Declaration

This thesis contains original work carried out by the stated author, with any collaboration stated and acknowledged within the corresponding text. The ZnO films and flat-bed reactor discussed in chapter 3.3 (ZnO nanowires) was developed and investigated by Dr Anyela Ramirez-Canon. X-ray diffraction (XRD) spectra were produced by Dr Gabriele Kociok-Kohn, X-ray photoelectron spectroscopy (XPS) spectra were produced by Dr David Morgan, Cardiff University, and inductively coupled plasma mass spectrometry (ICP-MS) was produced by Dr J. Andy Milton, University of Southampton. The TiO$_2$ Nanoparticles used in chapter 5 (TiO$_2$ nanoparticles) were developed and synthesised by Dr Maria Medina-Llamas.
Abstract

Current wastewater treatment is not able to efficiently treat trace micropollutants. These compounds include a wide range of biologically active compounds from various human sources, and are found in μg/L concentrations in domestic wastewater. Photocatalysis is an advanced oxidation process that can act as a polishing step after conventional treatment, which utilizes semiconductor materials that are activated by UV light to degrade these complex compounds. Currently most examples of commercial photocatalysts use them in slurry or powder form, however this requires post-treatment removal. Research increasingly focuses on the use of immobilized photocatalysts, while minimising disadvantages such as complexity of synthesis and reduced activity in comparison to systems using photocatalyst in suspension. Concentrating on the two most common semiconductors, TiO$_2$ and ZnO, the scope of this research was to develop and optimise immobilised wire photocatalysts, where the oxide layer was grown on the surface of their parent metal via electrochemical anodization. Conventionally films are used as the support, however a metal wire aimed to increase the availability of the surface area and improve mass transfer in the reactor, in comparison to the film systems. Thus sustainable methods for wire anodization were investigated, which included the development of a tubular photocatalytic reactor, to ensure high surface illumination, and an in-flow anodization rig for the wire support. A ZnO layer could be successfully synthesised by anodizing a Zn wire using KHCO$_3$ electrolyte, referred to as a ZnO wire, which demonstrated an increase in photocatalytic degradation of phenol, in comparison to an untreated Zn wire and increased quantum efficiency to ZnO films. The ZnO wire stability and photoactivity could be increase by the addition of oxygen to the reaction solution. Other parameters investigated, included reactor hydrodynamics, anodization time and the application of electricity to the metal core.

TiO$_2$ is the most widely used photocatalyst for water treatment. Producing immobilized TiO$_2$ catalyst from Titania via anodization requires the use of hazardous fluoride electrolytes. Limited research exists on investigating non-fluoride based TiO$_2$ anodization, specifically upon wires, and the photocatalytic activity of the produced oxide layer has not been studied. Different halide based electrolytes and additives were tested, and the optimum electrolyte solution was found to be potassium bromide with ethylene
glycol. These materials were characterised using a variety of analytical techniques, such as scanning electron microscopy and X-ray diffraction. Subsequently annealing temperatures were refined to obtain TiO\(_2\) crystal modification (rutile to anatase ratio) that provides best photocatalytic performance. This study demonstrated TiO\(_2\) nanostructures could be successfully anodized with mild anodizing conditions upon a Ti wire, which demonstrated photoactivity to degrade micropollutants, carbamazepine and phenol.

Also included in this thesis is a study on the photocatalytic activity of different types of TiO\(_2\) nanoparticles that were produced via a novel membrane emulsification-precipitation process. The photocatalytic activity of the nanoparticles was investigated under UV light and under visible light for nitrogen doped varieties. Latter tests required the application of UV filter solutions. The nanoparticles demonstrated an increased degradation of the model contaminant, phenol in comparison to photolysis alone, however the overall photocatalytic was lower than that of a commercial photocatalyst used as benchmark.

It is common for a study to focus entirely upon either the syntheses or investigate photocatalytic materials that are already available, this thesis has concentrated on various aspects; production, material characterization and investigating the photocatalytic activity. To conclude, non-hazardous anodization of immobilized photocatalyst, TiO\(_2\) and ZnO wires were successfully developed and demonstrated, with annealing temperature highlighted as a key preparation parameter to tailor the properties of the photocatalyst. These wires demonstrated higher photoactivity and increased surface availability in comparison to the conventional films used. The development of a suitable photocatalytic reactor was required to optimise surface illumination of the wire photocatalyst. Reaction conditions, such as atmospheric conditions and flow rate, were shown to play a key role in photoactivity, and further investigation found that the key pathway for degradation is using hydroxyl radicals. The research presented in this thesis has led to three published papers. A research project during the initial stage of this integrated PhD contributed to two publications on membrane ozonation for water treatment and on-going research projects. Further work, regarding immobilized ZnO wires would be to identify inconsistencies in the anodization process, to improve synthesis efficiency. The nitrogen-doped immobilized TiO\(_2\) photoactivity would be investigated using visible light, as well as optimising the nitrogen doping procedure. Finally, determine the relationship between physical properties and photoactivity of the TiO\(_2\) nanoparticles, in comparison to the photocatalytic benchmark, Evonik Aeroxide P25.
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Undertaking a PhD is a team sport and everyone mentioned below (and more) are my team; I’m so lucky to have you all.

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To you all, thank you.

Peace out xoxo
Dissemination

Publications


Conferences

**Apr 2017**  The 18th UK- International Water Association Young Water Professionals, Bath, UK. Poster presentation and organiser

**May 2018**  The 15th IWA Leading Edge Conference on Water and Wastewater Technologies, Nanjing, China. Poster presentation

**Sep 2019**  The 16th International Conference on Environmental Science and Technology CEST2019, Rhodes, Greece. Oral presentation
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- Organising and hosting bi-monthly symposiums

Mar – May 2019  Internship at Nanyang Technological University, Singapore
- Working under Professor Xiao Hu on photo-electro catalysis for immobilized photocatalysis.
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<th>Definition</th>
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<td>$C_0$</td>
<td>Initial concentration of pollutant</td>
</tr>
<tr>
<td>$C_t$</td>
<td>Concentration of pollutant at time, $t$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient [m$^2$ s$^{-1}$]</td>
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<tr>
<td>$E$</td>
<td>Band gap energy [eV]</td>
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<tr>
<td>$e^-$</td>
<td>Electron</td>
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<tr>
<td>$h$</td>
<td>Planck’s Constant [$6.63 \times 10^{-34}$ m$^2$ kg/s]</td>
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<tr>
<td>$h^+$</td>
<td>Charged hole</td>
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<td>$I_A$</td>
<td>Area of anatase diffraction peak</td>
</tr>
<tr>
<td>$ID$</td>
<td>Inner diameter [mm]</td>
</tr>
<tr>
<td>$I_R$</td>
<td>Area of rutile diffraction peak</td>
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<tr>
<td>$I_{o\lambda}$</td>
<td>Incident light Intensity [mW/cm$^2$]</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant [h$^{-1}$]</td>
</tr>
<tr>
<td>$L$</td>
<td>Length [cm]</td>
</tr>
<tr>
<td>$OD$</td>
<td>Outer diameter [mm]</td>
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<tr>
<td>$R$</td>
<td>Reflectance [%]</td>
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<tr>
<td>$Re$</td>
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<tr>
<td>$Pe$</td>
<td>Peclet number [-]</td>
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<tr>
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</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number [-]</td>
</tr>
<tr>
<td>$u$</td>
<td>Flow velocity [m.s$^{-1}$]</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Volume recieving UV dose per second [mL/s]</td>
</tr>
<tr>
<td>$V_R$</td>
<td>Entire reaction solution [mL]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Molar absorption coefficient [M$^{-1}$ cm$^{-1}$]</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Diffraction angle [$^\circ$]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength [nm]</td>
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<tr>
<td>$\tau$</td>
<td>Reaction time [s]</td>
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<tr>
<td>$\nu$</td>
<td>Frequency [Hz]</td>
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<tr>
<td>$\Phi$</td>
<td>Quantum yield [mol/Einstein]</td>
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# Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ACF</td>
<td>Activated carbon fibres</td>
</tr>
<tr>
<td>AO</td>
<td>Anodic oxidation</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced oxidation process</td>
</tr>
<tr>
<td>BDD</td>
<td>Boron doped diamond</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett Teller</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol A</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection by-products</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>EAOP</td>
<td>Electrochemical advanced oxidation process</td>
</tr>
<tr>
<td>EAPC</td>
<td>Electrical assisted photocatalysis</td>
</tr>
<tr>
<td>EDCs</td>
<td>Endocrine disrupting compounds</td>
</tr>
<tr>
<td>EF</td>
<td>Electro-fenton</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic retention time</td>
</tr>
<tr>
<td>ICP – MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>MPN</td>
<td>Most probable number</td>
</tr>
<tr>
<td>N-Doping</td>
<td>Nitrogen doping</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>NPOC</td>
<td>Non-purgeable organic carbon</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated biphenyl</td>
</tr>
<tr>
<td>PCR</td>
<td>Photocatalytic reactor</td>
</tr>
<tr>
<td>PEF</td>
<td>Photoelectro-fenton</td>
</tr>
<tr>
<td>PMR</td>
<td>Photocatalytic membrane reactor</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent organic pollutants</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>PZC</td>
<td>Point zero charge</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SPEF</td>
<td>Solar photoelectron-fenton</td>
</tr>
<tr>
<td>TA</td>
<td>Tubular Annular</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solids</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet radiation</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>WW</td>
<td>Waste water</td>
</tr>
<tr>
<td>WWTP</td>
<td>Waste water treatment plant</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
</tr>
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This doctoral thesis investigates the development of sustainably anodized TiO\(_2\) and ZnO immobilized photocatalysts and their photocatalytic performance, as well as the photocatalytic behavior of TiO\(_2\) and N-doped TiO\(_2\) nanoparticles.

This cumulative thesis comprises six chapters

Chapter 1. This provides a literature review of micropollutants, heterogeneous photocatalysis, formation of TiO\(_2\) and ZnO via anodization, as well as their application as photocatalysts in water treatment.

Chapter 2. This chapter summarizes and supplements methods, materials and experimental procedures used throughout this thesis, including characterization fundamental theories.

Chapter 3. The development of ZnO upon a wire. It was concluded that ZnO stability could be increased in oxygen rich conditions, and that the ZnO wire presented high efficiency than the ZnO film. Based on work published in: Enhancing the photocorrosion resistance of ZnO nanowire photocatalysts. Taylor, C. M., Ramirez-Canon, A., Wenk, J. & Mattia, D., 19 Jun 2019, In: Journal of Hazardous Materials. 378, 120799


Chapter 3-5: Research chapters include published manuscripts as well as context, experimental aims, supporting information and additional commentary.
Chapter 6. General conclusions of the presented research and an outlook for future research

Additional publications by the thesis author were based on work carried out during the Interdisciplinary PhD, and were not part of research undertaken in this thesis.


Chapter 1

Literature Review
1.1 Wastewater treatment
Modern wastewater treatment processes (WWTP) and technologies have been developing since the mid-18th century with the initial task to reduce water borne diseases such as cholera and typhoid, which had been caused by the cross contamination between waste and drinking water resources.¹ Today, every person in the UK produces on average 150 litres of wastewater daily, which will travel to a WWTP and require treatment before being released into the environment.² A conventional wastewater treatment scheme includes three stages (Figure 1.1); primary, secondary and tertiary. An optional disinfection step is not present in most treatment plants in the UK. Municipal wastewater is a complex matrix, with a wide spectrum of different compounds and inorganics present at the same time. Typical wastewater has a biological oxygen demand (BOD) of 100 – 300 mg.L⁻¹, salts content of 30- 100 mg.L⁻³ as well as nutrients such as nitrogen (10 to 100 mg/L)⁴,⁵ and phosphorous (levels typically range from 3.7 to 11 mg/L)⁶, pH (between 6.5 -9.0)⁷ and biological constitutes, such as bacteria and viruses (ranging from 10-10¹⁰ MPN/mL).⁶

**Figure 1.1:** An example of the three stages of wastewater treatment, including an optional disinfection step. [Image adapted from Center for Sustainable Systems, University of Michigan⁸]

The primary aim of wastewater treatment is to reduce BOD along with nutrients, such as nitrogen and phosphorous, so that effluent can be released into the environment.⁹ The first stage of treatment is the primary stage, which aims to remove total suspended solids (TSS) from the water and reduce its BOD via settling tanks.⁶,¹⁰ The secondary stage uses biological methods such as activated sludge treatment to remove the majority of BOD.
The activated sludge process can remove up to 90% of organic matter from the effluent nutrients and is one of the most widely used waste water treatment processes. Finally, water will pass through the tertiary treatment step, which aims to remove suspended solids and nutrients, using a variety of different treatment options such as surface/deep filtration or granular medium filters. Tertiary treatment was introduced in the 1970s as nitrogen and phosphorous discharge became linked to surface water eutrophication. Whilst WWTP successfully remove macropollutants, such as particulates, BOD, pathogens and nutrients; polar and non-volatile micropollutants are able to pass through conventional wastewater treatment plants with little to no change and be released into the environment, where they can be found at concentrations up to µg L⁻¹.

1.2 Micropollutants

Micropollutants are pollutants found at low concentrations (ng L⁻¹ to µg L⁻¹) in municipal wastewater reported globally, which compose of a variety of speciality chemicals including pesticides, pharmaceuticals and personal care products, of anthropogenic origin. This has led to an increasingly complex and diverse mixture of compounds passing through treatment plants. The presence of micropollutants has been shown to have serious and complex ramifications for ecosystems, for example the correlation between reproductive failure in female seals and polychlorinated biphenyl (PCB) contamination in the heavily polluted Baltic sea.

In general, polar and non-volatile compounds are more likely to escape WWTP because these compounds are mobile within the aquatic environment and the biological treatment stage is unable to remove them. Physicochemical treatment, such as a mixing and flocculation processes have been generally found to be unable to remove many synthetic compounds. Some micropollutants have even been shown to decrease the effectiveness of the WWTP. For example, biodegradation and adsorption by activated sludge is decreased by microbial inhibition by the presence of antibiotics. Due to the constant output of wastewater treatment, these contaminates are in steady state concentrations, which is known as pseudo persistent. As such wastewater acts as a sink and is primary source for these synthetic compounds. From wastewater discharge and waste sludge disposed, the micropollutants are able to enter both the aquatic and soil environments (shown in Figure 1.2).
The micropollutants can then be transferred to plants, move through the soil or reach ground water. The majority of micropollutants are hydrophilic, but pollutants which are hydrophobic have the potential to bio-accumulate within the food chain and it has been demonstrated that animals higher up in the food chain present higher levels of persistent pollutants. Hydrophilic micropollutants, may also enter drinking water supplies.

Micropollutants are generally spilt into six groups; industrial chemicals, personal care products, pesticides, pharmaceuticals, stimulant and generally illegal drug (steroids/hormones) and surfactants (examples shown in Table 1.1). Some of these compounds also exhibit endocrine disrupting characteristics and are known as endocrine disrupting compounds (EDCs). These compounds disrupt, mimic or block the effect of hormones in living organisms and cover an “extensive and expanding” spectrum of compounds. The EU has prepared a EDC priority list, including 564 compounds as potential ED, and 147 which are thought to be persistent in the environment. Increasing evidence shows the link between the presence of EDCs, health effects (including reproductive) for humans and other living things. Lasting effects include decreased fertility, increased birth defects, and increased cancer risk with significant concern towards foetuses and babies. Estrogen and its metabolites, are one of the most biological.
potent chemicals, with a predicted-no-effect concentration (PNEC) at only 0.1 ng/L, in comparison ibuprofen displays a PNEC of 5000 ng/L.\textsuperscript{13,32} Their presence in water bodies has led to the fermentation of male fish and even led to fish populations collapsing.\textsuperscript{33} According to Bolong \textit{et al.}\textsuperscript{30}, less than 10\% of natural and synthetic estrogens are removed via the biodegradation process in WWTPs and although a considerable amount is adsorbed to the sludge, most of the compounds remain soluble in the effluent.

\textbf{Table 1.1:} Example of micropollutants of emerging concern and their common use, including those found on the EU Watch List contaminants of emerging concern (highlighted by *).\textsuperscript{34–40}

<table>
<thead>
<tr>
<th>Main Category</th>
<th>Examples</th>
<th>Common use</th>
</tr>
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<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>Estrone (E1)*</td>
<td>Steroid estrogen</td>
</tr>
<tr>
<td></td>
<td>Estradiol (E2)*</td>
<td>Steroid estrogen</td>
</tr>
<tr>
<td></td>
<td>17α-Ethinylestradiol (EE2)*</td>
<td>Synthetic estrogen</td>
</tr>
<tr>
<td></td>
<td>Diclofenac*</td>
<td>Anti-inflammatory</td>
</tr>
<tr>
<td></td>
<td>Erythromycin*</td>
<td>Antibiotic</td>
</tr>
<tr>
<td></td>
<td>Carbamazepine</td>
<td>Anti-epileptic</td>
</tr>
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<td>Personal care products</td>
<td>Bisphenol A</td>
<td>Plasticizer</td>
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<tr>
<td></td>
<td>4-benzophenone</td>
<td>Sunscreen agent</td>
</tr>
<tr>
<td>Industrial chemicals</td>
<td>Butylated hydroxytoluene (BHT) *</td>
<td>Anti-oxidant</td>
</tr>
<tr>
<td></td>
<td>Polychlorinated biphenyls (PCBs)</td>
<td>Dielectric and coolant fluid</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Perfluorooctane sulfonate (PFOS)</td>
<td>Coatings</td>
</tr>
<tr>
<td></td>
<td>Cetrimonium chloride</td>
<td>Emulsifiers</td>
</tr>
<tr>
<td>Herbicides &amp; pesticides</td>
<td>Oxadiazon*</td>
<td>Herbicide</td>
</tr>
<tr>
<td></td>
<td>Methiocarb*</td>
<td>Pesticide</td>
</tr>
<tr>
<td></td>
<td>Diuron</td>
<td>Herbicide</td>
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<td>Illicit drugs</td>
<td>MDMA</td>
<td>Hallucinogen</td>
</tr>
<tr>
<td></td>
<td>Cocaine</td>
<td>Stimulant</td>
</tr>
<tr>
<td></td>
<td>Amphetamine</td>
<td>Stimulant</td>
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</tbody>
</table>

Pesticides such as atrazine and diuron were designed to be stable, persistent and active at low concentration,\textsuperscript{30} and have been shown to have harmful properties, for example have
shown a reduction in rats fertility. Despite atrazine being banned by the EU in 2003, it is still detected at levels thought to be toxic to humans and animals. Pharmaceuticals are one of the most common groups of micropollutants found and examples of penicillin, carbamazepine and many antibiotics, have been found to be persistent via standard wastewater treatment and therefore have been found unchanged in water bodies. Fluoxetine also known as Prozac, an example of an anti-depressant, has been linked to reduced feeding rates and other behavioural effects in fish populations. The persistence of antibiotics in water systems and the environment can contribute to antibiotic resistance. Trying to link one specific micropollutant to a certain effect should be avoided, because this severely underestimates the effect of the blend of compounds and also their biologically active metabolites. In conclusion, to avoid the release of micropollutants into the environment, there is a need for effective water treatment step to remove micropollutants from municipal wastewater.

1.3 Advanced Oxidation Processes

Advanced oxidation processes (AOP) were first proposed in the 1980s with the aim to utilise reactive radicals, specifically hydroxyl radicals (OH), to oxidise a recalcitrant contaminant in water. In theory, this would increase the biodegradability of the compound thus making it easier to remove, and reducing its toxicity. The final aim of an AOP is to achieve complete mineralisation of the micropollutant to carbon dioxide, water and mineral acids (Equation 1.1). However for most contaminants this is unlikely as it would require too much energy to achieve. Therefore AOP processes are usually combined with a subsequent biological treatment step to remove the partially oxidised micopollutant.

\[
\text{Organic pollutant} + \text{Hydroxyl Radicals} \rightarrow \text{Mineral acids} + \text{CO}_2 + \text{H}_2\text{O} \quad 1.1
\]

In most AOPs hydroxyl radicals are the primary radicals responsible for the oxidation reaction, in addition to a suite of other oxygen based reactive species and radicals. A few processes also utilise sulfate and chloride radicals. Hydroxyl radicals have a very high reduction potential, 2.70 V (vs. normal hydrogen electrode, NHE), which is much higher than other oxidants such as chlorine or hydrogen peroxide, which have oxidising potentials of 1.49 and 1.77 V respectively. With most substrates hydroxyl radicals have high reaction rate constants in the order of \(10^8\) to \(10^{10} \text{ M}^{-1}\text{s}^{-1}\) along with very short lifetime.
in water \( (10^{-6} - 10^{-9} \text{ s}) \). Hydroxyl radicals react with most organic compounds via four basic pathways: electron transfer, hydrogen abstraction, radical addition and radical combination. These reactions, occurring at double bonds and aromatic systems, will trigger a sequence of reactions that break down the molecules. Other compounds without electron rich functional groups still react, but at slower rates.

There are many examples of AOPs, but the most established are ozonation, UV-based and the Fenton-based processes (Figure 1.3). Ozone is a frequently used drinking water treatment method in Europe, however its application is limited by the formation of the toxic ozonation by-product, bromate (limited to 10 μg/L in drinking water). There are several examples of UV oxidation processes used in the pharmaceutical and chemical industry, to treat their wastewater. This includes GSK’s Amoxicillin manufacturing site in Singapore and BASF’s plant in Ireland to treat effluent from surfactant synthesis.

