

Although it took the LCPR-II 24 h to decompose the levofloxacin, one should keep in mind that the tested concentration far exceeded the concentration of antibiotics sampled in wastewater treatment effluents by a factor of 10³ to 10⁶. In photocatalysis, initial pollutant concentration is a significant contributor to the reaction rate, the lower the concentration, the faster the reaction. Furthermore, when the reactor was loaded with coated rods, it outperformed the "UV only" treatment, which is typically used as a last disinfection steps in wastewater treatment plants [15]. The results of this proof-of-concept highlight the potential of bismuth titanate coated rods, to improve the removal and inhibition of pollutants, such as antibiotics, through photocatalysis. We believe that developing an affordable, sustainable, efficient and scalable wastewater treatment reactor is a step in the right direction towards the adoption of photocatalytic systems in treatment plants.

In summary, a bespoke photocatalytic reactor was built from consumer market equipment and loaded with glass stirring rods coated with bismuth titanate by reactive magnetron sputtering. When loaded with 10 coated rods, the reactor proved effective at decomposing 90 % of an aqueous methylene blue solution, under UV-A, in 4 hours. During the reusability assessment, equivalent to 125 h of consecutive use, the time required to decompose 90 % of the pollutant, with the same concentration, dropped from 4 to 1 hour. This remarkable property is due to photoinduced vacancies, acting as electron trapping sites, and is characterised by a photocatalyst colour change from white to black. In pristine bismuth titanate coatings, superoxide (O_2^{-}) and holes (h^+) , were identified as the main drivers of the photocatalytic activity. Interestingly, in black bismuth titanate, superoxide (O_2^{-}) and holes (h^+) were not the only contributors, as electrons (e^{-}) also played a significant role. This last contribution is most likely due to the presence of newly formed oxygen vacancies, acting as traps and increasing the photocatalytic activity. Finally, the reactor was able to successfully degrade a concentrated solution of levofloxacin, whose antimicrobial potency was assessed by inhibition zone tests in the presence of E. coli, S. aureus and A. baumannii. This study demonstrates the potential of bismuth titanate based photocatalytic reactors for downstream wastewater treatment. This system could be used complementarily to UV disinfection, to decompose remaining traces of pollutants, to prevent the spread of antibiotic resistant bacteria in wastewaters.

Part 4. Synopsis

Chapter 10. Conclusions and future work

This chapter provides a summary of the main results presented in this thesis and discusses how the objectives laid out in Introduction section (Chapter 1) were achieved. In light of the presented findings, unexplored areas of interest for future research projects are suggested.

The main findings and achievements of the project are summarised in 10.1. The issues that require additional work and directions of further research in this area are discussed in Section 10.2.

10.1. Overall conclusion & discussion

The goal of this thesis was to produce a laboratory scale water treatment reactor, based on photocatalytic coatings produced by magnetron sputtering. This goal was achieved through two different approaches.

The first one consisted in optimising the deposition process of TiO_2 , the most popular photocatalyst, to reduce the production cost, simplify the deposition process and facilitate the process upscaling. This was achieved by studying two important deposition parameters, namely, coating pressure and magnetron power. When pressure and power were minimised and maximised, respectively, crystalline and photocatalytic TiO_2 coating were produced in a one-step process. Bench scale testing confirmed the high photocatalytic activity of the TiO_2 coated stainless steel mesh. The deposition process was then upscaled, to integrate the coated mesh in a bespoke photocatalytic reactor.

To remain consistent with the "low cost" approach, the bespoke reactor was built using components readily available in the computer hardware market. The Design of Experiment (DoE) method was used to optimise the photocatalytic reactor, by varying 5 factors: number of mesh, coating thickness, light intensity, flowrate and initial concentration. All independent parameters were significant except for flowrate.

Based on the built linear regression model, the variables were set to their optimum value, which led to the removal of more than 90 % of the initial pollutant concentration, in less than 5 h.

The second approach consisted in designing a new photocatalyst, more efficient than TiO_2 , regardless of the cost associated with target material and post deposition annealing. A bismuth titanate photocatalyst was produced, for the first time, by reactive magnetron co-sputtering. Not only was this photocatalyst more efficient at decomposing methylene blue from a solution and inactivating *E. coli*, but its performances also increased over repeated use. Its performances for MB degradation increased 6-fold over 15 consecutive photocatalytic degradation tests. This effect was attributed to oxygen vacancies, induced by UV-A irradiation and acting as charge carrier traps and improving the photocatalyst's activity. As oxygen vacancies form within the bismuth titanate, its colour changes from white to black, and was therefore termed "black bismuth titanate".