**Figure 1.3:** The five different classes of advanced oxidation processes: ozone based, photochemical based, chemical-AOP, electro-AOP and physical AOP. Treatments are categorised as; full-scale (green), pilot-scale (orange), and lab-scale (red) or undetermined (grey). These processes are identified as either homogenous or heterogeneous [Image adapted from Hübner et al. and Peres et al.]

AOPs demonstrate some superiority over conventional primary, secondary and tertiary wastewater treatments (discussed in section 1.1), such as higher degradation and non-
For example, AOPs have been shown to remove naproxen and carbamazepine, which are persistent during conventional water treatment. Physical processes, such as membranes or activated carbon, effectively remove pollutants but leave them chemically unaltered, thus producing a concentrated sludge which requires post-treatment and disposal.

AOPs can be costly, where ozonation and UV-based processes are energy intensive. Additional chemicals needed (e.g. H$_2$O$_2$ or catalysts) and post-treatment to remove catalysts or oxidation by-products may add additional costs. For example, UV photolysis is able to partially degrade 50-80% of micropollutants (dependent on wavelength), however this would require a UV dose that is 100 times higher than the typical UV dose necessary for disinfection. AOPs are also hindered by scavenger compounds present in the water matrix, such as dissolved organic matter or inorganic compounds such as bromides or carbonates. These compounds react with the hydroxyl radicals, and thus compete with the target organic micropollutants. Therefore there is growing research to investigate and improve the efficiency of AOPs.

1.4 Photocatalysis

1.4.1 Photocatalysis Theory

The term “Photocatalysis” was first used in 1911 by Eibner when he used illuminated zinc oxide (ZnO) to bleach a dye. However it was not until 1972 upon the discovery by Fujishima and Honda et al., that water could be spilt into hydrogen and oxygen using titanium electrodes with light, that the research in the area picked up significantly. Photocatalysis combines photochemistry with a catalyst to accelerate or cause a chemical reaction. Photocatalysis has been used for water splitting, sterilization, chemical synthesis, and for self-cleaning surfaces.

Photocatalysts are semiconductors, with a small band gap of 1-1.5 eV between the lowest unoccupied and highest occupied band, in contrast to a conductor which has continuous energy bands and an insulator whose band gap is much larger (> 4eV) (Figure 1.4).
The catalyst absorbs light with energy equal or exceeding to that of its band gap. This is described by the Planck-Einstein equation, which states energy of light is proportional to the frequency of light \((E = h\nu)\). Absorption of light causes an electron to jump up from the valence to the conductor band gap. Larger band gaps will require increased photon energy, which translates to lower wavelengths. When a photon is absorbed, an electron jumps between these bands, leaving a charged hole in the valence band and the electron in the conduction band. The charged holes produce the highly reactive, hydroxyl radical \((\bullet \text{OH})\) by oxidising water molecules (Figure 1.5). In other words, the electron is promoted from the bonding to the anti-bonding orbital and therefore displays much more reactive properties. Simultaneously, as oxidation occurs from photo-induced positive holes, reduction of oxygen present in the water will occur, from photo-induced negative electrons. This second step produces superoxide radicals such as \(\text{O}_2\bullet\), \(\text{HOO}\bullet\) and \(\text{HO}_2\)-, which are less reactive than hydroxyl radicals but can also be used for secondary degradation pathways, known as indirect oxidation. To be an effective photocatalyst, the reaction between electron/holes and the absorbed species must compete with the electron and hole recombination, where absorbed energy is released as heat.

**Figure 1.4:** The difference between insulators, conductors and semiconductors in terms of their band gaps.
Chapter 1: Literature Review

Figure 1.5: The formation of the hydroxyl radical and other superoxide radical, upon the absorption of light (\( h\nu \), where \( h = 6.63 \times 10^{-34} \text{ m}^2\text{ kg/s} \) and \( \nu \) is the frequency of light) on the semiconductor zinc oxide (ZnO) in water.

It is important to note that the effect of the valence and conduction bands edges on driving the redox reactions in photocatalysis. For example, for a species to be oxidized, it must have a more negative oxidation potential in comparison to the valence band potential. Whereas, for a species to be reduced, the species must be more positive than the reduction potential of the conduction band.\(^{81}\)

The quantum yield (\( \Phi \)) is a measure of how efficiently hydroxyl radical are produced upon the absorption of a photon in a photocatalytic system,\(^{82}\) as shown in equation 1.2:

\[
\text{Quantum Yield} = \frac{\text{Hydroxyl radicals emitted}}{\text{Photons absorbed}} \tag{1.2}
\]

Quantum yields are a characteristic property of a compound over a given wavelength range that can be compared across studies and used to predict real environmental fate, and is dependent upon chemical properties and light characteristics.\(^{61}\) The formal quantum of efficiency of photocatalysis can be described by the ratio of the rate of reaction over the incident of light intensity.\(^{81}\)

The reaction between the micropollutant and hydroxyl radicals (or other oxidising agents) in the system, is known as indirect oxidation. Micropollutants may also degrade via direct
1.4 Photocatalysis

oxidation, where the pollutant adsorbs on to the catalysts surface or via photolysis. Adsorption rate is typically slower than the photocatalytic rate and has five key steps:\n
1) The organic pollutant transfers through the liquid phase to the catalysis surface
2) The pollutant adsorbs onto the activated catalysis surface, which is activated by the absorption of a photon
3) The photocatalysis reaction for the adsorbed phase occurs on the catalysis surface
4) The transformation product desorbs from the catalysis surface
5) The transformation product mass transfers to the bulk liquid phase

Photocatalysis, can often be explained by Langmuir-Hinshelwood kinetics, where the rate of reaction, $r$ is proportional to the surface coverage of the reactants.\(^8^4\) The reaction rate ($r$) of adsorption is shown in equation 1.3:\n
\[-r = \frac{dc}{dt} = k_p \theta\] \hspace{1cm} 1.3

Where $c$ is the reactant concentration, $t$ is equal to reaction time, $k_p$ is the photoreaction coefficient and $\theta$ is the coverage ratio of pollutants on the photocatalysis surface.\(^8^5\) The coverage ratio ($\theta$) is described by the concentration of the reactant and adsorption capacity, which is shown in equation 1.4:

\[\theta = \frac{K_{LC}c}{1 + K_{LC}c}\] \hspace{1cm} 1.4

Where $K_{LC}$ is equal to the adsorption equilibrium constant to measure the adsorption capacity of the photocatalyst.\(^8^5\) There are also examples where a reaction takes place between a surface adsorbed molecule and a molecule, that remains in the bulk, which is described as Eley-Rideal mechanism.\(^8^6\) It is important to note; the rate of reaction of photocatalysis is dependent on light intensity (or radiant flux), as well as a significant impact upon temperature\(^8^4\) (discussed further in section 1.4.3).

Degradation by adsorption is known as direct oxidation and is key when the pollutants adsorb strongly to the surface with firm electronic contact. The importance of direct and indirect oxidation depends on the compound, and also affects the transformation products. Lv et al.\(^8^7\) highlighted that phenol produced different degradation transformation products during photocatalysis, depending on whether phenol was oxidised by the hydroxyl radicals or adsorbed onto the catalyst surface and reduced by the charged hole. Nejand et
al. discussed the role of adsorption in the photocatalytic degradation of toluene using ZnO. They suggest that at higher concentrations of pollutant, there is increased adsorption onto the catalytic surface and that this increases degradation rates. While Kamat et al. compared the emission spectrum of ZnO in chorophenols, and deionized (DI) water. They found the chorophenols hindered emission, suggesting the compounds absorb to the ZnO surface.

A photocatalyst for use in water treatment must meet some essential requirements such as chemical stability, non-toxicity, photocatalytic activity, non-solubility and be an inexpensive material. Semiconductors used for photocatalysis include a whole range of materials from tungsten oxide (WO3) and iron (III) oxide (Fe2O3). Sulphide semiconductors such as CdS and PbS are regarded unsuitable due to instability and toxicity or require expensive production costs such as graphene and carbon nitride (G-C3N4). However the field is dominated by two materials, titanium dioxide (TiO2) and zinc oxide (ZnO). These two materials are both relatively inexpensive in comparison to other materials and display similar photodegradation mechanisms. Oxide photocatalysts are less prone to deactivation, known as poisoning, where active sites become blocked, but these materials can be dependent on pH in comparison to non-oxide ones. Both TiO2 and ZnO are examples of wide band gap semiconductors (2 – 4 eV), in comparison to standard semiconductors, such as silicon which have band gaps of approximately 1 – 1.5 eV. Wide band gap semiconductors are increasing in prevalence because their properties fall between that of semiconductors and insulators and display more useable properties, such as stability at higher temperatures and voltages than semiconductors with smaller band gaps. A large band gap (> 3 eV) will prevent any absorption in the visible light spectrum and require absorption into the UV spectrum (<390 nm), and this only makes up approximately 5% of irradiation from the sun. Thus solar light cannot be used to excite their electron up to the conduction band, and dedicated UV sources are needed, making this an energy intensive process. The doping or modifying the catalyst surface, can be used to increase wavelength absorption in the visible light spectrum (400 – 600 nm) as well as hinder electron-hole recombination (discussed further in section 1.5.9).

As the photocatalytic process gradually breaks down the micropollutant molecules, no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. The catalyst itself is unchanged during the process and no
consumable chemicals or additional oxidants are required,\textsuperscript{98} as well as working at ambient conditions.\textsuperscript{99} Additionally, when the micropollutant is attracted strongly to the surface of the catalyst, the process will work even at very low concentrations.\textsuperscript{93} This could result in savings and a simpler operation of the equipment involved. UV based processes are already used to treat pharmaceutical wastewater in multiple plants\textsuperscript{65} and are used as a tertiary step in WWTP in Singapore.\textsuperscript{100} Photocatalysis specifically has been shown to successfully treat wastewater containing dyes\textsuperscript{101} and pharmaceuticals.\textsuperscript{102} However, as current UV processes are more expensive and energy intensive compared to other AOPs, the use of energy efficient LEDs in the future could aid to reduce to cost and increase feasibility of the process.\textsuperscript{63,66} Therefore, more research is required to improve the efficiency of the overall photocatalytic process.

\subsection*{1.4.2 Photocatalytic Reactor Design}
Currently research focus has been primarily on the photocatalytic material, whereas the reactor design in comparison has been overlooked. This has allowed for inefficient and out-date reactors to continually be used.\textsuperscript{103} Recently there has been an increase in interest into photocatalytic (PC) reactor design, as it has been found to have such a large impact of the efficiency (by increasing irradiated surface area for example) of the system.

There are four main type of reactors; slurry, immobilised, membrane and fluidised bed (shown in Figure 1.6). The most common type of photocatalytic reactor uses powder suspensions, also known as “slurry reactors”. These reactors utilise suspended photocatalyst particles which provide a higher contact area between the photocatalyst, the light source and the solution. This system offers high surface area of photocatalyst per unit volume to react with the UV light, however it requires catalysis separation afterwards (via methods such as settling tanks or external cross flow filtration systems\textsuperscript{83}), as well as leads to light scattering and catalysis aggregation\textsuperscript{68} and thus is impractical for WWTP due to cost and the concern of material leaching into the environment.\textsuperscript{104} For example, the Fenton process is the second most commonly used photochemical AOP, it utilise hydrogen peroxide, UV light and iron to produce the hydroxyl radical\textsuperscript{48}, and have been established in several industrial applications.\textsuperscript{65,105} However, more widespread application of the Fenton process is hindered by its restriction to be carried out at acidic pH and the need for the catalytic sludge to be removed afterwards,\textsuperscript{66} something immobilised catalysis do not require.
Figure 1.6: Graphical summary of the four main different types of photocatalytic reactions:
a) slurry b) immobilized c) membrane reactor d) fluidised bed[Image adapted from Loeb, et al.103]

In fixed bed, also known as immobilized, reactors the photocatalyst is coated onto either the reactor wall, a stationary support structure or spherical glass beads.106 The catalyst support should not excessively hinder the UV light as well as being resilient to oxidising and UV conditions. Suitable supports include; glass as it allows for high temperature during attachment and conditioning of photocatalysts,107 as well as concrete108,109 quartz110,111 and polymers.112,113 Immobilized photocatalysts are becomingly increasingly common as they allow for continuous operation of the reactors.68 The disadvantages of immobilized photocatalyst reactors include relatively lower contact area and lower light efficiency. Kim et al.114 compared two different scaled up reactors containing immobilized anodized TiO$_2$ films: flat type reactors (one film) and rotating tubular reactors (four films) at degrading three model pollutants (shown in Figure 1.7). They demonstrated that the rotating tubular reactor, despite a lower surface area than the flat type reactor (756 cm$^2$ and 900 cm$^2$ respectively), was most effective at degrading EDCs.
Also highlighted was the importance of hydraulic retention time (HRT), with increasing reactor efficiency with decreasing. HRT (thus increasing in flow rate), allowing for mass transfer to take place. However, the requirement for different films for the reactor makes it difficult to operate, and the mesh requires a lot of material for anodization.

Another growing area are photocatalytic membrane reactors (PMRs), this includes reactors with photocatalysts immobilized into/on top of the membrane, or reactors with membranes and the catalyst in suspension. By combining membrane separation with heterogeneous photocatalysis, downstream removal is not required. Also due to the photocatalyst present, membrane fouling should be reduced. Thus the advantages include ease of use, with the disadvantages of low permeate flux and potential membrane damage by hydroxyl radicals or UV light and membrane exchange when catalyst loses activity. Horovitz et al. deposited N-doped TiO$_2$ via sol-gel upon a ceramic Al$_2$O$_3$ microfiltration membrane, to degrade model micropollutant carbamazepine. They demonstrated the compromise between pore size, permeate flux and pollutant degradation. Smaller pores (200 nm) presented significantly reduced flux but better degradation in comparison to larger pores (800 nm).

The fourth reactor are fluidized bed reactors, which use the addition of an upward stream of fluid in the reactor to bring the immobilized photocatalytic particles from a stationary phase to a suspended state. Zulfakar et al. used a fluidized bed reactor utilizing immobilized TiO$_2$ to degrade phenol. These systems offer the advantages of a low pressure drop, a high permeate flux and high photocatalyst surface. However it’s
disadvantages include loss of particles within the system and necessary downstream treatment. There have been multiple investigations comparing the photocatalytic effectiveness of various reactor designs. Manassero et al. carried out a comparison between three different TiO₂ photocatalytic reactors; slurry, fixed-bed and fixed-film, degrading the model micropollutant, clofibric acid, with the UV lamp position at one side of the reactor. They found the fixed bed to provide a satisfactory quantum efficiency enough that it could be further optimised by increasing the thickness of the TiO₂ layer to increase absorption of photons, in comparison to the most efficient slurry reactor configuration. The fixed-film performed badly as was only illuminated on one side, thus a reduced contact area.

Van Grieken et al. also investigated, slurry, fixed bed, and wall (fixed film) reactors for E. coli deactivation using TiO₂ and UV, but with the UV lamp positioned in the middle of the reactor and thus within the reaction solution (shown in Figure 1.8). The immobilised systems did show a lower disinfection rate constant to that of slurries, however the immobilized system was less effected by organic matter. Thus slurry and immobilized systems required similar irradiation times. As the wall/fixed films were coated around the UV lamp, it increased absorption but also hindered transmission of UV light into the sample. This method also requires dip-coating the reactor wall and replacing the entire glass when catalyst loses activity.

![Figure 1.8: The two main type of photocatalytic reactors: slurry and immobilised (wall and fixed bed)](Image abstracted from Van Grieken et al.)

In both Manassero et al. and Van Grieken et al. examples, the slurry solutions required post treatment including centrifuging, filtering at 0.02 µm and filtering at 0.22 µm membranes respectively, which are very expensive and time consuming steps.
Akyol et al.\textsuperscript{111} coated the walls of a tubular reactor with a ZnO film, surrounded by six UV lights, which had comparable photocatalytic activity to that of ZnO powder. They demonstrated the relationship between the diameter of the reactor with pollutant degradation, narrower reactors displays higher rate constants, with 4 mm achieving the best and 12 mm the lowest. There are also many scale up examples of solar light plants, especially when employed with compound parabolic collectors (CPC).\textsuperscript{122} Reactor design is a critical factor in photocatalytic performance, the optimisation of the photocatalytic process via reactor design will allow for enhanced system performance and thus is a crucial area of investigation.

1.4.3 Key Process Parameters for Photocatalysis

There are various parameters, including the photocatalytic reactor, which affect the performance of the photocatalyst (shown in Figure 1.9). Light irradiation is a key parameter, but other parameters affecting degradation in a photocatalytic reactor include\textsuperscript{123}:

- Light source including wavelength and distribution
- Catalyst type including electron acceptor type
- Mass transfer efficiency within the system
- Micropollutant concentration
- Other components which can interfere such as scavengers

Catalyst loading is vital to degradation, with a range of between 0.04-5.0 g/L usually reported, but an average of 0.5 g/L of TiO\(_2\).\textsuperscript{102} This has been investigated thoroughly and is dependent on the photoreactor, and other parameters, with various groups reporting various different optimal catalyst loading for each system. Qamar et al.\textsuperscript{124} reported that for degrading vanillin, the initial reaction rates were found to be directly proportional to catalyst concentration (TiO\(_2\) and ZnO) indicating a heterogeneous regime, but also state that above a certain concentration rates become independent of concentration. However, it has also been reported that increasing catalyst loading can lead to light scattering and a reduction in light penetration, as well as catalyst agglomeration leading to reduced active surface.\textsuperscript{125} All of these cause a reduction of photocatalytic activity.
The micropollutant concentration impacts photocatalyst performance. High concentrations of micropollutants and natural organic matter (NOM) reduce process efficiency by saturating the photocatalyst surface, thus increasing the competition for active sites, and reducing irradiation of the surface, which can lead to the agglomeration of the photocatalyst particles. The concentration of suspended organic solids will increase the turbidity of the reaction solution, reducing light transmission through the solution and thus reducing photocatalysts activation available. In terms of light activation there is; visible light (400 – 600 nm), UV-A (315 – 400 nm), UV-B (280 – 315 nm) and UV-C (100 - 280 nm), which are suited to different photocatalysts with different band gaps. It has also been shown that an excess of light promotes a faster electron-hole recombination and the low activation energy of photocatalytic reactions (5–20 kJ/mol), compared with ordinary thermal reactions. It is important to note that photocatalytic degradation does not display a linear correlation with light intensity and that excess light promotes fast electron – hole recombination.

![Figure 1.9: Graphical summary of parameters that affect photocatalytic micropollutants degradation. [Image adapted from Lais et al.](126)](image)

The pH of the treatment effluent is a crucial and complex parameter, as this affects many factors such as the catalysts aggregation and the surface charge of the catalysis. The point
zero charge (PZC) is the pH value when the photocatalysis has no charge and thus there is minimal electrostatic attraction between the catalyst and the micropollutants. For example, when the pH of the point zero charge (PZC) is higher than the total pH, the catalysts has a positive surface and thus will attract negatively charged compounds. If the PZC is lower than the pH, the negative catalyst will repel the negative compounds.\textsuperscript{127} The PZC of ZnO nanostructures is approximately 9, and the electrical property change with the pH value of the dispersion.\textsuperscript{128} The PZC for TiO\textsubscript{2}, is 6.25, the effect of pH upon the surface charge is shown in equation 1.5.\textsuperscript{124,129}

\[
\begin{align*}
\text{TiOH} + H^+ & = \text{TiOH}_2^+ \quad \text{pH} < 6.25 \\
\text{TiOH} + \text{OH}^- & = \text{TiO}^- \quad \text{pH} > 6.25
\end{align*}
\]

This highlights the difficulty in treatment as the vast variety of compounds will react differently. Wastewater, in particular industrial wastewater, is discharged at various pHs which will compromise the process because the pH effects the efficiency of photocatalytic degradation.

The optimum temperature for photocatalytic degradation is between 20 – 80 °C, however increasing temperature can increase the rate of organic micropollutants degradation, but this increase in temperature can reduce the dissolved oxygen (DO) concentration and adsorptive ability of reactants upon the photocatalyst surface, therefore leading to an overall reduction of the photodegradation efficiency.\textsuperscript{9} Low temperatures (< 20 °C) can lead to increasing the apparent activation energy, increases the absorption of the reaction product but limits desorption of the final product from the photocatalyst.\textsuperscript{130}

Another key parameter is dissolved oxygen levels in the water, which help to reduce electron/hole recombination, by acting as an electron scavenger and thus producing further reactive oxygen species (ROS). Patterson et al. demonstrated that under oxygen rich conditions, the ZnO photocatalysis displayed increased photocatalytic activity as well as increased stability.\textsuperscript{131} Im et al. found that oxygen increased mineralization of carbamazepine under TiO\textsubscript{2}/UV conditions. This was due to the production of additional superoxide radicals (O$_2^-$), which aid electron and hole separation, and hydrogen peroxide.\textsuperscript{132} In addition to the stabilization and formation of radical intermediates, the presence of DO also plays a role as a buoyant force within the reaction solution.\textsuperscript{99}
Therefore as both chemical composition and pH of wastewater may vary, efforts should be made for the development of photocatalytic materials and reactor design, which can be useful in a wider range of operating conditions such as temperature, pH and micropollutants concentrations to ensure high photocatalytic performance, avoid excess cost and reaction time.