The bismuth titanate deposition process was scaled up to coat stirring glass rods, which were integrated into the bespoke photocatalytic reactor. Parameters such as initial pollutant concentration, light intensity and flowrate were chosen based on the previous reactor optimisation work. The number of coated rods was gradually increased to maximise photocatalytic activity, with a maximum of 10 rods integrated in the reactor. Afterwards, the reactor's durability was tested through 25 dye degradation cycling tests, equivalent to 125 h of consecutive use. During this time the bismuth titanate coating was converted into black bismuth titanate, which led to a reduction of the time require to decompose 90 % of the MB from 4 h to only 1 h. Finally, levofloxacin, a pollutant of concern in wastewater treatment plant effluents, was successfully degraded using the black titanate-based reactor. The decomposition of the antibiotic into harmless reaction intermediates was verified by zone of inhibition tests, in the presence of three different bacteria.

This work aimed at addressing the many challenges hindering the widespread adoption of photocatalytic wastewater treatment systems; namely cost, complexity and efficiency. The photocatalytic reactor was built from inexpensive and readily available components to maintain the upfront cost to a minimum. In chapters 6 and 7, titania was produced in a one step-process, to keep the cost down and simplify the photocatalyst manufacturing process. The downside of this approach is that titania is a well-known photocatalyst, with clearly defined weaknesses. In chapters 8 and 9, a different approach was taken by annealing the coatings and using cosputtering to produce a complex oxide, bismuth titanate. This resulted in a significantly more efficient photocatalyst, but this came at higher a cost and with an added layer of complexity. Regardless of the approach, both photocatalysts were integrated in a water treatment reactor and successfully used to decompose various model pollutant. This work clearly demonstrates the potential of such photocatalytic reactors, which will play an important role in addressing present and future challenges related to wastewater treatments.

Finally, this work demonstrates the relevance of magnetron sputtering for the deposition of efficient photocatalytic coatings and how it facilitates their integration into photocatalytic reactors. Several aspects require additional work to be carried out to improve the properties of the coating, the deposition process, the scale of the photocatalytic water treatment process and nature of tested pollutants.

10.2. Future work suggestions

Based on the main findings of this thesis, the following suggestions are proposed for future research work.

10.2.1. Investigate the deposition of doped TiO₂ in a one-step process

The results obtained when working on the deposition of TiO₂ are encouraging, as they open the door to large scale, energy efficient and economical manufacturing of photocatalytic TiO₂ coatings. However, its shortcomings are still preventing the widespread adoption of large-scale photocatalytic wastewater treatment systems based on TiO₂. Strategies to overcome these shortcomings exist and could be integrated in the deposition process. The deposition by magnetron sputtering of, for example, crystalline N-TiO₂ or C-TiO₂, in a one-step process, could be more efficient whilst remaining economical. This could easily be achieved by introducing nitrogen or carbon dioxide during the deposition process, which could be controlled by a Plasma Emission Monitoring (PEM) system.

10.2.2. Improve the deposition process of Bismuth titanate

As this work has shown, bismuth titanate is an interesting material with a lot of potential for photocatalysis. However, the deposition of such material, by reactive magnetron cosputtering, remains challenging as phase composition is influenced by several factors such as power delivered to each target, pressure, substrate-target distance, reactive gas flowrate etc. In its current state, co-sputtering of bismuth and titanium was carried with constant argon and oxygen flowrates of 50 and 25 sccm, respectively. Contrary to the work done on titanium dioxide, the system was not regulated with a PEM feedback system, which means that over long deposition times, targets would be progressively poisoned. This target poisoning may result in slower deposition time and Ti:Bi ratios imbalance, which would give rise to other, potentially undesirable, polymorphs. Furthermore, as of the writing of this thesis, bismuth titanate coatings produced by co-sputtering still require annealing to be crystalline. Future work should aim at integrating PEM feedback systems and produced crystalline coatings without annealing, to improve the reliability of the deposition process and make it more affordable, respectively.