1.5 Zinc Oxide & Titanium Dioxide

1.5.1 Zinc Oxide

ZnO is one of the most researched chemical compounds in nanotechnology\textsuperscript{133} and its properties are strongly dependent on its structure, including morphology, aspect ratio, size, orientation and density of crystal.\textsuperscript{134} ZnO is a wide band gap semiconductor (~3.3 eV, which corresponds to a maximum excitation wavelength of 380 nm\textsuperscript{135} and has a large exciton binding energy (60 meV) similar to TiO\textsubscript{2} but with least two orders of magnitude higher electron mobility\textsuperscript{136}, longer electron lifetime (and thus longer recombination time), therefore ZnO’s photocatalytic performance is able to match and in some cases, has been shown to exceed TiO\textsubscript{2}.\textsuperscript{128,137–142} Zinc oxide can be found in three different crystal structures, cubic structures such as zinc blende or rock salt, but its most stable and common phase is in hexagonal wurtzite\textsuperscript{135} (shown in Figure 1.10). To form rock salt requires very high pressures, and zinc blende is only formed from cubic structures.\textsuperscript{143}

![ZnO crystal structures](image)

**Figure 1.10**: ZnO crystal structures: rocksalt (a), zinc blende (b) and Wurtzite (c). [Image abstracted from Özgur et al.\textsuperscript{144}]
1.5 Zinc Oxide & Titanium Dioxide

ZnO has a large number of active sites, which makes it a highly active photocatalyst and is an example of an n-type semiconductor (excess electrons to holes). A disadvantage is that it is prone to light induced corrosion, which will cause a reduction in photocatalytic activity after using with UV light. Other issues include ZnO has a rather high solubility in water of 8.59 mg/L, compared to 0.13 μg/L for TiO₂. The solubility of these materials increases in acidic pH and in nano-materials compared to bulk.

Most research focuses on ZnO, but there are many examples of ZnO used as photocatalysts with the addition of dopants, as this reduces the electron/hole recombination thus improving photocatalytic activity as well as increasing versatility. The doped ZnO has also been shown to increase micropollutants degradation under visible light, and increase stability. ZnO can be doped with anionic, cationic and rare-earth dopant, but ZnO is a characteristically challenging material to dope.

1.5.2 Titanium Dioxide

TiO₂ is the most widely used photocatalyst, and is used for various applications such as water splitting and water purification. It has the advantages of good chemical stability, non-toxicity, long term photo stability and it does not suffer from photocorrosion (discussed in section 3.4.2). Additionally, TiO₂ can be used as both oxidative and reductive catalyst. The benchmark for photocatalytic activity under UV light is Evonik Aerioxide P25 (previously known as Degussa P25 TiO₂), which is widely available and displays a high specific surface area. However, P25 is used mainly in a powder form in slurries or requires immobilization. TiO₂ has three crystals structures: anatase, rutile and brookite (the rarest form) (shown in Figure 1.11).

**Figure 1.11:** The crystal structures of three mineral forms of TiO₂: Anatase, Brookite and Rutile [Image abstracted from Elkodous et al.]
Rutile is the most thermodynamically stable crystal structure of TiO$_2$, and anatase is the most photocatalytic active phase, but the use of a mixture of both rutile and anatase is the most photocatalytic effective. This increase in activity can be explained by the mineral forms displaying different band gaps, 3.2 and 3 eV for anatase and rutile, respectively. These can produce a heterojunction, which increases photocatalytic activity possibly by trapping electrons and preventing recombination and lowering the band gap. Another potential explanation is that the conduction band edge of rutile should be lower than that of anatase, resulting in more favourable conditions for electron transfer from anatase to rutile. Evonik Aeroxide TiO$_2$ P25 is composed of anatase and rutile crystals in an approximately 15:80 ratio (and 5% accounting for an amorphous phase).

1.5.3 Production of ZnO and TiO$_2$ Nanostructures
There are various methods to produce the ZnO nanostructures, such as vapour phase transport, hydrothermal and electrochemical. Currently, the most utilised methods for producing ZnO nanostructures are via vapour transport processes, in which zinc or ZnO powder mixtures react with oxygen vapour to form nanostructures. This covers any process that deposits a solid material from a gas phase onto a surface. Another method is hydrothermal treatment, which crystalizes mineral in situ onto a solid surface in an autoclave. The reaction between the native defects on the ZnO surface and water seen in hydrothermal treatment aids healing of surface defects, which can act as a scattering centre and reduce electron mobility. The deposition method impacts the nanostructures which are formed, other parameters include source material composition, growth temperature and diffusion rates. Elamin et al. used the hydrothermal method to produce ZnO nanosheets and nanotubes, using the same method and conditions, the only difference being a longer time to produce nanotubes rather than nanosheets. Cao et al. successfully produced photocatalytic active N-doped titania nanoparticles via a mild hydrothermal method, without the need for a crystallizing step.

These methods also require the photocatalytic layer to be deposited on to a support such as glass, activated carbon and quartz. The material used as a support must meet strict requirements, such as strong immobilisation between catalyst and support, maintaining high surface area and the support must not susceptible to oxidation.
1.5.4 Anodization
Electrochemical synthesis of nanostructures is increasingly common, due to its simplicity, low temperature requirement, flexibility, and low cost.\textsuperscript{153} Anodization is a well-known route to synthesize low-dimensional self-organized structures.\textsuperscript{153} By supplying a current to a conducting metal (the cathode), an oxide layer is formed on the anode surface in the presence of an electrolyte, which aides in the dissolution of the metal surface (as shown in Figure 1.12).

\begin{center}
\textbf{Figure 1.12:} Schematic illustration of the anodization process of metal anode in electrolyte solution.
\end{center}

It is easier to produce nanowires on an industrial scale in comparison to the other methods which require high temperature environments for example.\textsuperscript{160} Formation of the photocatalytic active oxide layer via anodization, will allow for the catalyst to act as its own support, therefore requiring less material and making the process more efficient.

1.5.5 ZnO Anodization and Nanostructures
ZnO nanostructures can be produced via anodization using various basic electrolytes such as sodium hydroxide (NaOH)\textsuperscript{161} and sodium bicarbonate (NaHCO\textsubscript{3}).\textsuperscript{160} Mattia \textit{et al.}\textsuperscript{162} highlighted the effect of different electrolytes on the formation of various ZnO nanostructures, for example, the use of H\textsubscript{3}PO\textsubscript{4} to produce nanoflakes, HCl to form nanoflowers and KHCO\textsubscript{3} to form nanowires. Shetty \textit{et al.}\textsuperscript{163} used water as a more sustainable electrolyte to anodize a ZnO layer, but this required much longer anodization time (6-12 hours), and produced nanoporous structures. Various parameters have been shown to affect the morphology of the ZnO structures that form such as pH, applied
voltage, time, concentration\textsuperscript{161,162} as well as different electrolytes\textsuperscript{160} used and different morphology produced.\textsuperscript{164}

ZnO nanostructures can be found in many different morphologies such as nanorods, nanowires, nanosheets, nanodumbbells, nanobelts, nanoflowers, etc.\textsuperscript{9} There are four different groups of nanostructures based on dimensions (Figure 1.13); 0D which include nanoclusters and nanoparticles, 1D such as nanowires and nanorods, which have higher surface volume ratio in comparison to nanoparticles.\textsuperscript{134} There are also 2D and 3D structures such as nanoplates and nanotetrapods respectively, however these are less common. 0D and 1D structures are known for light scattering and high surface area.\textsuperscript{165} Surface area and defects play an important role in the photocatalytic activity of metal oxide nanostructures. At the nanoscale (1–100 nm), materials demonstrate significantly different physical and chemical properties from their bulk counterparts. Furthermore, a higher surface to volume ratio provides a dramatic increase in the surface reactivity.\textsuperscript{99}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nanostructures.png}
\caption{The four different dimensional groups of Zinc Oxide nanostructures: a) Nanoparticles (0D),\textsuperscript{214} b) Nanotubes (1D),\textsuperscript{215} c) Nanosheets (2D),\textsuperscript{216} d) Nanotetrapods (3D),\textsuperscript{217} shown using scanning electron microscopy micrographs.}
\end{figure}
ZnO nanowires have become the most widely researched structure, with five times more publications on wires in comparison to other structures as a whole being published in 2011 for example, as wires have been shown to have more applications than the other 2D and 3D structures. This is because ZnO nanowires have a high surface to volume ratio, and thus more active sites available.

The ZnO layer is formed by a redox reaction (Figure 1.14), which shows the two simultaneously competing reactions occurring during anodization, the formation of the ZnO layer (Figure 1.14.2) and then the ZnO is dissolved by the electrolyte solution (1.14.3), resulting in nanostructures. High electrolyte concentrations result in thicker oxide layers forming, while the lower concentrations led to more defined nanostructures formed. However the exact mechanism for the formation of the ZnO layer is still not entirely understood. For example, it is unknown whether the ZnO nanostructures form by deposition onto the zinc surface or grow outward from the base of the zinc. Mah et al. suggested that the nanostructures develop from pits formed on the surface of the zinc wire by zinc dissolution, caused by the presence of Zn$^{2+}$ ions. They suggest the nanofibres form laterally at the side wall of pits, and then coalesce into the focal point which forms the nanoplatforms and from this the nanowires grow out. This occurs with super saturation of the electrolyte, where the concentration of Zn(OH)$_4^{2-}$ exceeds the solubility ($k_{sp}$) of Zn(OH)$_2$ resulting in the precipitation of Zn(OH)$_2$ onto the anode surface.

\[
\text{At steel cathode: } 2H^+ + 2e^- \rightarrow H_2 \quad (1)
\]

\[
\text{At zinc anode: } Zn \rightarrow Zn^{2+} + 2e^- \\
Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (2) \\
Zn(OH)_2 \rightarrow ZnO + H_2O
\]

\[
\text{Dissolution: } ZnO + HX^* \rightarrow ZnX^* + H_2O \quad (3)
\]

Figure 1.14: Anodization redox reaction to produce ZnO layer

Previously it has been found that different nanostructures translate into different photocatalytic behaviour. As found by Patterson et al. by using hydrothermal solution deposition to produce the ZnO nanostructures, various different structures could be
produced such as nanowires, nanoballs and nanorocks. It was found that varying the
different structures did effect photocatalytic degradation for an azo dye, with nanowires
displaying the highest degradation 75% over six hours in oxygen rich conditions, despite
not having the highest estimated surface area. However, these were the tallest and most
aligned structure, in comparison the smallest-least aligned structures. Similar results were
shown by Zhang et al.\(^{167}\), who found that ZnO nanorods with a higher aspect ratio (longer
and thinner rods) with more surface defects, displayed significantly better photocatalytic
performance with the longer wires having the fastest degradation of the dye, methylene
blue. They found that these longer and thinner nanorods where produced at lower post
annealing temperatures (350 °C) in comparison to higher annealing temperatures (500
°C). Gao et al.\(^{161}\) investigated how various anodization parameters impacted the ZnO
nanostructures which formed upon Zn foils using NaOH electrolytes. They found that
time had a minor effect on the ZnO nanorods produced. With an increasing anodization
time, leads to stripping of the initial anodized layer, a secondary anodization happens on
the newly exposed surface. This leads to changing nanostructure morphology as well over
time. With increasing anodization time, an equilibrium between oxide formation and
dissolution, led to increased regularity. Elamin et al.\(^{134}\) also demonstrated that while ZnO
nanosheets and nanotubes produced by the hydrothermal method (shown in Figure 1.15)
had similar degradation behaviour for the dye, methyl orange, they degraded at different
times with nanosheets displaying higher degradation time than nanotubes (an 20 % higher
removal rate over a two hour period).

![Scanning electron microscopy micrographs of ZnO a) nanosheets and b) nanotubes [Image abstracted from Elamin et al.\(^{134}\)]](image)

*Figure 1.15: Scanning electron microscopy micrographs of ZnO a) nanosheets and b) nanotubes [Image abstracted from Elamin et al.\(^{134}\)]*

In this example, the nanosheets have suggested higher surface area in comparison to the
nanotubes. Therefore, this will increase contact area between target material and the ZnO,
as well as increasing UV absorption. In all the above discussed examples, they are able to tune the ZnO morphology which form by tailoring one or more parameters (such as annealing time, anodization time, electrolyte concentration, electrolyte composition). These examples highlight the relationship between nanostructure morphology and photocatalytic degradation, however the impact of time upon the photocatalytic behaviour or the effect of nanostructures formed upon a Zn wire, instead of a Zn film has not been fully investigated.

1.5.6. ZnO in Photocatalysis & Photo-electrocatalysis for water systems
ZnO has been used successfully as a photocatalyst for many years. Habba et al.\textsuperscript{145} used ZnO nanowires for water purification to degrade dyes, and showed a clear increase in degradation upon the use of a ZnO in conjugation with UV, in comparison to just UV. Over a three hour period, there was 90% removal of acid red dye compared to 10% using photolysis alone. Tian et al.\textsuperscript{168} showed ZnO had significantly higher photocatalytic degradation of the dye, methylene orange in comparison to Evonik Aeroxide TiO\textsubscript{2} P25. ZnO has also successfully been used to degrade ibuprofen,\textsuperscript{169} vanillin\textsuperscript{124} and other EDCs.\textsuperscript{170} Juan et al.\textsuperscript{9} discussed recent developments, with modified ZnO such as doping showing much promise and overall there is clear intent to increase ZnO photocatalyst ability by using it in tandem with other technologies. The use of ZnO has been limited due to susceptibility to photocorrosion, a process where the formation of molecular oxygen from oxide anions is more favourable, than from the water that the ZnO is in.\textsuperscript{72} Key factors in this are the vacant sites on the ZnO surface and the reaction between surface oxygen and charged holes in the valence band (VB) oxidation (shown in equation 1.6).\textsuperscript{9}

\begin{align*}
\text{ZnO} + 2h^*_B & \rightarrow \text{Zn}^{2+} + \frac{1}{2} \text{O}_2 \quad 1.6
\end{align*}

Various steps have been investigated to reduce ZnO photocorrosion, this includes surface modification such as graphene oxide\textsuperscript{171} or polyaniline.\textsuperscript{172} The formation of a passive layer on the ZnO surface, suppresses the rate of photocorrosion and can also lead to increased photocatalytic activity.\textsuperscript{128} As well as surface modifications, there are also system parameters which can reduce photocorrosion. For example, Patterson et al.\textsuperscript{131} found that using oxygen rich conditions reduced ZnO photocatalyst degradation under UV light as
well as increased methylene blue degradation, in comparison to oxygen limited conditions which saw the instability of the ZnO films increase.

Electrochemical advanced oxidation processes (EAOP) generates hydroxyl radicals electrochemically to degrade micropollutants, usually in an electrochemical cell. There are two routes that the micropollutants are degraded in EAOP: direct and indirect oxidation. In direct oxidation, the pollutant is degraded on the surface of the anode, while for indirect oxidation a strong oxidising agent is produced from the anode surface which reacts with the pollutant.\textsuperscript{173} Hydrogen peroxide, a very reactive oxidising agent, is also produced at the cathode surface via the reduction of water.\textsuperscript{174}

EAOP systems are robust, versatile and require low pressure and low temperature.\textsuperscript{173} A disadvantage however is that organic material can be deposited on the electrode surfaces and wastewater has a low conductance, therefore additional electrolyte is required. One of the most developed large scale examples of EAOP is in automated disinfection of swimming pool water using boron doped diamond (BDD) anodes.\textsuperscript{174,175} Panizza \textit{et al}.\textsuperscript{174} discussed the two main challenges for EAOP were reducing electrode price and also incorporating the use of renewable energy into the process.

Therefore it is clear both photocatalysis and EAOP would be very beneficial if joined together. For example, Ochiai \textit{et al}.\textsuperscript{176} successfully produced a novel electrochemical–photocatalytic sequential water treatment system using a BDD electrode and a TiO\textsubscript{2} photocatalyst and increased pollutant degradation. However the two systems can further be combined. An electro-assisted photocatalytic system combines photocatalysis with electrochemical water treatment. It applies an electrical field between an anode, which has a photocatalyst surface, and a cathode, that increases the separation of the photogenerated electrons and holes. Electrons and holes move in opposite directions inside the electrical field and this increases their separation by transferring the electrons to the cathode and leaving the holes in the photocatalyst.\textsuperscript{177} The theory is that applying a positive bias to photoanode, it will reduce hole and electron recombination. Huang \textit{et al}.\textsuperscript{178} used TiO\textsubscript{2} with activated carbon fibres (ACF) in a electrochemical cell to electro-photocatalytic degrade acid orange. This system was able to degrade 91 \% of an acid solution over a period of 180 minutes with the addition of 0.5 V to the electrode.
With regards to ZnO specifically, Aber et al.$^{177}$ demonstrated the use of electro-assisted photocatalytic degradation of a dye, reactive navy blue, with ZnO nanoparticle immobilized on a titanium anode. Applying potential difference of 4 V between the electrodes caused decolourization to increase from 39 % in a standard photocatalytic system to 81 % process. The area of electro-assisted photocatalysis has been investigated, but with regards to the simply application of electricity to a cathode and anode and the system acting as an electrochemical cell. The effect of simply applying electricity to a single metal electrode, with the aim to aid charge separation, has not been investigated.

### 1.5.7 TiO$_2$ Anodization

TiO$_2$ anodization is dominated by the use of hazardous and toxic fluoride based electrolytes such as hydrofluoric acid (HF) and ammonium fluoride (NHF$_4$).$^{179,180,181}$

Titania anodization is shown in equation 1.7:

$$Ti \rightarrow Ti^{4+} + 4e^- \quad \text{(Oxidation of Ti)}$$

$$Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+ \quad \text{(Formation of oxide layer)}$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \quad \text{(Dissolution of oxide layer)}$$

Regonin et al.$^{181}$ describes the process as the Ti$^{4+}$ being driven from the Ti substrate towards the electrolyte where they combine with the F$^-$ ion to from a stable titanium hexalfuroide complex. Additional ions from the electrolyte will also migrate towards or away from the anode depending on their electrostatic charge and can be incorporated within the film. The presence of F$^-$ ions, capable of partially dissolving the oxide, is believed to be crucial in forming porosity in the film and possibly act to sustain the porosity during the formation of the nanostructures. After establishing a steady state between oxide formation and dissolution, an equilibrium situation can be achieved leading to nanotubular or nanoporous oxide layers.$^{182}$ This process usually takes up to several hours.$^{182}$ There are a few examples of more sustainable halide based electrolytes such as sodium chloride (NaCl)$^{183}$, hydrochloric acid (HCl)$^{184}$ and perchloric acid (HClO$_4$)$^{182}$ as well as potassium bromide (KBr)$^{183}$ to produce the TiO$_2$ layer via anodization. Other halide based electrolytes (non-fluoride) are able to produce oxide layers quicker but with less order.$^{181}$ Richter et al.$^{185}$ successfully used a range of different organic acid electrolytes including oxalic and formic, containing chlorine salts to produce the harsh conditions necessary to produce TiO$_2$ nanostructures. Allam et al.$^{186}$ used HCl
and H₂O₂ on Ti foil, at room temperature to produce the conditions required to form TiO₂ nanostructures. They also carried out these anodizations in ethylene glycol, which incorporated carbon into the nanostructures as the EG was oxidised. The use of viscous electrolytes, such as ethylene glycol and glycerol, results in wall smoothness by damping local spikes in the flux of reaction species by locally different pH values within the tubes.¹⁸⁷ However, it has been observed that viscous electrolytes result in a lower current density, and local acidification, thus lowering the amount of competing chemical dissolution, thereby increasing the nanostructure length.¹⁸⁸,¹⁸⁹ Similar to ZnO, key parameters are electrolyte composition, temperature, pH, voltage and time are key, to tailor which nanostructures form.¹⁹⁰,¹⁹¹

1.5.8 TiO₂ nanostructures
Like ZnO, TiO₂ nanostructures can exist in various different morphologies such as nanoparticles,¹⁹² nanorods and nanoflowers.¹⁹³ However these structures are formed during synthesis methods such as microwave treatment, hydrothermal or vapour deposition methods. Titanium anodization carried out using halide based (fluoride, perchlorate, chloride, bromide), will develop porous/tubular morphology¹⁸¹ as the oxide layer is soluble in the electrolyte. Nanotubes are an attractive structure because they display high surface area, high cation exchangeability and less recombination sites in comparison to nanoparticles.¹⁹⁰ Nanotubes can also display high light scattering effects, by allowing for high electron mobility through the nanotubes, which prevents surface h⁺/e⁻ recombination and enhances photocatalytic efficiency in comparison to nanoparticles.¹⁹⁰,¹⁹⁴ The use of any other electrolyte, such as sulphuric acid and phosphoric acid, will lead to barrier type structure forming are common barrier layer type electrolytes.¹⁹⁵,¹⁹⁶ These barrier type structures are thin (a few hundred nm in length) and compact, reducing surface area. The difference between nanotubes and barrier structures are shown in Figure 1.16.

The formation of nanopores/nanotubes using fluoride electrolyte, an initial barrier forms which then acts as the foundation for the formation of pores which transition into nanotubes, and their diameter is proportional to applied voltage.¹⁸¹ These pores form at weak spots (such as pits and crack) present on the oxide layer. These pores allow for current to move through the insulating oxide layer to the metal core, which can then
produce the nanostructures. Local current at these points could lead to heating and thus increase the rate of TiO$_2$ dissolution.

![Figure 1.16: TiO$_2$ anodized nanostructures: a) Anodic titanium oxide nanotube produced by Zhou et al. b) Barrier type pore structure produced in 0.1 M sulphuric acid at 50 mA/cm$^2$ for 30 minutes, by Masahashi et al.](image)

The other halide based electrolytes are examples of rapid breakdown conditions, so are much faster than fluorides processes (1000 x faster) and result in tubes with significantly smaller diameters, and incorporate electrolyte species into the anodic films. In these examples, the nanostructures are not affected by the morphology and develop at specific nucleation points, which is proportional to the applied potential, and thus the growth rate. Hahn et al. produced TiO$_2$ nanotubes using HClO$_4$ and NaClO$_4$. Cheong et al. formed disordered TiO$_2$ nanotubes using ethylene glycol and sodium chloride, highlighting the advantages of using ethylene glycol to increase the photocurrent density efficiency of nanotubes were found to increase with increasing ethylene glycol ratio to DI water. The macrostructures in this study resemble flake structures. Hassan et al. produced nanotubes using HCl, H$_2$O$_2$ and ethylene glycol with ethylene glycol acting to decelerate the decomposition process. Devine et al. also used NaCl and ethylene glycol to successfully produce nanotubes, producing similar flake like structures to those produced by Cheong et al. (comparison demonstrated in Figure 1.17). They also demonstrated the formation of similar nanostructures using KBr electrolyte, but suggested the use of ethylene glycol dampened nanostructure growth, but produced tube structures rather than fibres formed using DI water alone. This was at 40 V and for an anodization time of 60 seconds.
Figure 1.17: Scanning electron microscopy micrographs of anodized TiO$_2$ nanostructures produced by: (a-b) Cheong *et al.*\textsuperscript{198} using 0.3 M NaCl at a 6:4 ratio with ethylene glycol respectively, a) flowerlike-nanostructure at 10 µm b) nanotubes at 500 nm. Devine *et al.*\textsuperscript{183} (c-d) synthesised nanostructures in 50:50 ratio of water and ethylene glycol at a 0.3 M NaCl at 40 V for 60 seconds c) cluster on nanostructures on the compact TiO$_2$ layer at 10 µm d) nanotubes at 200 nm.

Potentiostatic anodization is the most commonly used method in the literature for the formation of TiO$_2$. Casado *et al.*\textsuperscript{200} demonstrated that using galvanostatic allows fine control of the electrical current resulting in improvement in nanostructures growth due to slower dissolution of the TiO$_2$ compact layer. In the examples, the photocatalytic behaviour of structures produced using non fluoride electrolytes or galvanostatic anodization, was not investigate or only partially demonstrated.
1.5.9 TiO$_2$ in Photocatalytic systems & Doping

TiO$_2$ has been the benchmark of photocatalysis, with use usually in the form of Evonik Aeroxide P25 slurry reactors. It is widely researched and understood material, e.g. in 2017 alone, out of 1356 articles published regarding photocatalytic water treatment, over half (761) were based upon TiO$_2$. Achilleos et al. compared the effectiveness of six commercially available photocatalysts, including Evonik Aeroxide P25, in a batch UV reactor. They highlighted irradiation time, photocatalyst type, catalyst to substrate concentration ratio and the water matrix were key to degradation.

Van Grieken et al. highlighted the TiO$_2$ immobilized systems had lower activity for *E. coli* deactivation and methylene blue degradation in comparison to TiO$_2$ slurry, but also demonstrated that the immobilized systems displayed lower inhibition and thus required less irradiation time, in comparison to the slurry. Furthermore, as previously discussed in section 1.4.2, slurries require expensive post treatment.

In terms of immobilized, photocatalysts there are many examples of TiO$_2$ powder immobilized on to supports or titania grown on to supports, e.g. via such as anodization. The vast majority of anodized samples are flat films. Subramanian et al. prepared TiO$_2$ nanotubes via anodization using fluoride electrolytes on Ti wire instead of foil (reactor set up shown in Figure 1.18).

**Figure 1.18:** The photocatalyst configuration of TiO$_2$ foils vs TiO$_2$ wires used by Subramanian et al. They suggest the improved photocatalytic performance per cm$^2$ demonstrated by the anodized TiO$_2$ wire is due to the wire geometry, and the nanotubes on the surface to Absorb Reflected (IRL) and Refracted (IRF) Light [Image abstracted from Subramanian et al.]
They found that degradation of the dye, methyl orange increased from 19 to 40% from nanotubes on one Ti foil in comparison to four Ti wire (with a surface area of 2 and 1.26 cm\(^2\) respectively). The higher photocatalytic activity of the anodized wires (over the films), despite the reduced surface area, can be attributed to the efficient capture of reflected and refracted light by the radially outward oriented TiO\(_2\) nanotubes formed over the circumference of the titanium wire.

Titania has the disadvantage of very fast electron-hole recombination, as well requiring UV light activation (wavelengths <385 nm).\(^6\) This can be resolved via doping, which by incorporating foreign ions or impurities into the metal oxide results in the coordination environment of the lattice being altered.\(^1\) It adds localized electronic energy levels within the band gap, narrowing the band gap and thus lowering the energy required to excite an electron from the valence band up to the conduction band.\(^9\) This allows for the catalyst to absorb in the visible light spectrum but also to reduce recombination by enhancing the charge separation between electrons and holes. The dopants may also trap the electrons,\(^9\) preventing the electron falling back in to the valence band. Examples of dopants include carbon,\(^2\) fluoride, sulphur or other metals dopants such as iron and silver. Nitrogen doping (N-doped) is one of the most common dopants, because it has a small ionization energy and atomic size comparable with oxygen, is stable and to from metastable centres. This reduces the band gap from approximately of 3.2 eV for undoped TiO\(_2\) to 2.5 eV with N-doped TiO\(_2\).\(^3\) The higher the dopants atomic number, the lower the energy of its 2p state, caused by the increase in effective nuclear charge.\(^4\)

Other dopant examples such as fluoride, enhance photocatalytic performance by reducing the Ti\(^{3+}\) ions due to charge compensation between F\(^-\) and Ti\(^{4+}\).\(^5\) Sulphur on the other hand is very difficult to insert into the lattice, due to its large cationic radius,\(^5\) while iron has been used successfully as a dopant because it has a similar atomic radius to that of titanium (0.65 A vs 0.605 A respectively), so can be inserted into the crystal lattice.\(^6\)

Nitrogen doped samples usually exhibit enhanced absorption in the visible light spectrum 400-510 nm.\(^7\) There are two classes of processes for nitrogen doping: A first one, involves a single step via sol-gel method,\(^8\) nitrogen annealing,\(^9\) or anodization with a nitrogen precursor in ethylene glycol such as urea, or ammonium fluoride.\(^7\) Second two step processes occurs when the amorphous titania layer has already been produced, followed by the addition nitrogen via, e.g. immersion in ammonia solution,\(^10\) chemical
vapour deposition\textsuperscript{211} or anodization.\textsuperscript{212} Cao \textit{et al.}\textsuperscript{157} produced N-TiO\textsubscript{2} nanoparticles by a mild hydrothermal method at 150 °C for two hours, which saw an increase in phenol degradation of 47 \% under visible light in comparison to undoped samples (which achieved just 10 \% degradation over ten hours). Thus highlights the effectiveness of N-doping, and how it can reduce cost of TiO\textsubscript{2} photocatalysis by using visible instead of UV light.
1.6 Summary of the Literature and Thesis Aims
This chapter has introduced photocatalysis and its potential role in wastewater treatment. The first section provided an overview of municipal wastewater treatment, and, their inadequacy to treat micropollutants, with a promising solution laying in the use of advanced oxidation processes. The second section introduced photocatalysis, and discussed the fundamental theory, as well as highlighted key parameters in the reaction and in reactor design upon the photocatalytic efficiency. The third and final section presented the two catalytic materials studied in this thesis, TiO$_2$ and ZnO, and the electrochemical synthesis method of anodization to produce them. This section also highlighted how varying the anodization parameters can tailor the oxide structure produced and provided examples of the successful use of TiO$_2$ and ZnO as photocatalysts to degrade micropollutants.

Throughout the chapter, questions and areas of novel research have been highlighted and listed as the following:

- The anodization of metal oxides has been studied intensively and almost exclusively upon flat film surfaces. This use of film anodization leads to material wastage and limited irradiation efficiency. The use of a wire support could be an effective alternative. This would require optimisation of the anodization conditions to suit the wire over film.

- The use of a wire photocatalyst would require the development of a suitable tubular reactor, attempting to address the disadvantages that immobilized photocatalysts face as well highlighting key system parameters which impact photocatalysis efficiency.

- The relationship between anodization parameters (such temperature and time), surface morphology and whether this translates to change in photocatalytic efficiency of the oxide layer has yet to be studied intensively. It is crucial to determine the stability of oxide layer and investigate, if needed, how to increase stability further.

- Conventional two to three cell electrochemical system used in tandem with photocatalysis, have been well documented and studied. However, the application of electricity to the metal core of the photocatalysis to increase activity has not. This could be a simple and effective alternative. The hypothesis behind this experiment is that the addition of electricity could minimize electron-hole
recombination, as well as alter the wettability of the catalysts surface and increase direct oxidation, thus increasing photoactivity of the material.

- A very limited example of TiO$_2$ anodized upon wires or synthesised with the use of non-fluoride electrolytes exist. These examples also fail to investigate fully the photocatalytic activity of an oxide layer developed.

The aim of this thesis was to answer these open questions, and address the highlighted gaps in the literature by providing a deeper understanding of the relationship which exists between immobilised photocatalyst synthesis via anodization and photocatalytic activity. As well as the effect of physical properties of the catalyst and photoactivity.
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Chapter 2

Materials & Methods
2.1 Context

This chapter provides a detailed overview of the different techniques and methods which were used to investigate the anodization of metal oxide layers for use as photocatalysts, including information above and beyond available in the corresponding chapters or submitted manuscripts. The chapter is spilt into: the development of the experimental procedures (section 2.2), the theoretical background to the characterization methods used (section 2.3), and the development of the tubular photoreaction suitable for the wire photocatalyst (section 2.4). Once fabricated, the materials were analyzed by a variety of characterization techniques and their photocatalytic behavior was studied. The production, characterization and use of the photocatalytic wires is shown in Figure 2.1. This includes the mandatory steps of cleaning the wires, then the electrochemical step of anodization to produce the oxide layer. This is followed by the post thermal treatment annealing to stabilize the crystal structure of the oxide layer. Finally, the material is tested for the degradation of micropollutants in a suitable photoreactor to determine photocatalytic activity. Optional stages such as pre-anodization steps, including electro-polishing and characterization, are shown above the main trail on the flow diagram.

Figure 2.1: Schematic diagram of the steps required to anodize the metal to produce the photocatalytic active oxide layer.

2.2 Experimental Procedure

2.2.1 Reagents
Ultrapure water was supplied from a PURELAB®, ELGA LabWater purification system (18.2 MΩ cm) and used un-buffered. All chemicals and organic solvents were purchased from major suppliers and used without further purification, unless otherwise stated in the corresponding chapter.
2.2.2 Preparation of Wires
The metal wires were cut to 25 cm, and thoroughly cleaned with acetone and ethanol to remove oil, grease and other external contaminants before anodization, and then straightened by hand or via rolling blocks. If a preparation step, such as pre-annealing or electro-polishing, was investigated it would be carried out at this stage. Annealing allows for the material to release internal stress and improve microstructure of the metal by removing crystal defects and grain boundaries.1 Electro-polishing, the reverse of electro-plating is a solvent consuming process, used to increase the hydrophilic nature of the metal surface and achieve a smooth surface.2,3 Electro-polishing is carried out in a electrolyte solution of ethanol (> 99.8%) and perchloric acid (60-62%) in a volumetric ratio of 2:1 at -70°C and 20 V for 15 minutes. The metal wire acts as the anode and a metal beaker containing the reaction solution acts as cathode. Both wire and steel beaker were attached to a power supply (Figure 2.2). The beaker was submerged within a solution of dry ice and acetone, to maintain the reaction temperature of -70°C. The metal wire (anode) had no contact with the metal beaker (cathode).

![Figure 2.2: Electro-polishing set-up.](image)

Samples were annealed within a quartz tube, in a tubular furnace (Carbolite CTF 12/75/700). Unless otherwise stated, no preparation step was carried out, except for being cleaned with acetone and ethanol to remove oil and grease.
2.2.3 Development of Wire Anodization Reactor and Cleaning

The active oxide layer (TiO$_2$ and ZnO) is formed upon a bare titanium and zinc wire surface respectively, using as electrochemical process, known as anodization (discussed in section 1.5.4). This unique flow-through anodization rig (Figure 2.3) was developed so that the metal wire would not require bending. Previous systems have been designed to anodize films$^4$, which require a different set up to that of the wire anodization.

![Figure 2.3: Developed flow wire anodisation rig](image)

In this two annular electrode system, the metal wire acts as the anode and is suspended within a steel cathode tube with both connected directly to the power supply. The wire anode was between 0.81 – 1 mm diameter and the steel cathode tube was 10 mm in diameter. The steel cathode tube is 20 cm in length, with holes at 12 cm in length, to allow for electrolyte to flow out of the top, so it will not become saturated (shown in Figure 2.4).

The wire was suspended within the steel cathode tube using a rubber stopper at the top and bottom, to ensure the anode and cathode never made any contact. The bottom rubber stopper allowed for electrolytes to flow through the cathode. A flow through anodization
rig allows for reduced electrolyte solution to be used. Additionally, a magnetic stirrer was used to mix the electrolyte reservoir solution.

**Figure 2.4:** Anodization set up: a) cathode and b) close up of anode and cathode

Electrolyte volume and temperatures were set according to the anodization metal. Other anodization parameters include electrolyte flow rate, which was set to 15 rpm. The two main metals anodized in this thesis were Zinc (chapter 3) and Titanium (chapter 4), and investigated anodization experimental conditions are given in Table 2.1

**Table 2.1:** Experimental conditions for the anodization of Zinc and Titanium

<table>
<thead>
<tr>
<th>Anodization parameters</th>
<th>Metal support</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zinc</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>KHCO₃</td>
</tr>
<tr>
<td>Concentration</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Temperature / °C</td>
<td>8</td>
</tr>
<tr>
<td>Time/minutes</td>
<td>5, 10, 15, 30, 35 &amp; 60</td>
</tr>
<tr>
<td>Applied power</td>
<td>1.5 V</td>
</tr>
</tbody>
</table>
Chapter 2: Materials & Methods

The steel tube cathode was electrochemically cleaned regularly, where it was immersed in oxalic acid (0.3 M, 300 mL) for 30 minutes with 0.5 A/20 V applied to the steel tube (acting anode) and a substitute steel wire (acting cathode).

2.2.4 Post anodization thermal treatment

Post thermal treatment is a process of heating, and slowly cooling to remove defects from the metal. Additionally this process increases the crystalline size. The annealing temperature corresponds to one-half to two-thirds of the metal melting point, and is different for bulk or nanoparticle materials, thus is different for zinc, titanium and tungsten. Unless otherwise stated, all samples were annealed post anodization in a tubular furnace.

2.3 Material Characterisation

This section provides an explanation of the techniques used to characterise the photocatalyst throughout this thesis and their fundamental principles. The characterisation techniques include microscopy, structural and chemical analysis of the material, as well as photocatalytic analysis.

2.3.1 Structural analysis

2.3.1.1 X-Ray Diffraction

X-Ray diffraction (XRD) is a common technique used to characterise crystalline materials and their atomic spacing. It measures the scattering of X-rays from the planes of atoms within a crystalline material, to produce a diffraction pattern which can be used to identify the material.

Constructive interference of the scattered waves, results in Bragg’s law, which describes the relationship between wavelength radiation, angle of X-rays and the internal spacing in the crystals, shown in equation 2.1:

\[ n\lambda = 2dsin\theta \]  \hspace{1cm} 2.1

Where \( n \) is the order of reflection (an integer), \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the spacing between the planes of the atomic lattice and \( \theta \) is the diffraction of angle in
degrees. A schematic figure of the Bragg’s law is shown in figure 2.5.

**Figure 2.5**: Schematic diagram of X-ray diffraction and its relationship to Bragg's law [Image adapted from Sarrazin et al.]

The smaller the spacing between atomic lattice ($d$) or the larger the wavelength ($\lambda$), the larger the diffraction angle ($\theta$). The recorded intensities are plotted against the diffraction angle $2\theta$. The diffraction spectra can then be used to characterise the material, by peak position and height. The Scherrer equation describes the inversely proportional relationship between the peak width and its crystalline size, as shown in equation 2.2:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

Where $\tau$ is equal to the mean size of the crystal size, $K$ is the dimension shape factor (0.9) and $\lambda$ is the x-ray wavelength (0.154 nm). $\beta$ is known as full width at half maximum (FWHM), and is the peaks width at half maximum intensity in radians. The peaks Bragg angle is represented by $\theta$.

The ratio of crystal phases, anatase to rutile, in the TiO$_2$ samples was calculated using the following equation 2.3:

$$\text{Rutile Phase}\% = \frac{100}{1 + 0.8 \left(\frac{I_A}{I_R}\right)}$$

Where $I_A$ is the area of the anatase diffraction peak ($2\theta = 25.4^\circ$) and $I_R$ is the area of the rutile diffraction peak ($2\theta = 27.5^\circ$).
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XRD was used in this thesis to characterise the anodized photocatalyst (including effect of annealing temperature), demonstrate crystallinity and calculate crystal size. XRD spectra used in this thesis were produced by Dr Gabriele Kociok-Kohn (Department of Chemistry, University of Bath), using a Philips X-ray generator PW 1710 diffractometer, set in plate mode. Measurements were carried out between 20 values of 10° and 80°.

2.3.1.2 X-Ray Photoelectron Spectroscopy
X-ray Photoelectron spectroscopy (XPS) is a surface analytical technique which provides the chemical composition of a material by measuring the characteristic binding energy of the elements present. XPS is carried out in vacuum, and uses X-rays to provoke a photoelectric effect from a materials surface. The emitted photoelectrons, act as a fingerprint for the elements, are detected to produce a spectrum. The relationship between these variables is shown in equation 2.4:

\[ E_{\text{binding}} = h\nu - E_{\text{Kinetic}} - \phi_{\text{spec}} \]  

Where \( h\nu \) is equal to the photon energy of the X-ray beam (Joules), \( \phi_{\text{spec}} \) is equal to the spectrometer work function (eV), \( E_{\text{Kinetic}} \) is the kinetic energy measured of photoelectron by the XPS. \( E_{\text{binding}} \) represents the unique binding energy of the electron, which correlates with the elements and bonding present in the sample.

XPS in this thesis was used to identify the elemental composition of the photocatalyst samples, and determine the success of nitrogen doping of the samples. XPS spectra reported in this thesis were carried out by Dr David Morgan at Cardiff University, performed on powdered samples using a Thermo Fisher Scientific K-alpha+ spectrometer. The samples were analysed over an area of approximately 400 μm, using a micro-focused monochromatic Al x-ray source (72 W). Pass energies of 150 eV for survey scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes respectively, to record data. Charge neutralisation of the samples used both low energy electrons and argon ions. Data analysis and characterisation was performed in CasaXPS using a Shirley type background and Scofielde cross sections.
2.3.2 Microscopy

2.3.2.1 Scanning Electron Microscopy
Scanning electron microscopy (SEM) is an example of microscopy used to provide qualitative analysis of a materials surface. SEM uses a high energy- electron beam to scan the surface of a sample, schematic of SEM shown in Figure 2.6. The electron beam penetrates the sample to the depth of μm, depending on accelerating voltage and density of sample. As the electrons interact with the material, secondary and backscattered electrons are produced, as well as characteristic X-ray, which are collected to produce a micrograph. SEM uses the same fundamental theory as light microscopy, but as the wavelengths of the electrons are smaller than that of light, a higher resolution micrograph can be produce.  

SEM micrographs in this thesis was carried out to produce qualitative analysis of the oxide nanostructures produced during anodization, and the impact of photocatalyst upon them. Micrographs were obtained using a JEOL JSM64801V Scanning electron microscopy (SEM)

![Figure 2.6: Schematic figure of a scanning electron microscopy (SEM) [Image abstracted from Zhu et al.]](image_url)

2.3.2.2 Transmission Electron microscopy
Transmission electron microscope (TEM) uses a similar principle to SEM, but requires electrons to be transmitted through a sample to produce a micrograph. This provides information on the inner structure of the sample, such as morphology, crystal structure and size, whereas SEM provides detail information regarding the outer structure of the
sample. TEM micrographs and data were obtained in this thesis to provide crystal data and further characterise the material. A Jeol 2100 Plus LaB6 Transmission Electron Microscope was used. Samples were prepared by suspending the material in ethanol and sonicated for 10 minutes prior to bring dropped onto a carbon film copper grid (EMResolutions C200Cu100, 300 mush copper (100)).