10.2.3. Investigate the mechanism behind photoinduced oxygen vacancies.

Light induced oxygen vacancies were identified as responsible for the colour change and photocatalytic activity increase in bismuth titanate, but the mechanism resulting in their formation is not yet clear. Further analysis using XPS, TRPL and EPR would provide a better understanding behind the oxygen vacancies formation process. Additionally, although long cycling experiments were performed, the depth of penetration and concentration of the oxygen vacancies hasn't been investigated. A long-term study should be performed, to assess whether oxygen vacancies keep forming, how far within the coating do they form, and if it can reach a point of diminishing return on the photocatalytic activity.

10.2.4. Use the laboratory scale reactor to treat WWTP effluents.

In this thesis, the bespoke photocatalytic reactors were used to treat dye and antibiotic solutions. Effluents from wastewater treatment plants (WWTP) are known to contain a wide variety of organic pollutants and micro-organisms. Although the developed reactor has shown promising results when treating one type of pollutants at a time, it is yet to be seen how it would perform when exposed to a mixture of pollutant and what interactions might occur. Forming a partnership with local WWTP, to obtain samples of effluents, would be a first step toward the adoption of photocatalytic reactors in WWTP.

10.2.5. Upscale the bespoke photocatalytic reactor from laboratory to pilot scale.

The bench scale testing of photocatalytic coatings was performed with volumes of 50 mL, while the laboratory scale reactor was able to treat volumes of 500 mL. This represents an order of magnitude increase, but it is still a far cry from the volume that wastewater treatment plants would require. Future work should aim at upscaling further the process by one or two orders of magnitude to reach the pilot scale. This could be achieved by increasing the size of the reactor, but it would be limited by the reservoir size in computer stores. Another way of achieving the same results would be to put several reservoirs in series, each connected by the PVC tubing, and loaded with coated rods or stainless-steel mesh. Due to the new space requirement, the irradiation system should be revisited.

Ideally, sunlight should be used as an irradiation source, which would exclude TiO_2 , as only bismuth titanate, or doped TiO_2 , would have an appropriate bandgap. This new system could be set outdoors with the coated rod loaded reservoirs installed on concave reflective surfaces. The system would be self-reliant, as a commercial cheap solar panel could power the 5V pumps and sun tracking system, such as the Arduino Solar Tracker. New promising photocatalysts, produced by magnetron sputtering, could then easily be upscaled from bench scale to laboratory scale, and finally, to pilot scale.

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Annexe

A.XRD analysis



Figure 87. XRD analysis of different bismuth titanate samples used for Pawley refinements.

B.DoE Analytical tool

i. Main effect plots

A main effect plot can be defined as the mean response value of an output at different levels of a process. It provides information on the type and magnitude of response resulting from a change of parameters [206]. Two important information can be extracted from a main effect plot:

- The sign or direction of the effect
- The magnitude or strength of the effect

For example, in the case of a catalytic reaction, the main effect plot illustrated by Figure 88 shows that increasing the temperature increases the yield of the reaction (positive effect). The main effect plots' magnitude can be compared for different factors by comparing the angle they form with the line of the mean value (red dotted line in Figure 88). The steeper the main effect line, the greater the magnitude of the effect and vice versa.

The estimate effect of a process's parameter can be calculated with the equation (44), where $\overline{F_{(+)}}$ and $\overline{F_{(-)}}$ are the average responses at respectively the high- and low-level settings of a factor.



Figure 88. Main effect plot of temperature on the yield of a catalytic reaction

$$E_f = \overline{F_{(+)}} - \overline{F_{(-)}} \tag{44}$$

ii. Interaction plots

Almost any kind of experiment or process is subject to parameter interactions, which in some cases is the root cause of a problem rather than the individual effect of different factors [206]. Interactions occur when the effect of a parameter at a certain level changes at different levels of another parameter. To study the interactions among process parameters, one does need to vary all the factors simultaneously [206], [326]. Therefore, appropriate arrays must be used, such as the ones recommended by Dr. Taguchi [211]. Then, interaction graphs such as the ones illustrated in Figure 89 can be plotted. If the lines of the interaction plot are parallels, then there are no interactions. In this example, the lines are not parallel which mean that there is an interaction between the pH and the temperature, and that this interaction affects the reaction's yield. Furthermore, it is possible to estimate the second order interaction effects using the equation (45), by calculating the difference between the average responses of the high levels and low levels of factors A and B.

$$A \times B = \frac{\overline{A_{(+)}} + \overline{B_{(+)}}}{2} - \frac{\overline{A_{(-)}} + \overline{B_{(-)}}}{2}$$
(45)



Figure 89. Example interaction plot between temperature and pH on reaction yield

iii. Pareto plots

Pareto plots are used to identify the factors and interaction effects that have the most significant impact on the process or experiment. It displays the absolute values of the effect which can be compared to a reference line [206]. As shown on the example (Figure 90), the factors A, B, C, D and the interaction $A \times C$ are potentially important. However, Pareto plots only display the absolute value of the effect of each factor and interaction on the response. It doesn't give any indication on the magnitude or direction of the effect these parameters have on the response. Therefore, it is usually used conjointly with a normal probability plot (NPP) [206].