2.3.3 Photocatalytic characterisation

2.3.3.1 Ultraviolet-Visible (UV-Vis) spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is used to measure the absorption (or transmission) of a material in the UV-Vis spectrum (200-800 nm). A beam of light of various wavelengths is passed through a solution, the intensity of light is measured before and after passing through the analyte solution. Light Absorbance can be described by the Beer-Lambert Law, shown in equation 2.5:

\[ A = \log_{10} \frac{I_0}{I} = \epsilon l c = -\log_{10} T \]  

Where A is absorbance (dimensionless), \(I_0\) is incident light and I is transmitted light, \(\epsilon\) is the molar absorption co-efficient (M\(^{-1}\) cm\(^{-1}\)), \(l\) is the optical path length (cm) and \(c\) represents molar concentration (M). T is transmission of the sample (%). A schematic of UV-Vis spectroscopy is shown in Figure 2.7.

![Figure 2.7: Schematic figure of UV-Vis spectroscopy [Image adapted from Sobarwiki et al.28]](Image)

The energy of a photon of light (E, in joules) can be described by the Planck-Einstein relationship (shown in equation 2.6):

\[ E = h \nu \]  

2.5

2.6
Where \( v \) is equal to the frequency of light (s\(^{-1}\)) and Planck constant \( h \) is \( 6.62 \times 10^{-34} \) J/s. The optical band gap of the semi-conductor can be determined using a Kubelka-Munk reflectance spectra.\(^{14}\) This can be produced using equation 2.7:\(^{15}\)

\[
\frac{k}{s} = \frac{(1 - R)^2}{2R} = F(R)
\]

Where \( k \) is the absorption coefficient, \( s \) is the scattering coefficient. The Kubelka-Munk reflectance spectra can then be produced, with the energy (eV) or wavelength (nm) along the x-axis, against the y-axis, \((F(r)hv)^2\). The band gap or optimum wavelength (depending on the x-axis) can then be calculated from the plots linear region.

Ultraviolet-Visible (UV-Vis) spectroscopy was used in this thesis to characterise the photocatalytic material properties (such as band gap and minimum wavelength absorption) and determine absorption of UV filter solutions. UV-Vis spectroscopy was carried out using a Cary 100 UV-Vis plot and ultrapure water was used as the reference sample.

2.3.3.2 Inductively coupled plasma mass spectrometry
Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive analytical tool able to measure trace metals up to ng/L or parts per billion (ppb) in an environmental sample. The vaporized sample is passed through a high temperature plasma source (such as Argon), which ionizes the sample atoms. The mass spectrometer then separates and order the ions according to their mass/charge (m/z) ratio, followed by an electron multiplier tube director which identifies the ions and quantifies.\(^{11}\) Ion currents are converted into electrical signals, the magnitude of the electrical signal is proportional to the number of ion present in the sample. This method is superior to that of atomic absorption spectroscopy (AAS), which is not as sensitive with a minimum detection limit of 1 \( \mu \)g/L.\(^{16}\)

In this thesis, ICP-MS was used to measure the stability of the photocatalyst in water and under UV light, by measuring the levels of photocatalyst present in the water. The ICP-MS spectra presented in this thesis was recorded by Dr J.A Milton at the University of Southampton, performed on Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Thermo Fisher Scientific X-Series II instrument in the School of Ocean and Earth Science, University of Southampton. All samples, standards and blanks were spiked with internal standard elements Be, In and Re.
2.3.3.3 High performance liquid chromatography

High performance liquid chromatography (HPLC) is a highly selectivity analytical tool used to separate, identify and quantify the molecules in a sample. A liquid mobile phase is used to transport the analyte sample through the stationary phase (column), shown in Figure 2.8. As the sample passes through the column, the sample will separate out into individual analyte bands, depending on their chemical composition, which will either be attracted or repulsed by the very porous hydrophobic stationary phase. The mobile phase will also be made up of different polarity solvents, which will aid separation of the analytes. The analytes bands are detected by UV or fluorescence, which provides each analyte band as a quantifiable peak, and if retention time is known allows for the compound to be characterised.\textsuperscript{17}

![Figure 2.8: Schematic diagram of High-performance liquid chromatography [Image adapted from Ibsen Photonics\textsuperscript{18}]]

In this thesis, HPLC was used to monitor the degradation of micropollutants, carbamazepine and phenol, as a tool to examine the photocatalytic activity of the photocatalyst synthesised. Micropollutant degradation was calculated using equation 2.8:

\[
\frac{C_t}{C_0} \times 100 = \% 
\]

Where \(C_t\) is the peak area, from the chromatogram of micropollutant, at time, \(t\) and \(C_0\) is the peak area of the initial micropollutant before the reaction (time 0 minutes). The HPLC analysis used in this thesis was performed on a HPLC-UV chromatograph (Agilent, series 1200) with a C-18 column (column Poroshell 120 EC-C18, 2.7 μm, 4.5 x 50 mm). Specific analysis conditions are provided in each chapter.
2.4 Tubular Photoreactor Design and Development

2.4.1 Photoreactor Measurements and Fluence

The photo-catalytic reactor used has a tubular structure (Figure 2.9) which increased the UV irradiation onto the catalyst surface as well as increased the mass transfer between the reaction solution and the catalyst surface, in comparison to flat reactors seen previously.\(^1\) This system allows for a zinc wire to be suspended within a quartz tube surrounded by up to three UV-C lamps, and for the pollutant to be recycled around the batch system. If voltage is applied (0.2V-1.5V using DC power supply), it is applied to the top and bottom of the wire suspension as shown in Figure 2.9b. Both ZnO and TiO\(_2\) absorb in the UV-A region, however throughout this study UV-C lamps were used. These lamps were chosen due to low cost, past experience with UV-C lamps as well as previous studies demonstrating that UV-C lamps enhanced photocatalytic degradation in comparison to UV-A lamps.\(^{19,20}\)

![Figure 2.9: The photocatalytic rig designed and developed in this thesis: a) total set up and b) close up of photoreactor](image)

1. 2019, 2020
2. ZnO, TiO\(_2\)
3. UV-A, UV-C
This reactor was developed and optimised based on a previous reactor design by Dr Anyela Ramier-Ancon. The total photoreactor length was 20 cm, with the active photoreactor space of 8 cm, 5 cm between each UV lamp, 3.5 cm between the tubular quartz tube and each UV lamp. The inner diameter of the tubular quartz tube was 0.4 cm, with an outer diameter of 0.6 cm. A 1 mm diameter poly vinyl chloride (PVC) wire was used as a model wire for use in all photolysis experiments, to maintain consistent flow dynamic conditions. The reactors were benchmarked with the model pollutant and herbicide, atrazine to determine the fluence rate of the reactor. This was calculated using equation 2.9, shown below:

\[
E_p^0(254 \text{ nm}) = \frac{k_{p,atr}}{2.303 \cdot \phi_{atr} \cdot \varepsilon_{atr,\lambda}}
\]  

Equation 2.9 was used to calculate the photon fluence rate, \(E_p^0\) (einstein m\(^{-2}\) s\(^{-1}\)), \(k_{p,atr}\) represents the pseudo first order rate constant of Atrazine (s\(^{-1}\)), \(\phi_{atr}\) is equal to the quantum yield of atrazine depletion (0.046 mol einstein\(^{-1}\)) and \(\varepsilon_{atr,\lambda}\) is the molar absorption coefficient of atrazine at the wavelength \(\lambda\) (3860 m\(^2\) mol\(^{-1}\)). This measures the efficiency of the photoreactor and allows for different systems to be compared. The quantum yield is the ratio of photons absorbed to photons emitted via fluorescence. This found a \(k\) value of 0.027 s\(^{-1}\) and a fluence rate of 6.60 \(\times\) 10\(^{-5}\) Einstein m\(^{-2}\) s\(^{-1}\).

Conditions were kept constant for all photocatalytic experiments unless otherwise stated: pollutant chilled to 10 °C, flow rate: 250 mL/min, 80 to 100 mL of 10 μM of phenol and carbamazepine reaction solution respectively. If voltage was applied, it was kept constant at 0.2 V/0.9 Amps. The system was washed through with 250 mL of DI water after each experiment. Micropollutant degradation was monitored using HPLC (section 2.3.4.3).

### 2.4.2 Atrazine preparation and detection conditions

Atrazine is well known herbicide, which is used in this study to benchmark the photocatalytic ability of the reactor, known as the fluence rate. There are a few different classic actinometres\(^{22}\) that could be used in this study, including potassium iodide (KI)\(^{23}\) and ferrioxalate.\(^{24}\) Atrazine was used in this study for three reasons; it has a well-defined quantum yield and has been shown to be successfully used for energy calculations for UV-based treatment systems\(^{21,25}\). Also as a pesticide, Atrazine is structurally similar to other micropollutants.\(^{26}\) Therefore, it can be also used at the same concentrations in ‘optically’ thin solutions (>98% transmittance), while some of the classic actinometries
may create stronger absorbance and require calculating a correction factor for application in diluted solutions where target compounds occur at μM concentrations or below. Finally, Atrazine can be detected and measured using HPLC, which is the analytical used throughout this study to measure a suite of other compounds.

To prepare a 1 mM stock solution of atrazine, 0.053 g was dissolved in 250 mL in DI water. To aid dissolving, the solution was stirred for seven days, and sonicated twice a day. This was filtered using a nylon membrane, and produced a 173.5 μM solution. This was detected using HPLC. A calibration curve was produced from 5-200 μM, using methanol as an aid to dissolve atrazine at higher concentrations.

A 10 μM solution was prepared by diluting 5.76 mL of the stock solution into 100 mL DI water. This solution was used in the photoreactor, and degradation monitored over three hours to benchmark the system. A sample was taken every 15 minutes for the first hour, and there after every 30 minutes. The HPLC conditions used were 50% MeCN and 50% DI water, with a retention time of 7 minutes, flow rate of 1 mL/min and UV detection at 235 nm.
2.5 References


2.4 Tubular Photoreactor Design and Development

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Chapter 3

Immobilised ZnO nanowire photocatalyst

The work presented in this chapter has been published to Journal of Hazardous Material in June 2019.

3.1 Context

Previous work has demonstrated that flat film ZnO nanostructures and their photocatalytic activity could be tailored using anodization parameters such as pH, voltage, time and electrolyte composition. Preliminary results found that a ZnO wire could serve as an alternative to the well-researched flat films, as they offer the benefits of less material waste and increased surface area coverage, thus increasing the efficiency of the material. This chapter investigates and compares the differences between ZnO films and wires, including nanostructures and quantum efficiencies. Photocatalytic activity was determined by monitoring the degradation of the model pollutant, phenol. As discussed in section 1.5.6, ZnO is unstable in water and prone to photocorrosion, thus methods for increasing the stability of the ZnO layer in both film and wire systems have been developed. This work highlights how photo-corrosion of the ZnO nanowire immobilised photocatalyst can be enhanced by manipulating material synthesis, reaction conditions and reactor design. Section 3.2 sets out the experiments required to meet the aims, section 3.3 is the published manuscript and 3.4 is the supporting information for the manuscript. Section 3.5 is additional commentary and unpublished data regarding the ZnO wire photocatalytic activity and reactor, with section 3.6 providing chapter conclusions and further work.

This chapter is presented in an alternative format in accordance with Appendix 6A of the “Specifications for Higher Degree Theses and Portfolios” as required by the University of Bath. The research presented in this chapter was produced by the author with the exception of the following:

The ZnO flat film development, anodization and photocatalytic investigation (including Fig.5) were carried out entirely by Dr Anyela Ramirez-Canon, co-author on the published manuscript.

Research supervised by Dr Jannis Wenk and Professor Davide Mattia.
3.2 Experimental Aims

The following experiments formed the foundation of this chapter regarding the ZnO wire photocatalyst, to meet the aims and objectives:

- Develop anodization conditions suitable for a Zn wire, rather than a film. Determine the importance of synthesis parameters such as preparation steps (pre- and post-annealing) and anodization time upon photocatalytic activity.
- Determine key reaction parameters upon photocatalytic behaviour, such as flow rate or the addition of electricity to the metal core of the wire.
- Determine the reusability of the ZnO photocatalysis over multiple experiments, and the reproducibility of the photocatalyst activity and nanostructures.
- Investigate and enhance the stability of the ZnO photocatalyst wire, by measuring catalyst leaching into reaction solution via ICP-MS.
- Examine and compare the efficiency of the systems, flat film and tubular wire, including the quantum efficiency

References

3.3 Published Manuscript

Enhancing the Photo-corrosion Resistance of ZnO Nanowire Photocatalysts

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GRAPHICAL ABSTRACT
Post-treatment annealing and oxygen-saturated environments enhance the photo-corrosion resistance of ZnO nanowire films in batch and continuous flow reactors.

ABSTRACT
Zinc oxide (ZnO) displays superior properties as a photocatalyst, compared to the more widely used TiO₂. However, widespread application of ZnO is hampered by its high photo-corrosion in aqueous environments under UV irradiation. A systematic investigation of the effect of (i) post-production annealing, (ii) dissolved oxygen levels during photocatalysis and (iii) reactor configuration on the stability and photocatalytic activity (PCA) of ZnO nanowires, grown on either flat or circular supports, was
conducted. Results show, for the first time, that it is possible to significantly enhance the photo-corrosion resistance of ZnO in water under UV irradiation while also increasing PCA. Oxygen plasma post-annealing of ZnO nanowire films led to a 46% higher photocatalytic degradation of phenol compared to as-produced films. In oxygen-saturated solutions, both thermally and oxygen plasma annealed ZnO revealed similar photo-corrosion resistance. Switching from a batch to a flow-through reactor, tripled phenol photodegradation under the same irradiation conditions from 19 to 57% due to enhanced mass transfer, while significantly increasing the stability and re-usability of the ZnO, with 5 repeat uses over 3 days showing no decrease in PCA. These results pave the way to more widespread use of photo-corrosion resistant ZnO in the degradation of organic pollutants in water.

Keywords: zinc oxide; photocatalysis; flow reactor; photo-corrosion; phenol; anodization

Introduction

Zinc oxide (ZnO) is an attractive material for photocatalytic applications due to a combination of high excitonic stability, a direct band gap of 3.2 eV, high electron mobility, good transparency and strong luminescence at room temperature [1]. As such, ZnO has been used in a wide range of applications from water treatment [2, 3] to solar cells [4-6]. Under UV irradiation, ZnO has been successfully used to degrade organic pollutants including aromatic [7] and phenolic compounds [8], and dyes [9], in many cases outperforming TiO$_2$ [10]. Furthermore, ZnO can absorb visible light over a wider range of the solar spectrum compared to TiO$_2$ [11], resulting in the full degradation of multiple organic compounds under visible light [12,13]. Despite these superior properties, the use of ZnO in wastewater treatment is severely limited by its instability in water, attributed either to the formation of Zn(OH)$_2$ in aqueous solutions [14], or to changes in morphology from the use of its molecular oxygen during photocatalysis[15]. Furthermore, due to its amphoteric properties, ZnO can be dissolved in both acidic (forming metal cations) and in alkaline solutions (forming oxyanions of Zn such as zincates) [16]. Environmental factors such as UV irradiation, pH of the solution, dissolved oxygen level and material properties, such as morphology and stability, have a significant effect on the stability of ZnO during photocatalysis. UV light accelerates the dissolution of ZnO in aqueous environments [17], due to the residual photo-generated holes on the
Chapter 3: Immobilised ZnO nanowire photocatalyst

ZnO surface that are able to attack the Zn-O bond, dissociating Zn$^{2+}$ as summarized in Eq. 1a-c [16]:

- **photocatalysis:** \( \text{ZnO(s)} + \text{hv} \rightarrow \text{ZnO(s)} + \text{h}^+ + \text{e}^- \) (Eq. 1a)
- **re-combination:** \( \text{h}^+ + \text{e}^- \rightarrow \text{hv} \) (Eq. 1b)
- **photo-dissolution:** \( \text{ZnO(s)} + 2\text{h}^+ \rightarrow \text{Zn(aq.)}^{2+} + \frac{1}{2}\text{O}_2 \) (Eq. 1c)

Higher intensities of incident light produce higher ZnO dissolution rates, due to the relationship between the number of electron-holes and the number of photons that reach the ZnO surface which, in turn, is proportional to the light intensity [16]. The photocorrosion of ZnO thin films is strongly dependent on pH, with minimum dissolution around pH = 10 and maxima at both very high and very low pH values [16]. Dissolved oxygen levels also play an important role in the photocorrosion of ZnO, since in oxygen-poor conditions, progress of the photocatalytic reaction drives molecular oxygen out of the ZnO catalyst, leading to structural erosion [18]. An oxygen-rich environment, on the other hand, preserve the original ZnO catalyst structure at the nanoscale [15].

The development of different methods for fabrication of ZnO nanostructures, including chemical vapour deposition [19], epitaxial growth [20], and electrochemical methods [9, 21, 22], has opened the possibility of improving the photo-response and stability of ZnO by controlling the material’s physicochemical properties via structuring at the nanoscale [23]. For instance, it has been shown that the dissolution rate of ZnO is dependent on its particle size [24]. For ZnO nanostructured films, it has been reported that the photocorrosion of ZnO layers immersed in a 3.5% NaCl solution and exposed to white light (130 mW/cm$^2$) decreased as the oxide thickness increased [14]. Modification of the ZnO lattice by doping with a range of elements such as C [25], Fe [26], Nd [27], Co [28], Cu [29], and Al [30], also improved the photocatalytic activity of zinc oxide nanostructures, albeit without any significant increase in stability. Post-treatment processes, such as thermal or surface plasma treatments have also been used to improve specific properties of ZnO but not its resistance to photo-corrosion. For example, thermal annealing at 400 °C in inert and oxygenated environments led to increased optical transparency as well as increases in electrical resistivity [31]. Similarly, it was shown that annealing (30 minutes, 250 °C) of ZnO nanowire arrays, produced via anodization of zinc foil using aqueous potassium bicarbonate (KHCO$_3$(aq)) electrolytes, could change their reflectance spectra.
3.3 Published Manuscript

in UV and visible light [32]. Annealing of anodized ZnO nanowire arrays (also at 250 °C) showed a 10-fold increase in photo-response across the visible range\(^1\) [33]. Hydrogen plasma was used to enhance the thermal stability of ZnO thin films [34], and the photo-response of Al-doped ZnO nanorod arrays [35]. Oxygen plasma was also used to improve optical detection properties of thin ZnO epitaxial films [36, 37], and the wetting behaviour of ZnO nanorod arrays [38], as well as the electrical and optical properties of Ga-doped ZnO thin films [39].

Although these studies have improved the understanding of the material and process factors affecting ZnO photo-corrosion stability, no studies, to the authors’ knowledge, have focused on improving the photo-corrosion resistance of the ZnO nanostructures themselves.

In the present work, the effect of (i) post-production annealing conditions (thermal and plasma), (ii) dissolved oxygen levels during photocatalysis (atmospheric and saturated) and (iii) reactor configuration (batch or flow) on the stability and photocatalytic activity of ZnO nanowire films has been investigated.

Materials and Methods

**ZnO nanowire film fabrication**

ZnO nanowire films were produced via the electrochemical anodization of zinc foil and zinc wire to obtain ZnO-F and ZnO-W nanowire structures, respectively.

**Fabrication of ZnO-F:** High purity zinc foil (99.98%, 0.25 mm thickness, Alfa Aesar) was pre-annealed in air at 300 °C (CWF1100, Carbolite) for one hour at 1 °C/min, followed by cleaning with acetone (HPLC grade, 99.5+%, Fisher) in an ultrasonic bath for 10 minutes. Anodization was performed in a 2-electrode cell with 8 mm spacing, using the zinc foil as the anode and stainless steel (SS316 grade) as the cathode. ZnO nanostructured films were obtained with KHCO\(_3\) [0.01M] as electrolyte applying 1 V provided by a DC power supply (Agilent E3634A) for 1 hour. The temperature of the electrolyte was kept constant throughout anodization at 10 °C using a water-cooled bath

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\(^1\) Correction; should state across the “UV-visible range”
(Thermo Scientific HAAKEC 10-K10, DC10-K20 or DC50-K35). After anodization, the samples were thoroughly rinsed with ethanol and deionized water and left to dry at room temperature. Details about the relationship between anodization process parameters and the morphology of the ZnO nanostructures produced can be found elsewhere [21, 22].

Fabrication of ZnO-W: ZnO nanowire-coated zinc wires were prepared by adapting the above method to a bespoke wire anodization setup (Fig. S1): Zinc (Zn) wires (Goodfells ZN005131, diameter = 1 mm, purity = 99.9%) were cut to 35 cm length, and manually cleaned with acetone and ethanol to remove oil and grease. No electropolishing was performed. The anodization was conducted using an annular electrode system, with the zinc wire as the anode within a steel cathode tube connected directly to a DC power supply (1.5V). Potassium bicarbonate (KHCO₃, 0.05M) in ultrapure water was circulated as the electrolyte. The temperature of the electrolyte was kept constant at 8 °C during anodization using a water-glycerol cooling system (Agilent). The anodization times ranged from 5-15 minutes at 5-minute intervals, and 30-60 minutes at 15 minute intervals.

Post-annealing
Both ZnO-F and ZnO-W films were exposed to thermal annealing at temperatures ranging from 200 to 350 °C and for 1 to 72 hours in air with a 1 °C/min ramp. Films annealed with oxygen plasma were placed for 20 minutes in the chamber of a Diener plasma generator with a power of 50 W, oxygen flow rate of 50 mL/h at 2 bar and at room temperature. Subsequently, the annealed films were stored in darkness in a desiccator cabinet until use.

ZnO nanowire film characterisation
The surface morphology of the ZnO nanowire films was studied using a JEOL 6301F field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDX, Oxford, ONCA x-ray analyser, Oxfordshire, UK). The films’ crystal structure was investigated using an X-ray diffractometer (Philips Xray generator – PW 1710; flat plate mode; 20 values from 0° to 100°) and a transmitted electronic microscopy (Philips CM200 FEGTEM Field emission gun TEM/STEM) fitted with a supertwin Objective lens, cryo-shielding (Oxford Instruments) and UTW EDX
detector running ISIS software and Gatan GIF200 Imaging Filter for EELS/EFTEM. Composition analysis was carried out through X-Ray Photoelectron Spectroscopy (XPS - GV Escalab 250) equipped with a high intensity monochromated Al Kα source, focused to a spot 120-600 μm in diameter on the sample surface.

**Photocatalytic experiments**

Phenol was selected as a model compound to measure the photocatalytic activity (PCA) of ZnO due to its well-characterized photodegradation pathway [40]. PCA reactions were studied in unbuffered ultrapure water (18.2 MΩ·cm, PURELAB®, ELGA LabWater) at 50 or 80 mL volume of solution with phenol (5 or 10 ppm) at 10 ± 1 °C in a batch recirculating reactor, consisting of a jacketed vessel of 100 mL (reservoir) with a magnetic stirrer (1000 rpm) where temperature was controlled using a water-cooled bath (Thermo Scientific), under two distinct configurations (Fig.1a):

**Configuration I for ZnO-F:** The ZnO-F film was placed inside the vessel on an open superstructure above the stir bar. UV light was provided from the top at a fixed distance of 3 cm between the solution and the UV-lamp (UVG-54 Handheld UV lamp, 254 nm, 6W) with an intensity of light of 0.90 ± 0.01 mW/cm², measured using a UV light meter (HHUV254SD – OMEGA engineering).

**Configuration II for ZnO-W:** PCA experiments were carried out using an in-house designed flow-through reactor (Fig.1b) consisting of three UV lamps (UVH101, Pisces, 254 nm, 5W) evenly spaced at a distance of 5 cm around a central quartz glass tube (OD = 5 mm, ID = 4 mm, light intensity 11.95 ± 0.01 mW/cm²) containing the ZnO-coated zinc wire and the recirculating model contaminant solution. The recirculating flow rate was varied between 100 mL and 570 mL min⁻¹.

In a previous publication [40], the batch reactor was optimized to ensure that (i) the stirring speed was sufficiently high to ensure that data was collected in the kinetic regime, with no influence on photocatalytic degradation arising from mass transfer limitations; (ii) the effect of photolysis was less than 5% of the total degradation of phenol [41]; and (iii) although complete mineralization of the phenol required up to 12 hours, recording of the changes occurring in the first 4 hours was sufficient to establish a clear relation.
between changes in material properties and their effect on the films’ photocatalytic degradation activity [40].

Photocatalytic experiments were performed either in unsaturated DO conditions, obtained by natural absorption of oxygen from the environment in the open batch reactor or in saturated oxygen, obtained by saturating the reaction solution with oxygen (100 mL/min) for 20 minutes before, and continuing during the experiment. Before and after each experiment, the reactor system was rinsed with 250 mL pure water.

**Fig. 1.** a) Schematic of the two-configuration reactor used to test the photocatalytic activity of both ZnO-F (configuration I) and ZnO-W (configuration II) nanowires. Differences in light emission intensity have been calculated for each reactor to compare results. b) Photograph of the configuration II reactor.

**Analysis**

To determine phenol degradation, samples of 1 mL were withdrawn during irradiation at different times and then filtered using a PVDF Millex-VV Syringe Filter Unit (pore size: 0.1 μm, diameter: 33 mm). The samples were sufficiently small avoid any significant changes in the phenol concentration, ensuring reproducibility. Changes in concentration of phenol and its products were measured by HPLC using either Shimadzu SCL-10A or Agilent 1200 machines equipped with 150 mm x 2.0 mm, (Thermo, Germany) and 50 mm x 4.6 mm (Poroshell 120, 2.7 μm, Nacalai Tesque, Japan) reverse phase C18 columns,
respectively. The full degradation pathway of phenol using ZnO nanowires was studied in a previous publication [40].

Isocratic mobile phase conditions were 20-25% acetonitrile and 75-80% water with 5 mM phosphoric acid (pH 2) at flow rate of 0.5-1.0 mL/min. UV detection was set to 220 nm [42]. Additional measurements such as pH, conductivity and dissolved oxygen (DO) were conducted using a bench top multi-parameter meter (Versa-Star®). Measurements of dissolved zinc were carried out by atomic absorption spectroscopy (Perkin Elmer Analyst 100) using air-acetylene with a flow of 7-10 mL/min, and by ICP-MS (Thermo Fisher Scientific ELEMENT 2XR), with 1 mL samples prepared using 0.25 mL reaction solution and 0.75 mL of Ultrapure water, then diluted to 6.25 mL and spiked 3% HNO₃ (a factor of 6.25).

To enable comparison between the two irradiation systems, PCA results were normalised to account for the different light intensity. This was considered by presenting degradation data as a function of UV dose (mJ/cm²), rather than reaction time. UV dose was calculated by multiplying the time the solution was exposed to UV light by the effective light intensity of the system [43]. In the case of configuration I, this required subtracting the intensity of light absorbed by the medium. For configuration II, absorption by the medium was negligible due to the thin liquid layer surrounding the ZnO=W; however, due to the continuous nature of this configuration, the results had to be normalised by the fraction of solution volume receiving the dose at any given time. Details of the calculations are provided in Table S1.

**Results and Discussion**

Anodization using KHCO₃ electrolytes produced nanowire structures, in agreement with literature results [32]. In previous publications, the authors have shown (i) how anodization process parameters (voltage, electrolyte type and concentration, temperature and time) determine the films’ morphology [21, 22]; and (ii) how this then affects the photocatalytic activity of the nanowire films, by determining crystal structure, nanowire shape and light absorbance [40]. The formation of the nanowire structures is the result of competition between the formation of Zn ion complexes (Zn²⁺) that oxidise into ZnO, and
an etching process that dissolves the formed ZnO layer [21]. Some of the Zn(II) soluble species produced during the dissolution of Zn and ZnO can react with dissociated ions from the electrolyte (i.e. HCO$_3^-$) to form salt or Zn complexes. Some of these ions are deposited on the surface while others are attracted to the electrodes and incorporated into the newly formed layers of ZnO. The latter phenomenon has been observed during the formation of alumina via anodization [44].

XPS analysis showed that the main components of the as-produced films were Zn (34%) and O (55%), with traces of other compounds (C and Fe). The carbon atoms are likely the result of incorporation into the nanowire structure of electrolyte ions, well documented in the case of anodic alumina nanostructures [45], while the iron is attributed to post-synthesis contamination of the samples used for analysis.

XRD analysis of the as-produced ZnO nanowire structures showed they contained some wurtzite-type crystals (Fig. 2). Annealing at temperatures ranging from 200 to 350 °C for 1h showed a progressive increase in ZnO peaks with no further change observed beyond 350 °C. Longer annealing times at 350 °C (up to 24h) showed marginal increases in the ZnO peaks, while further annealing up to 72h produced no further change in XRD patterns (not shown). For thermal treatment, the increase in the intensity of the ZnO (100), (002) and (101) peaks revealed that the material became more crystalline after treatment; additionally, the peaks become broader indicating an increase in the grain size [46, 47]. An overlap of the (101) ZnO peak with the (002) Zn peak occurred, limiting the analysis of the preferential orientation of the crystallites. These results agree with other studies on ZnO produced via anodization [31, 48, 49]. For the plasma annealed films, changes in crystallinity were less pronounced: although ZnO peaks increased and became broader, the intensity of the ZnO (100) and (002) peaks was lower compared to the thermally annealed samples, indicating a preferential orientation on the (101) peak.
Fig. 2. XRD spectra for as-produced, thermally and plasma annealed ZnO-NFs. Key: ♦ ZnO (100); ■ ZnO (002); ● ZnO (101); □ ZnO (102); ★ ZnO (110); ○ ZnO (103); ✕ ZnO (112); unlabelled peaks belong to the Zn metal substrate, with the exception of the small peak at $2\theta = 13$ deg, for which an attribution could not be found.
FESEM analysis for the as-produced, thermally and plasma annealed samples revealed that neither post-treatment affects the films’ morphology prior to photocatalytic testing (Fig. 3a-c).

However, TEM analysis revealed significant changes in the morphology of individual nanowires resulting from the two annealing treatments (Fig. 3d-f). As-produced films (Fig. 3d) had a smooth surface with no individual crystallites observed. In thermally annealed ZnO, increases in crystallinity were observed in the TEM micrographs (Fig. 3e), with the formation of slit-type porosity, as reported elsewhere for thermally annealed ZnO nanowires produced with an ammonium carbonate, rather than potassium carbonate, as used here [22].

On the other hand, nanowires exposed to oxygen plasma (Fig. 3f) did not display any porosity on the surface, but rather showed an increase in surface roughness.

The changes produced in the ZnO-F by the thermal and plasma annealing processes resulted in an increase in the photocatalytic degradation of phenol of 33% and 46%, respectively, compared to the as-produced samples (Fig. 4). A significant change in the morphology of the as-produced and thermally annealed samples was observed after 4 hours of photocatalytic phenol degradation in the batch re-circulating reactor (Fig. 1, configuration I), with the initial nanowire morphology changing to a flake-like appearance (cfr. Fig. 3a vs. 3g and Fig. 3b vs. 3h, respectively). In contrast, the plasma annealed samples retained the nanowire morphology (cfr. Fig. 3c vs Fig. 3i), with some secondary nanostructure growth observed. These morphological differences agree with the value of dissolved zinc in the solution after 4 hours, with the as-produced film having the highest value and the plasma annealed film the lowest (Table 1).

### Table 1

Physico-chemical and kinetic parameters after 4h photocatalytic degradation of phenol: change in conductivity (\( \frac{\sigma - \sigma_0}{\sigma_0} \)) and dissolved zinc [Zn], first order reaction rate constant (k) and final degradation (C/C_0).

<table>
<thead>
<tr>
<th></th>
<th>( \frac{\sigma - \sigma_0}{\sigma_0} )</th>
<th>[Zn] (ppm)</th>
<th>k (h(^{-1}))</th>
<th>C/C_0</th>
<th>SEM</th>
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<tbody>
<tr>
<td>as-produced</td>
<td>4.5</td>
<td>5.4</td>
<td>0.10</td>
<td>0.24</td>
<td>g</td>
</tr>
<tr>
<td>thermally annealed</td>
<td>5.3</td>
<td>5.2</td>
<td>0.25</td>
<td>0.57</td>
<td>h</td>
</tr>
<tr>
<td>plasma annealed</td>
<td>6.7</td>
<td>3.8</td>
<td>0.31</td>
<td>0.70</td>
<td>i</td>
</tr>
</tbody>
</table>
As the photocatalytic reaction progresses, and depending on the pH of the solution, ZnO is dissolved into the electrolyte forming $\text{Zn}^{2+}$, $\text{Zn(OH)}_3^-$ or soluble $\text{Zn(OH)}_2$. Herein, the pH of the phenol solution was in the range of 6.2 to 6.5, indicating that the predominant chemical species in solution was $\text{Zn}^{2+}$. According to the thermodynamic speciation of zinc (Fig. S2) [50], increases in the concentration of this ion causes the formation of insoluble $\text{Zn(OH)}_2(s)$ which precipitates resulting in the formation of new nanostructures (cfr. Fig. 3g).

![Fig. 3. SEM and TEM micrographs](image)

**Fig. 3.** SEM and TEM micrographs of (a, d) as-produced, (b, e) thermally annealed and (c, f) plasma annealed ZnO-FF before photocatalytic tests; SEM micrographs of (g) as-produced, (h) thermally annealed and (i) plasma annealed ZnO-FF after photocatalytic degradation of phenol for 4 hours.
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The reduction in the dissolved Zn for the plasma annealed sample indicates less photocorrosion of ZnO and therefore higher stability of the material that was expressed in a higher stability of the nanostructures. As such, the increase in the relative conductivity of the thermal and plasma annealed ZnO nanowire compared to the as-produced equivalent can be attributed to the enhancement of photocatalysis and thus higher production of phenol degradation products and CO$_2$ [40]. Oxygen plasma is also known to vary the hydrophobicity of the material [51], and suppresses the presence of chemisorption sites (oxygen deficiency sites) and oxygen vacancies [36], which can contribute to improving the photocatalytic activity of ZnO.

![Fig. 4](image)

**Fig. 4.** Photocatalytic degradation of phenol using as-produced (■), thermally annealed (○ – 30 min; △ - 1h; □ - 18h; ◊ - 72h) and plasma (♦) annealed ZnO-NFs.; error is below 5% for all data points.

**Zn/ZnO wire catalyst reactor system**

To test the ZnO nanowires in a flow configuration, a zinc wire rather than a flat film was used as a substrate on which to grow the nanowires. The non-planar geometry of the zinc wire substrate, however, introduced curvature-induced radial tension in the ZnO-W samples, which required some changes to the anodization procedure with respect to the flat ZnO-F photocatalysts. In particular, it was observed that the pre-anodization electropolishing treatment step led to significant embrittlement of the ZnO/Zn wire structures, making them unusable. Therefore, electropolishing was forgone, with the rest...
of the procedure remaining the same as for the flat-film samples. It is hypothesised here that this difference is due to the different morphology resulting from the wire forming process as opposed to the flat film [52]. The result, after post-anodization annealing, was the formation of a robust and uniform ZnO layer on the Zn wire (Fig. 5) that could be used under flow conditions (Fig. 1) without any measurable loss of oxide material.

![Fig. 5. SEM micrograph of a ZnO nanowire layer grown on Zn wire (ZnO-W).](image)

The shape change had a significant effect on the photocatalytic activity of the ZnO-W, with the samples reaching similar degradation (~60%) in 1 hour (Fig. 6) rather than 4 h as for the ZnO-F catalysts (Fig. 4). The difference is even larger when one considers the UV dose received by the samples in the two reactor configurations (Table 2): if one compares the ZnO-F and ZnO-W both thermally annealed for 1h, after 1 hour of photocatalysis, the former has received a 40% higher UV dose while producing a phenol degradation that is 38% lower. Alternatively, for the same UV dose (2276 mJ/cm²), the ZnO-W showed a 46% higher degradation than the ZnO-F (C/C₀ = 0.43 and 0.81, respectively).
Table 2
Phenol degradation and UV dose for ZnO-F and ZnO-W after 1h of photocatalytic degradation.

<table>
<thead>
<tr>
<th></th>
<th>ZnO-F, annealed</th>
<th>ZnO-W, annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>thermal plasma</td>
<td>Zn wire thermal</td>
</tr>
<tr>
<td></td>
<td>atm. O₂ sat</td>
<td>atm. O₂ sat</td>
</tr>
<tr>
<td>UV dose [mJ/cm²]</td>
<td>3192</td>
<td>2276</td>
</tr>
<tr>
<td>C/C₀</td>
<td>0.81 0.88</td>
<td>0.75 0.59 0.43 0.35 N/A</td>
</tr>
</tbody>
</table>

Details of the calculations of the UV dose for all samples in Fig. 4 and Fig. 6 can be found in Table S1. Data for the UV dose and phenol degradation in Fig. 4 and Fig. 6 can be found in Tables S2 and S3, respectively. Fig. S3 directly compares the data from the two reactor configurations.

**Fig. 6.** Degradation of phenol in flow reactor by photolysis (■), photocatalytic degradation by; untreated Zn wire (□), ZnO-W in air (♦) and O₂-saturated atmosphere (◊); error is below 5% for all data points. Inset shows the first order reaction kinetics as a function of the flow rate (Reynolds number).
For the ZnO-W reactor configuration, significant degradation was also observed for the bare Zn wire. As previously discussed, electropolishing was forgone for this geometry, leaving a native and photoactive oxide layer on the surface of the wire. In addition, the cylindrical geometry of the wires prevented the ZnO-W from being subjected to a uniform and consistent plasma annealing process, thus no data can be reported here.

**Fig. 7.** SEM micrographs of ZnO nanowire layer on Zn wire (ZnO-W) (a) before photocatalysis and after photocatalysis under (b) atmospheric and (c) saturated oxygen environments.

The difference in performance between the two reactors can be convincingly attributed to hydrodynamic effects in the flow reactor [53]. In fact, changing the flow rate of the phenol solution significantly affected degradation, with an optimum at 250 mL/min (Fig. 6 inset). For the lower flow rates, increasing the flow rate increased the reaction kinetics, clearly showing that the process is in mass transfer-limited regime. This is a well-known effect, with the diffusion through the boundary layer at the liquid-catalyst interface limiting the rate of degradation [53]. As the flow rate increases, the laminar boundary layer thickness will decrease, thereby increasing the rate of mass transfer. A similar effect has been observed for the photocatalytic degradation of azo dyes using TiO₂ slurries [54]. At higher flow rates, when diffusion is no longer the limiting factor, adsorption of phenol on ZnO becomes the rate limiting step, with reaction kinetics becoming independent of flow rate (Fig. 6 inset). Comparable behaviour has been observed and fully modelled for phenol degradation in immobilised titania flow reactors [53]. Values well in excess of unity for the Peclet number (the ratio of convective to diffusional mass transfer), and a doubling of the Sherwood number (the ratio of convective mass transfer to the rate of diffusive mass transport) from 57 to 128, further support this analysis. All values and calculations are reported in Table S4 in the SI.
In Fig. 6, the effect of saturating the pollutant solution with oxygen is also shown. This results in increased degradation, from \( C/C_0 = 0.43 \) for the sample in air to 0.35 for the one under \( O_2 \) saturation. This can be attributed to an increased formation of superoxide radicals present in solution [18]. A similar effect was observed for the ZnO-F configuration (Table 2).

As already observed for the ZnO-F, the structure of the ZnO-W changed significantly during the photocatalytic experiments, with dissolution of the initial ZnO-W structures and re-deposition of nanosized super-structures onto the underlying nanowire surface when photocatalytic experiments were conducted under atmospheric conditions (cfr. Fig. 7a and 7b). The secondary nanostructures observed are similar to those observed for the ZnO-F (cfr. Fig. 5 and Fig. 3a-b). However, under an oxygen-saturated environment, structural changes were significantly smaller (cfr. Fig. 7a and 7c). This difference in behaviour is attributed to a reduced dissolution of the zinc into the solution as a consequence of photocorrosion [18]. This interpretation is confirmed by the concentration of Zn in the solution after the photocatalytic flow reaction for 1 hour which is \(~1 \text{ ppm}\) for the ZnO-W under atmospheric conditions and \(~0.1 \text{ ppm}\) for the oxygen saturated experiment. Both values are significantly lower than those observed for ZnO-F in the batch system (Table 1). It is noted here that while the Zn concentration value under atmospheric conditions is one order of magnitude higher than the one obtained under oxygen-saturated environment, it is well below the 3 mg/L threshold recommended by the WHO, above which water assumes an unpleasant taste, greasy feel and opalescent colour [55].
Stability and reusability of the ZnO-W photocatalysts in flow

The re-usability of the ZnO-W wires was investigated by using the same sample over a period of three days and monitoring the photocatalytic degradation over five different irradiation cycles. The ZnO wire displayed very low dissolution of ZnO into the water, with maximum values over an hour period of 1 ppm. It was found that the ZnO-W was reusable, with no significant reduction in photocatalytic activity (Fig. 8). This level of performance is comparable to that observed for ZnO nanowires produced via hydrothermal synthesis [49]. The result in Fig. 8 is particularly promising, as both air and light have been known to deteriorate the oxide layer, leading to a reduction in photocatalytic effectiveness [56].

Fig. 8. Stability and reusability of the thermally annealed (1h) ZnO-W after five repeat uses over three days. The first reading was repeated five times with an error of less than 5%, and the following readings were taken once.

In fact, while surface area can be directly linked to photocatalytic activity in particle slurries [57], this is not the case for immobilized photocatalysts: in a previous publication, the authors have shown that photocatalytic activity can be quantitatively correlated to the light absorbance and crystal structure of the individual ZnO nanostructures, but not to their overall surface area or thickness, as one would normally expect for slurries of photocatalytic nanoparticles [40]. The present results appear to qualitatively support this
view: while the super-structures might in fact be changing the thickness of the films and their surface area, they appear to not be blocking access to the underlying structure (Fig. 7b), thereby having a limited effect on light absorbance.