Source	LogWorth	PValue
С	10.318	0.00000
D	9.414	0.00000
Α	8.850	0.00000
В	5.378	0.00000
A*C	2.391	0.00406
B*D	1.619	0.02402
A*D	1.024	0.09470
A*B	0.317	0.48222
C*D	0.225	0.59533
B*C	0.035	0.92203

Figure 90. Example of a Pareto plot of the standardised effects.

iv. NPP

NPPs are used to plot main and interaction effects of a process's factors against cumulative probabilities (%). As shown in Figure 91, points that follow the straight blue line with a slope σ are inactive main effects or interactions [206], [327]. On the other hand, points that diverge from the blue line such as B, A, D and C are statically significant active effects with a significance level of 5%, meaning that there is a 5% chance that the observed significance level is due to pure chance only. Furthermore, because these points are positioned on the positive part of the normal quantile axis, it can be asserted that those factors have a positive effect on the output.



Figure 91. Example of an NPP of effects

v. NPP of residuals

Normal probability plots of residuals are used to check the normality of a dataset *i.e.* verify if the distribution is normal [206]. When the data points follow a straight line such as illustrated in Figure 88, the data can be considered as coming from a normal distribution. If one is in presence of a non-normal set of data, variance stabilising transformations such as a logarithmic one can be applied [206]. However, gross deviations can be serious and should require attention and further analysis.



Figure 92. Example of an NPP of residuals

vi. Response surface plots

Response surface and contour plots are visual tools useful to identify the best operating conditions to obtain a desired response [206]. Contour plots such as the one illustrated by Figure 93 are two-dimensional graphs where all points with the same response are connected to form contour lines of constant responses. Similarly, surface plots are three-dimensional representations where the response is displayed as a continuous surface on the z-axis relative to two selected parameters on the x-y plane such as illustrated in Figure 94. Surface plot generally can provide more information than contour plots. For example, in the case of a first order model, if the surface plot describes a flat plane, then the process contains only main effects and is not affected by interactions. Whereas, if process contained interactions, the contour lines would be curved and not straight [206].



Figure 93. Example of a contour plot



Figure 94. Example of a surface plot

vii. Model building

Building a regression model is useful to predict the response for different combinations of process parameters at their best levels which were not necessarily included in the array [206]. To develop a regression model based on significant main or interaction effects, the regression coefficients have to be determined. In the case of a 2-levels experiment, the regression coefficients are obtained by dividing the estimates of effects E_f by 2. A regression model as the one presented in equation (46) can then be used, where β_0 is the average response of the factorial experiment, β_i is a regression coefficient, β_{ij} is the interaction between the process parameters χ_i and χ_j , and ' ε ' is the random error component. A concrete example of calculated response prediction is shown in Figure 95. The value obtained from the regression model can then be compared to the one from confirmation experiments to assess the validity of the model.

$$\hat{y} = \beta_0 + \beta_1 \chi_1 + \beta_2 \chi_2 + \dots + \beta_{12} \chi_1 \chi_2 + \beta_{13} \chi_1 \chi_3 + \dots + \varepsilon$$
(46)



Figure 95. Prediction of the response for optimised conditions of an example experiment using a regression model

viii. Confidence interval

A confidence interval (at 99% confidence limit) can be calculated with the equation (47) to verify the validity of a regression model, where \bar{y} , *SD* and *n* respectively are the average response obtained from the confirmation runs, the standard deviation for each run and the number of confirmation runs [206]. If the value obtained from the regression model falls within

the limit of the *CI* then the model can be considered to be valid. Otherwise, sources of error should be investigated such as (47):

- Erroneous choice of experimental design
- Erroneous choice of response or output
- Excessive presence of noise
- Omission of important process parameters or interactions
- Measurement errors, etc.

$$CI = \bar{y} \pm 3 \left\{ \frac{SD}{\sqrt{n}} \right\}$$
(47)