Conclusions
The effect of (i) post-treatment annealing, (ii) oxygen level and (iii) reactor configuration of ZnO nanowire films on photocatalytic activity was studied for the photocatalytic degradation of phenol. ZnO undergoes significant morphological changes during the photocatalytic reaction, with dissolution of zinc into the aqueous solution and concurrent reprecipitation of novel ZnO and Zn(OH)$_2$ nanostructures onto the original ZnO structure. The photocatalytic activity and stability of the films were enhanced by the thermal and oxygen plasma treatments. Switching from a flat film (batch reactor configuration) to a wire (tubular flow reactor) significantly enhanced the photocatalytic activity of the films. This is attributed to improved mass transfer for the same UV dose received by films, with a phenol degradation of 57%, compared to only 19% after 1 hour of exposure, for thermally annealed films. Oxygen plasma treatment and a saturated O$_2$ environment further enhanced the stability and resistance of the films. Finally, the ZnO-W films in the tubular flow reactor showed remarkable stability, with no loss in photocatalytic activity after 5 consecutive uses over 3 days. These results show that the combination of novel ZnO nanowire structures grown by anodization on zinc wires and a tubular flow reactor have high activity and can be an effective configuration for the degradation of pollutants in water.

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All data used in this manuscript is available from https://doi.org/10.15125/BATH-00675
References


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3.4 Supporting information for “Enhancing the photo-corrosion resistance of ZnO nanowire photocatalysts”

![Diagram](image)

**Figure S1** Anodization rig (Annular electrode system)

![Graph](image)

**Figure S2** Speciation of zinc as a function of pH at fixed zinc concentration of $1 \times 10^{-3}$ M (top) and as a function of zinc concentration at 25 °C showing only the dominant species (bottom) [1]
Table S1. UV dose calculations for the two reactor configurations

$I_{0\lambda}$ = incident light intensity [mW/cm$^2$] = 0.9

$I_{\alpha\lambda}$ = intensity of light absorbed by the medium [mW/cm$^2$]

**UV dose for reactor configuration I:**

UV dose = irradiation time (s) * ($I_{0\lambda}$ - $I_{\alpha\lambda}$) [mJ/cm$^2$]

\[
I_{\alpha\lambda} = I_{0\lambda} \left(1 - 10^{\left(\varepsilon_{H_2O}[H_2O] + \varepsilon_{phenol}[phenol]\right) L}\right)
\]

where:

$I_{0\lambda}$ = incident light intensity [mW/cm$^2$] = 0.9

$\varepsilon_{H_2O}$ = Molar absorptivity [M$^{-1}$ cm$^{-1}$] = $1.44 \times 10^{-8}$

$[H_2O] = [M] = 55.345$

$\varepsilon_{phenol}$ = [M$^{-1}$ cm$^{-1}$] = 326.1099

$[phenol] = [M] = 0.00001$

$L = \text{Path length [cm]} = 2$

The value is then integrated over the distance of 0 – 2 cm to achieve the total intensity of light absorbed by the medium, $I_{0\lambda}$ = 0.01345 mW/cm$^2$

Equation obtained from Leifer$^1$

**UV dose for reactor configuration II:**

As a flow-through system, the entire volume solution does not receive the entire UV dose at any one time (as is done in the UV reactor I). To calculate the UV dose:

UV dose = irradiation time (s) * $I_{0\lambda}(\tau \times \frac{V_R}{V_0})$ [mW/cm$^2$]

$I_{0\lambda}$ = incident light intensity [mW/cm$^2$] = 11.95
3.4 Supporting Information

\( \tau = \) Reaction time [s]

\( V_R = \) Volume receiving UV dose per second [mL/s] = 4.23

\( V_0 = \) Entire reaction solution [mL] = 80

Light absorbed by the medium is negligible in this configuration.

**Fig. S3** Phenol degradation as a function of UV dose for both ZnO-F and ZnO-W samples.

**Table S2.** UV dose and phenol degradation data for reactor configuration I – ZnO-F

<table>
<thead>
<tr>
<th>time (s)</th>
<th>UV Dose (mJ/cm(^2))</th>
<th>( \frac{C}{C_0} ) as-produced</th>
<th>( \frac{C}{C_0} ) thermal anneal</th>
<th>( \frac{C}{C_0} ) plasma</th>
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<td>0</td>
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<td>1596</td>
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### Table S3. UV dose and phenol degradation data for reactor configuration II – ZnO-W

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<th>time (s)</th>
<th>UV dose (mJ/cm²)</th>
<th>C/Co</th>
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<th>ZnO-W atm</th>
<th>ZnO-W O₂-sat</th>
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### Table S4 Hydrodynamic data and calculations

<table>
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<tr>
<th>flow rate (ml/min)</th>
<th>flow rate (m³/s)</th>
<th>flow velocity (m/s)</th>
<th>Re_Dh</th>
<th>Pe</th>
<th>Sc</th>
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<td>128</td>
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</table>
3.4 Supporting Information

\[ D_h = 4 \frac{\pi (R^2 - r^2)}{2\pi (R + r)} \]

\[ Re_{D_h} = \frac{\rho u D_h}{\mu} \]

\[ Pe = \frac{u D_h}{D} \]

\[ Sc = \frac{\mu \rho}{D} \]

\[ Sh = 1.029 \times Sc^{0.33} \times Re_{D_h}^{0.55} \times \left( \frac{L}{D_h} \right)^{-0.472} \]

where R is the internal diameter of the quartz tube and r the diameter of the Zn wire; D = 5.43E-10 m²s⁻¹ at 277 K, diffusion coefficient for phenol in water at 277 K [2]; L is the length of the ZnO section of the wire; \( u \) is the flow velocity of the phenol solution in the annulus; \( D_h \) is the hydraulic diameter of the annulus; and \( Re, Pe, Sc \) and \( Sh \) are the dimensionless numbers, Reynolds, Peclet, Schmidt and Sherwood. The correlation for the \( Sh \) number in an annulus is from [3].

References:


3.5 Additional Commentary

The published manuscript presented in this chapter (section 3.3) demonstrated that the addition of oxygen (either in material synthesis or reaction conditions), increased stability of ZnO nanowire layer anodized on to a support (film or wire), but also increased the photocatalytic activity of the ZnO. This section acts to expand upon certain aspects of the published manuscript as well as the wider research carried out on the ZnO wire, which were not included in the submitted manuscript. This includes the development and growth of ZnO nanostructures, and effect upon photocatalytic activity (section 3.5.1), ZnO photocorrosion (3.5.2), Photo-electro-catalysis (3.5.3) and hydrodynamics in the tubular reactor (3.5.4).

3.4.1 Development and growth of ZnO nanostructures
As discussed in section 1.5.5, the anodized nanostructures can be tailored by varying the electrolyte composition, with various examples demonstrating KHCO$_3$ based electrolyte will produce nanowire nanostructures. The growth of the ZnO nanowires over five minutes was investigated (shown in Figure 3.9). An oxide layer is formed after one minute (3.9.a), with cracking of the layer occurring after two minutes, and the development of nanowires after minutes (3.9.c). The nanowires further grow and cover nanoslate structure, after five minutes small examples of nanoslates remain under nanowire structures (3.9.e).

![Figure 3.9](image_url)

**Figure 3.9:** Scanning electron micrographs of nanowire anodized on a Zn wire in KHCO$_3$ electrolyte: 1 minute (a), 2, (b), 3 (c), 4 (d) and 5 minutes (e).
ZnO nanostructures have been previously studies with the same methodology as used in this work.\textsuperscript{1} Cracking of the initial layers formed was also observed by others \textsuperscript{2,3} and attributed to the evolution of oxygen underneath the films.

The impact of anodization time on nanostructures formation was also investigated. Increasing anodization time leads to increased nanowire growth from 30 to 60 minutes (Figure 3.10). After 30 minutes the slate like structure is no longer visible, and the nanowire structure cover the entire zinc metal surface. As anodization time increase the nanowire structures, form nanoflower structures (Figure 3.10.b) and then begin to converge to form nanoweb structures (Figure 3.10.c). Similar structures were also found by others.\textsuperscript{2,4}

\textbf{Figure 3.10:} The effect of anodization time upon ZnO nanostructures formed: a) 30 minutes b) 45 minutes c) 60 minutes.

Altering anodization time affects the ZnO nanostructures formation\textsuperscript{5} and a positive relationship was shown between ZnO layer thickness and its photocatalytic activity.\textsuperscript{6} It is suggested that a thicker ZnO layer provides a larger surface area and porosity, thus providing extra space for absorption upon to the surface, as well reducing electron/hole recombination.\textsuperscript{6}

Nanoflowers have previously been shown to have high photocatalytic efficiency in comparison to nanorods or nanoparticles.\textsuperscript{7} Thus, it was hypothesised in this study that increasing anodization time would increase nanowire length, therefore increasing surface area of the photocatalyst leading to higher photo activity. It was found that increasing anodization time from 5- 60 minute had no impact upon photoactivity (as shown in Figure 3.11)
There are many examples of Zn films requiring anodization times of at least one hour,\textsuperscript{8,9} whereas the results from this study suggest this is unnecessary to achieve efficient photocatalyst production. The relationship of anodization time and nanostructures formed was previously discussed.\textsuperscript{10} In general it was found that increasing anodization time leads to increased density of the nanostructures. In this study, the anodization time was not found to obviously correlate with photocatalytic activity, despite producing different nanostructures (shown in Figure 3.9 & 3.10). This could be due to the differing nanostructures demonstrating a similar overall surface area, due to the increasing density of nanostructures (at longer anodization times) blocking the oxide layer reacting with the UV light as well as hindering the porous layer beneath to absorb micropollutants. It should also be noted that increasing oxide layer thickness can increase instability and cracking, caused by tension within the material.\textsuperscript{11}

After the publication of “Enhancing the photo-corrosion resistance of ZnO nanowire photocatalysts” (section 3.3), a study regarding ZnO multi-dimensional architecture found that nanords (1D structures) demonstrated the most efficient photocatalytic activity in comparison nanoparticles (0D), nanosheets (2D) and nanoflowers (3D).\textsuperscript{12} The lowest photocatalytic degradation was demonstrated by nanoflowers (3D), which has been

\textbf{Figure 3.11:} The effect of anodization time (5, 30, 45 and 60 minutes) of a ZnO wire upon photocatalytic degradation of phenol (10 μM).
previously been shown to have very effective photocatalytic activity.\textsuperscript{7} Notably, they highlight that photocatalytic efficiency cannot be attributed to one physical property, but is due to a combination of multiple properties (surface area, pore diameter crystalline size).

Also to be noted within this study was the high standard deviation when a Zn wire (untreated) was use as a photocatalyst (42\% ± 5.18). Any increased phenol degradation using an untreated zinc wire is suggested to be due to the native oxide layer on the zinc surface, which will be photocatalytic active. This source of unconformity in the samples, will cause an increased uncertainty within the treated ZnO wire (58 \% ± 8.34). This difference is due to a native oxide layer which forms on the Zn wire. This layer can be removed using a process known as electro-polishing (discussed section 2.1.2), however when used upon the Zn wire, this increased the fragility and brittleness of the zinc wire, which makes the zinc support difficult to use and anodize.

### 3.4.2 Photocorrosion

As discussed in section 3.3, oxygen plasma annealing increased the photoactivity and stability of the ZnO film. The oxygen plasma utilises an electrified oxygen gas stream to convert Zn(OH)\textsubscript{2} to ZnO. There have been multiple examples of oxygen plasma annealing being used to enhance the properties of photocatalysts including ZnO.\textsuperscript{13,14} Plasma energy has been shown to increase relaxation of internal stress and grain boundaries, thus increasing stability.\textsuperscript{15} However, the same oxygen plasma procedure did not result in the same benefits for the ZnO wire as for the ZnO film (section 3.3). Plasma annealing of ZnO wire, caused a reduction in photocatalytic activity (32 \% in comparison to 58 \% for the thermally annealed wire). The photocatalytic degradation of phenol for the plasma annealed ZnO wire was similar to that of an unannealed ZnO wire (32 \% and 37 \% respectively). Thus, highlighting the difference in the behaviour between the wire and film material, and therefore the ZnO wire could require significantly longer plasma annealing time. The ZnO-wire was plasma annealed for longer than the ZnO-film (1 hour compared to 20 minutes respectively).
3.4.3 Photo-electrocatalysis of ZnO

Another parameter which was investigated to increase photocatalytic effectiveness was the addition of electricity. As discussed in section 1.5.6, there are many examples of electro-photocatalysis, where the photocatalyst is one out of two or three probes in an electrochemical cell, with efficiency is enhanced by minimising electron/hole recombination. However, the effect of simply adding electricity to the photocatalyst has not been investigated. It is important to note this is different to electro-assisted photocatalysis or photo-electrochemical degradation, which uses an anode and cathode suspended in solution with the catalytic nanoparticles. This prevents the electron and hole from recombining as they move in opposite direction.\textsuperscript{16}

Due to the anodizing process, the metal core remains within the photocatalytic active oxide layer, which allows for the application of electricity to the photocatalyst (method discussed in section 2.4). The fundamental theory behind the passing of current through the metal wire core, was that it would increase charge separation between electrons and holes, cause a change in wettability of the catalyst surface as well as increase potential direct oxidation. All of these potential effects leading to an increase in photoactivity.

![Figure 3.12: The effect of electricity upon degradation of phenol (10 μM) over 1 hour using a ZnO wire (anodized for 60 minutes) under UV-C conditions.](image)
3.5 Additional Commentary

The effect of electricity applied in this manner was preliminary investigated\textsuperscript{11}. It was found that applying a small voltage (0.2 V/0.9 Amps) to an untreated zinc wire in conjunction with UV-C light increased degradation of phenol (10 μM) by 20 %. It was important to investigate whether the application of electricity to the anodized ZnO would increase activity in addition to photo-activation. Our first results initially supported the findings of the earlier study (Figure 3.12) showing an increase in phenol degradation when voltage (0.2V) was applied to the zinc wire. However, these initial results were not reproducible and overall electricity was found to not enhance pollutant degradation, including at higher voltages, phenol degradation remained at 58 %. 
3.6 Chapter Conclusions and Further Work

This chapter demonstrated a ZnO photocatalyst, produced via anodization, can have both photocorrosion and leaching into reaction solution minimised using oxygen based methods. These methods included introduction of oxygen; either in the synthesis (oxygen plasma annealing) or during the reaction (oxygen saturation of reaction solution). The addition of oxygen was also shown to enhance growth of nanostructures.

Using wires in a tubular reactor setup was shown to increase photocatalytic activity compared to films in a flat reactor configuration, with a 57% to 19% of phenol degradation respectively over 1 hour. This is suggested to be due to the tubular reactor improving mass transfer for the same UV dose received by the films. The ZnO wire was shown to be reusable (consistent photoactivity after five uses), and photocorrosion was minimised upon the addition of oxygen. As well as oxygen, another key reaction parameter which was highlighted was flow rate. The development of nanostructures growth was also investigated, with no correlation found between anodization time and photocatalytic activity. This was suggested to be due to increased anodization time, increasing the oxide layer, however not leading to significantly increased visible surface. This would be due to the layers below would being hidden, thus unable to react with the UV light and for adsorption of the phenol contaminant. This study has focussed on the anodization of the ZnO wire, further research could concentrate on a mesh material, which could be able to under-go electro-polishing without becoming brittle and improve reproducibility of the ZnO photocatalysis. Other methods to investigate increase ZnO stability could involve hybridization using carbon, which has been shown to enhance photocatalytic activity but also activity in the visible light spectrum.

Passing electric current (0.2V - 1.5V) through the zinc wire was found to have no impact of increasing photocatalytic activity of the ZnO wire. The ZnO immobilised support could be investigated in a conventional two-three probe electrochemical cell, to determine if this could enhance the photocatalytic activity of the material and the effect on photocatalyst stability.
3.7 References


Chapter 4

Photocatalytic immobilised TiO$_2$ nanostructures via fluoride-free anodization

The work presented in this chapter has been published to Journal of Environmental Chemical Engineering in February 2020.

Chapter 4: Photocatalytic immobilised TiO$_2$ nanostructures

4.1 Context

The previous chapter demonstrated the increase in efficiency for the tubular/wire reactor setup over the flat film catalyst/reactor configuration. As discussed in section 1.4, the most commonly used photocatalysts are ZnO and TiO$_2$, however the anodization of TiO$_2$ conventionally requires the use of hazardous fluoride electrolytes and is carried out upon flat films. Any examples of non-fluoride TiO$_2$ anodization films, have not investigated photodegradation activity of the material. In the previous chapter, phenol was the main model pollutant used, however demonstrated high sensitivity to UV light ($\Phi_{254} = 2.55 \times 10^{-2}$ mol/Einstein). Thus a more photo-resistant model pollutant was chosen to be investigated as well, Carbamazepine ($\Phi_{254} = 0.06 \times 10^{-2}$ mol/Einstein), a well-studied pharmaceutical used to treat epilepsy, which is known for its high persistency and is one of the most frequently reported compounds found in surface water.

This chapter investigates the development and optimization of a fluoride-free TiO$_2$ anodization method for a Ti wire, and the resulting photocatalytic activity of the oxide layer. Section 4.1 provides context for the chapter, section 4.2 sets out experimental aims, 4.3 is the submitted manuscript, 4.4 supporting information and 4.5 is additional commentary, including a chapter conclusions and future work (section 4.6).

This chapter is presented in an alternative format in accordance with Appendix 6A of the “Specifications for Higher Degree Theses and Portfolios” as required by the University of Bath. The research presented in this chapter was produced by the author with the exception of the following:

ICP-MS data was obtained by Dr J.A. Milton, University of Southampton

X-ray diffraction spectra was obtained by Dr Gabriele Kociok-Kohn, University of Bath

XPS spectra was obtained from Dr David Morgan, Cardiff University

Research supervised by Dr Jannis Wenk and Professor Davide Mattia.
4.2 Experimental Aims

The following experiments formed the foundation of this chapter, to meet the aims and objectives:

- Optimise TiO$_2$ anodization conditions without the use of fluoride electrolyte upon a Ti wire and characterise with XRD, XPS, SEM. Determine the effect of anodization conditions, such as electrolyte composition and temperature, upon TiO$_2$ nanostructures formed.

- Explore the importance of thermal treatment (such as pre- and post-annealing temperature for the TiO$_2$ wire).

- Investigate the resulting photocatalytic activity of the optimum TiO$_2$ layer, monitored via degradation of micropollutants, carbamazepine and phenol. Including reproducibility of the photocatalyst, and if photocatalytic behaviour can be tailored via anodization conditions.

- Determine the reusability and stability of TiO$_2$ wire photocatalyst, including consistent activity after multiple uses and investigating if the photocatalyst leaches into the reaction solution.

- Determine the carbamazepine and phenol by-product pathway, by monitoring transformation products produced and whether direct or indirect oxidation is dominant, using methanol as hydroxyl radical scavenger. Also investigate whether the pollutants are undergoing transformation or mineralization by measuring total organic carbon (TOC) levels.

References


4.3 Published Manuscript

Photocatalytic immobilised TiO₂ nanostructures via fluoride-free anodisation

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Keywords: photocatalysis, immobilised titanium dioxide, potassium bromide, UV and advanced oxidation, hydroxyl radical, electrochemical anodisation, fluoride free

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Graphical Abstract

Highlights
- Titanium (Ti) anodisation method based on alternative halide electrolytes developed
- Structure and photocatalytic activity of resulting immobilised TiO$_2$ characterised
- Fluoride-free electrolytes yield stable photoactive immobilised TiO$_2$ on Ti wire

Abstract
Current methods for anodising titanium to produce immobilised titanium dioxide (TiO$_2$) photocatalysts require the use of hazardous fluoride electrolytes. A fluoride-free electrolyte anodisation method was developed, using bromide- and chloride-based electrolytes and ethylene glycol as an additive. Under optimised anodisation times and temperature conditions, the alternative electrolytes led to the growth of stable immobilised TiO$_2$ nanostructures layers on titanium wires used as a support. Crystal phases and topography of the produced TiO$_2$ layers were characterised using scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoelectron spectroscopy (XPS). The photocatalytic activity of fluoride-free anodised immobilized TiO$_2$
photocatalysts is reported here for the first time, showing that differences in the crystal phases had a strong effect on the degradation of the model aquatic contaminants, carbamazepine and phenol. These results show that effective immobilised TiO$_2$ nanostructures photocatalysts can be obtained using electrolytes without fluorine paving the way to more sustainable and safer production methods for photocatalyst for pollutant abatement in water.

1. Introduction

Modern lifestyle has been accompanied with an increasing usage of pharmaceuticals [1], hormones [2], drugs and pesticides [3]. After their use, many of these compounds, termed as micropollutants, end up in municipal wastewater. Micropollutants are difficult to remove by conventional waste water treatment methods due to their low concentration [4], and yet, even at concentrations in the ng/L to µg/L range, micropollutants may adversely affect aquatic ecosystems and reach drinking water supplies when released into the environment [5] [6]. Therefore, additional treatment is needed to remove these micropollutants from wastewater [7].

Advanced Oxidation Processes (AOP) are among the most promising treatment approaches for the removal of micropollutants [8]. AOPs utilise highly reactive species, especially hydroxyl radicals (•OH), to oxidise micropollutants resulting in oxidation products with increased biodegradability and reduced toxicity [9] [10] [11]. Such oxidation products can readily be further degraded and mineralised, for example, via biological post-treatment [12, 13]. Photocatalytic AOPs produce •OH through the absorption of light by a photocatalyst [14], in which case light initially creates electron-hole pairs that then react with chemical species at their surface [15]. The charged hole reacts with water, forming mostly •OH, while other reactive species include superoxide radical anions (O$_2$•-), perhydroxyl radicals (HOO•) and hydro peroxide ions (HO$_2$•) [16]. Target micropollutants may also degrade directly at the surface of the photocatalyst [14].

TiO$_2$ is the most commonly used solid state heterogeneous photocatalyst due to its high efficiency in comparison with other photocatalysts, and photo stability, including chemical and biological inertness [17, 18]. Most studies employ TiO$_2$ and other types of photocatalysts as suspended slurries [19, 20]. However, slurries have several disadvantages including reduced efficiency due to the turbidity of the solutions and light
scattering, aggregation of catalyst and the need for separation after treatment [21]. To overcome these issues, immobilised TiO$_2$ photocatalysts have been investigated as an alternative to slurry systems [22]. Moreover, immobilised catalysts can be applied in continuous reactors since the catalyst separation step can be omitted [23].

The production of immobilised TiO$_2$ photocatalyst is challenging, usually requiring complex or costly procedures including the sol-gel process [24], chemical vapour deposition (CVD)[25] or facile methods such as the alkali-hydrothermal technique or direct oxidation via H$_2$O$_2$ [26-28] to deposit the photocatalytic layer on a support such as glass or quartz [29]. Anodisation is an electrochemical method used for the controlled production of oxide layers on metal surfaces [30]. By applying a defined current to the metal, acting as anode in an electrochemical cell, two competing processes take place: The oxidation of the metal with subsequent dissolution of metal ions, and the formation of the oxide layer [31], shown for titanium in a halide (X) electrolyte below:

\[
\text{Ti} \rightarrow \text{Ti}^{4+} + 4e^- \quad \text{Oxidation via electrolysis (1)}
\]

\[
\text{Ti}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ \quad \text{Formation of oxide layer (2)}
\]

\[
\text{TiO}_2 + 6X^- + 4\text{H}^+ \rightarrow [\text{TiX}_6]^{2-} + 2\text{H}_2\text{O} \quad \text{Dissolution of oxide layer (3)}
\]

During anodisation, a steady state between oxide formation and dissolution can be established permitting growth of defined photocatalyst micro- and nanostructures, including nano-tubular and nano-porous oxide layers [32]. Most TiO$_2$ anodisation methods require the use of hazardous fluoride-based electrolytes [33], such as hydrofluoric acid (HF) and ammonium fluoride (NHF$_4$) [34, 35], to produce an environment which mildly dissolves the anodic oxides while the applied current continuously provides new oxide growth [32]. Fluoride has been the favoured electrolyte, because its small ionic radius allows it to act as a dissolution agent by entering the growing TiO$_2$ crystal lattice [31]. There are a few examples of the use of halide-based electrolytes such as sodium chloride (NaCl) [36], hydrochloric acid (HCl) [37] and perchloric acid (HClO$_4$) [32] as well as potassium bromide (KBr) [36] to structure the TiO$_2$ layer. NaCl aqueous electrolytes buffered at pH 4 have also been used to produce both TiO$_2$ and tungsten oxide (WO$_3$) via anodisation [32], however, this resulted in extensive pitting of the parent metal, due to certain locations at the electrode exhibiting high current densities. Electrolyte composition, temperature, pH, applied voltage and anodisation time [38, 39] are key to tailoring which nano structures are formed during the
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anodisation [31, 40]. For example, studies have found that anodisation at lower voltage produces fewer pits in the parent titanium metal with a photocatalyst layer that consists of thin nanotubes, while higher voltage results in surface dissolution and smoother nanostructures [41]. To aid anodisation and further improve the TiO$_2$ crystalline nanostructures, ethylene glycol or glycerol are frequently added to electrolytes as viscosity enhancers to decrease mobility of ionic species and create locally high acidity conditions for improved Ti dissolution [42, 43]. Although the use of viscous solvents produces smooth nanotube structures, it also slows down crystal growth [36]. An advantage of anodisation is that the parent metal anode can act as its own support without the need for complex deposition processes, making it simpler, quicker and less costly than other immobilisation methods [44]. Anodisation creates a strong adhesion of the formed TiO$_2$ to the titanium surface that provides photocatalyst stability in reactors [45].

After anodisation, annealing is a necessary thermal treatment, to remove crystal defects by releasing internal stress [46], [47]. Thermal treatment has been also reported to affect the photocatalytic activity of TiO$_2$ by altering the crystalline phases present [39]. Annealing can be carried out both before and after anodisation or exclusively after anodisation. Despite these advantages, titanium is expensive, with planar film geometries leading to material wastage and limited irradiation efficiency [48]. The use of Ti wire allows for a larger relative surface area to be covered with active photocatalyst and may lead to reduced scattering due to the radial direction of nanostructures rather than the parallel arrangement that has been reported for Ti films. TiO$_2$ nanostructures formed on wires exhibited a two-fold increase in photocatalytic activity compared to TiO$_2$ nanostructures formed over Ti foil, despite the illuminated surface area of the TiO$_2$ wires being half of that for the TiO$_2$ foil [48]. In this study, a novel titanium wire anodisation protocol without the use of fluoride electrolytes was developed to produce immobilised TiO$_2$ nanostructures for the photocatalytic degradation of two model micropollutants carbamazepine and phenol in a continuous flow photoreactor. Carbamazepine (CBZ) was used because it is recalcitrant towards direct photo degradation by UV-light [49] and phenol was chosen because it is a frequently used model micropollutant [50, 51].
2. Materials & Methods

2.1. Chemicals

All chemicals were purchased from commercial suppliers and used without further purification. Aqueous stock solutions including the electrolyte were prepared from ultrapure water (resistivity >18 MΩ/cm) from Milli-Q (Merck) or ELGA (Veolia) water purification systems. Titanium (Ti) wires (diameter 0.81 mm and 0.25 mm) were purchased from Sigma Aldrich 99.7% trace metals basis. The Ti film was purchased from Alfa Aesar (CAS no. 7440-32-6) and was cut to 20 x 13 mm, with a thickness of 0.127 mm. Unless otherwise stated all experiments were carried out on the Ti 0.81 mm wire.

2.2 Wire preparation, anodization and post-annealing

The wires were cut to 25 cm length and cleaned with acetone and ethanol before further processing. Wires were either pre-annealed at 500 °C for 3h [52] or directly submitted to anodisation. For anodisation, a previously developed platform was used [53]. The anodisation was conducted using an annular electrode system, with the Ti wire as the anode within a steel cathode tube (separated by a distance of 10 mm) connected directly to a DC power supply under galvanostatic conditions of 0.2 A, which resulted in an applied voltage of 7.2 V, and a continuously recirculated electrolyte with total volume of 200 mL. The electrolyte consisted of 0.3 M sodium chloride (NaCl; >99 %) or 0.3 M potassium bromide (KBr; >99 %) either in aqueous phase or in a 50:50 volume ratio with ethylene glycol. Anodisation temperature ranged from -10 to 22 °C. Constant temperature was maintained using a water-glycerol cooling system (DC-10, Thermo). Anodisation time ranged from 30 to 60 minutes. The annular system ensured the Ti wire was not bent to avoid breakage during anodisation and damage of the oxide layer that formed. To crystallize the TiO$_2$ layer, wires were annealed post anodisation between 250-900 °C at 5 °C/min for three hours. The TiO$_2$ wire was washed briefly with ultrapure water to remove water soluble impurities. The Ti film was produced using batch anodisation, by using the cleaned foil pieces as the anode of a two-electrode cell and a 3 mm-thick stainless-steel piece as the cathode. The anodisation area was restricted to a round area of 10 mm in diameter by using rubber and Teflon templates [54].
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2.2 Characterisation

The crystal structure of initial and anodised wires after annealing was determined by X-ray diffraction (XRD) using a Philips X-ray generator PW 1710 diffractometer, set in plate mode. Measurements were carried out between 20 values of 10° and 80°. The Scherrer equation was used to determine mean crystal sizes:\[^{[55]}\]

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (4)

Where $D$ is the mean crystalline size, $K$ is the shape factor (0.9), $\lambda$ is the wavelength of XRD (0.15 nm), $\beta$ conforms to the full width half maximum and $\theta$ is the diffraction angle of the dominant diffraction peak. The ratio of crystal phases, anatase to rutile, in the TiO$_2$ samples was calculated using the following equation:\[^{[56]}\]

$$\text{Rutile Phase \%} = \frac{100}{1 + 0.8 \left( \frac{I_A}{I_R} \right)}$$  \hspace{1cm} (5)

Where $I_A$ is the area of the anatase diffraction peak ($2\theta = 25.4^\circ$) and $I_R$ is the area of the rutile diffraction peak ($2\theta = 27.5^\circ$). The oxide layer nanostructures were investigated using a JEOL JSM6480IV Scanning electron microscopy (SEM). The crystal structure was also investigated with the use of transmission electron microscopy (Jeol 2100 Plus LaB$_6$). Samples were suspended in ethanol and sonicated for 10 minutes prior to being dropped onto a carbon coated copper grid (EMResolutions C200Cu100, 300 mesh copper (100)). The powdered samples were characterized by X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher Scientific K-alpha+ spectrometer, using a micro-focused monochromatic Al x-ray source (72 W) over an area of approximately 400 micrometres. Pass energies of 150 eV for survey scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes were used, respectively. A combination of both low energy electrons and argon ions was used for charge neutralisation of the sample. Data analysis was conducted with CasaXPS applying a Shirley type background and Scofield cross sections, and an energy dependence of -0.6.

2.4. Photocatalytic experiments

The photocatalytic activity of the TiO$_2$ coated Ti-wires was evaluated using a bespoke continuous flow photoreactor (Fig. S1)\[^{[53]}\] consisting of three UV lamps (UVH101,
Pisces, 254 nm, 5W) evenly spaced at a distance of 5 cm around a central quartz glass tube (OD = 6 mm, ID = 4 mm, light intensity $7.80 \pm 0.01$ mW/cm$^2$) containing the TiO$_2$-coated titanium wire and the recirculating micropollutant solution. For the direct photolysis experiments, a PVC (polyvinyl chloride, 1 mm diameter, 25 cm length) dummy wire was used to replace the Ti wire. The recirculating flow rate was set at 250 mL/min [53]. All irradiation experiments were conducted in unbuffered ultrapure water with phenol or carbamazepine as model micropolllutants at 10 μM starting concentration. Experiments were conducted at a constant temperature of 10 °C, with 80 - 100 mL recirculating reaction solution, with a 1 mL sample taken every six minutes. Unless otherwise stated experiments were carried out over 1 hour, to ensure degradation was in the linear range. Inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Fisher Scientific ELEMENT 2XR) was used to determine the Ti levels in solution using 0.5 mL of sample volume, 10-fold diluted to 5 mL with 3% HNO$_3$.

### 2.5 Micropolllutant Analysis

Isocratic high-performance liquid chromatography (HPLC) on an Agilent 1200 machine equipped with a Poroshell 120 column (EC-C18, 2.7 μm, 4.5 x 50 mm) and a UV detector was used to follow removal of model micropolllutants with irradiation time. Conditions were 20% acetonitrile and 80% aqueous phase (5 mM phosphoric acid, pH 2) for phenol (detection wavelength 220 nm) and 30/70% for carbamazepine (285 nm), respectively. For determination of phenol transformation products, conditions were 15% acetonitrile and 85% aqueous phase (5 mM phosphoric acid, pH 2), at 40 °C with a detection wavelength of 220 nm, a flow rate of 0.5 mL and injection volume of 20 μL and identified by comparing retention times with those of literature data and standards of known transformation products (Tab.S2). Transformation products of CBZ were identified using literature data, retention time, mass accuracy and MS/MS fragmentation patterns (Tab. S3).

The concentration of total organic carbon (TOC), as non-purgeable organic carbon (NPOC), was measured with a TOC analyser (Shimadzu TOC 5000A, Kyoto, Japan). For TOC measurements, photodegradation experiments with CBZ and phenol were conducted at 90 μM and 210 μM, respectively, (equal to 15 mg C/L) to ensure carbon removal due to mineralisation could be quantified.
3. Results & Discussion

3.1. The effect of the type and concentration of electrolyte upon nanostructure formation

The effect of electrolyte conditions on oxide layer formation and corrosion of titanium wires during anodisation was investigated for post-annealing procedures. An exemplary set of wire photographs and associated SEM micrographs for different anodisation conditions is shown in Figure 1. The use of NaCl (aq) electrolyte showed uneven oxide formation, and severe wire corrosion, with the formation of flake- or web-type microstructures, consisting of nanofibre structures (Fig. 1 a-c). The use of ethylene glycol at a 50:50 volume ratio with NaCl (aq), reduced oxide formation and increased wire corrosion, reducing the anodization time window, with similar microstructures formed to those produced in the pure NaCl aqueous phase (Fig. 1 d-f). While the anodisation of Ti using both the aqueous and ethylene glycol based NaCl electrolyte showed some similarities, the structures and oxide formation were mainly heterogeneous and inconsistent. These results indicate that in NaCl based electrolytes, the rate of chemical dissolution of TiO$_2$ was higher than the rate of electrochemical formation, including the oxidation of Ti and etching of TiO$_2$ induced by the electric field. For KBr based electrolytes, no wire corrosion and an increased oxide layer formation compared to NaCl electrolytes was observed, producing repeatable sponge or foam like microstructures, though without complete coverage (Fig. 1 g-i). The combination of KBr and ethylene glycol at equal ratio during anodisation delivered a homogeneous oxide layer of flake-like microstructures across the wire surface (Fig. 1 j-l). Both NaCl and KBr are strong electrolytes with similar conductivity values, however KBr was found to be a less aggressive electrolyte in comparison to NaCl, reducing corrosion and allowing for nanostructures to form. A possible explanation to this, is the increase in size of the bromide ion in comparison to the chloride ion. The addition of ethylene glycol prevented corrosion and produced more uniform TiO$_2$ coverage.
3.2. The effect of temperature upon nanostructure morphology

To investigate the influence of anodisation temperature on wire corrosion and oxide layer formation, a series of experiments was conducted between -10 and 22 °C for NaCl and KBr electrolytes in both the aqueous phase and mixed at 50:50 volume ratio with ethylene glycol. It was found that reduction of temperature from 22 to 0 °C caused a decrease in corrosion and improved the formation of the oxide layer. As previously discussed, NaCl-
based electrolytes caused severe corrosion and very little oxide layer formation, however, by decreasing temperature (0 °C), the oxide layer formation could be increased while corrosion of the wires was still significant. For KBr, no corrosion was found at any of the tested temperatures, however, the oxide layer that was produced at both 22 °C and 10 °C was patchy and heterogeneous. Reducing the temperature down to 0 °C resulted in complete coverage of the Ti wire with a uniform oxide layer. Further reducing the electrolyte temperature to -5 and -10 °C did not increase coverage further or led to additional improvements of the photocatalytic activity, respectively (results shown in Fig. S4). Therefore, 0 °C was used as the electrolyte temperature throughout the rest of the study.

At higher temperatures, wire surface dissolution and oxide layer formation are not in equilibrium and rapid dissolution corrodes the Ti wire before significant oxide layer formation can occur [57], in particular with the NaCl electrolyte. This can be explained by the relationship between wire conductivity and temperature: Titanium has a resistance of 39·10^{-8} \ \Omega \ \text{m}^{-1} \ at \ 273 \text{ K}, which is an order of magnitude higher than other commonly used anodisation metals, such as zinc and tungsten [58]. However as increasing conductivity is necessary to produce a sufficient oxide layer during anodisation, lowering the temperature reduces the resistivity of metals and, therefore, results in better conditions for oxide layer development. In addition, the lower temperature reduces the conductivity of the electrolyte solution and prevents wire corrosion. In each example, reducing electrolyte temperature from 22 to 0 °C resulted in an increase in voltage (1 V in KBr examples and 7 V in NaCl). Higher anodisation temperatures were found to be detrimental to producing TiO_2 nanotubes but were advantageous for higher growth rates of the nanotubes [57]. Increasing electrolyte temperature from 0 to 70 °C led to a decrease in outer diameter (50 nm to 30 nm) and a decrease in length (1.25 nm to 0.1 nm) due to enhancement of chemical dissolution. The thickest and longest nanotubes could be produced at an electrolyte temperature of 0 °C [31, 57].

### 3.3. Formation of nanostructures

The nanostructures formed during the identified optimum anodisation conditions (KBr:EG, 0 °C, 0.2 A, 30 minutes anodisation time) were further investigated via SEM (Fig. 2). At higher magnification, the flake-like structures shown in Fig.1 are made up of
cuboid nanostructures (Fig 2a) with a disordered crystals (Figure 2b – c). Figure 2d shows a very different morphology from Figure 2a, the result of anodisation of a flat Ti film rather than a wire. This shows that the geometry of the metal has a significant effect on the resulting anodised layer, as previously shown for alumina [59]. The overarching flake-like structures are similar to the flower like TiO$_2$ structures produced via anodisation on Ti foil at 0.3 M NaCl at 6:4 ratio of H$_2$O:EG at room temperature and 40 V, described by others [41]. However, [41] reported nanotubes as the underlying structure rather than nanocuboids. This difference could be due to the different anodisation systems used (continuous vs batch), different electrolyte temperature and the different substrate (Ti wire vs Ti film). Use of the wires in photocatalytic experiments did not result in a change of nanostructures (SEM micrographs before and after experiments are shown in Fig. S6) and there was also no obvious corrosion neither of the Ti wire nor of the oxide layer after photocatalytic experiments. The TiO$_2$ layer was characterised by XPS (Fig. S7 and atomic concentration in Tab.S8), TEM (Fig. 9) and XRD (Fig. S12). TEM micrographs (Fig. 2 b-c) shows disordered crystals after removal from the titanium wire. Average particle size of the TiO$_2$ oxide layer was found to be 30 nm (Text. S10), d-spacing of 0.35 nm; and selected area electron diffraction (SAED) confirms TiO$_2$ crystal (characterised data shown in Fig.S11). As previously stated, Ti films have been extensively studied, but limited examples exist of anodisation of Ti wires.

To further understand the difference in nanostructures formation between wires and films, additional experiments were conducted with titanium films to highlight any differences in material behaviour. For these experiments, the same anodisation conditions as for the Ti wire (0.2 A and 0.3M KBr: EG at 50:50 volume ratio, at 0°C for 30 minutes) were used on a Ti film. The Ti film displayed a smaller anodised surface area compared to the Ti wire but a comparable total surface area (wire total area: 6.37 cm$^2$, anodised area: 2.55cm$^2$, film total area: 5.28 cm$^2$, anodised area: 0.79 cm$^2$). As such the Ti film anode displayed a higher voltage (30 V) than the Ti wire (7 V), resulting in different nanostructures (cfr. Fig.2d and Fig. 1g), with varying thicknesses as a function of the anodisation parameters.
Figure 2: (a) SEM micrographs of TiO$_2$ nanostructures anodised on Ti wire, using KBr:EG (50:50 ratio, at 0.3 M); (b-c) TEM micrographs of TiO$_2$ crystals from wire and (d) TiO$_2$ structures grown on Ti film.

3.4 Photocatalytic Activity of TiO$_2$ structures

For both micropollutants, post-annealed wires had the best photocatalytic performance with 17% and 40% of removal for carbamazepine and phenol, respectively (Figure 3). Pre-annealed wires, on the other hand, showed a slower photo-transformation, attributed to reduced conductivity of the Ti wires, caused by an increase in grain boundaries [59]. This limited the current that could be applied during anodisation compared to unannealed wires and thus reducing oxide formation of the Ti wire. Without post-annealing, the TiO$_2$ layer produced via anodisation remains amorphous (shown in XRD Fig. S12), with little photocatalytic activity and may in fact hamper the photocatalytic degradation of micropollutants [31] [60]. Therefore, post-annealing only was applied to all samples. Complete phenol (10 μM) degradation was achieved within 6.5 hours (shown in Fig.S13). The photocatalytic performance of both the untreated Ti and the anodised TiO$_2$ wire showed good reproducibility, with errors of ± 1.3 % and ± 2.0 % respectively, and reusability over five uses (Fig.S14). An overview on Ti anodisation studies using different
electrolytes followed by photocatalytic experiments is provided in Table S21. ICP-MS analysis of reaction solution confirmed the stability of the TiO$_2$ photocatalyst, showing that both under UV and in the dark, Ti levels in solution remained below 10 µg/L. The Ti wire itself showed similar stability, suggesting the oxide layer did not alter Ti stability (complete data shown in Tab. S14). Currently, there are no Ti limits set by water standard agencies, however Ti is known to be toxic at high levels [62-65].

**Figure 3:** Photocatalytic degradation of a) Carbamazepine (10 µM) and b) phenol (10 µM), using bare, untreated Ti wires, un-annealed TiO$_2$ wires, a pre- and post-annealed TiO$_2$ wires and a post-annealed (700 °C) only TiO$_2$ wire over one hour in a continuous photocatalytic reactor. Error bars show standard deviation of three replicate experiments.

### 3.5. The effect of post-annealing temperature

The post-annealing temperature had an important effect on the structure and photocatalytic activity of the TiO$_2$ nanostructures (Fig. 4). XRD was used to measure the rutile-to-anatase ratio, showing that an increase in the temperature leads to an increase in the rutile-to-anatase ratio, with an optimum at 700 °C. For the degradation of both micropollutants investigated (XRD data shown in Fig. S12). The 700 °C optimum has a mix of both anatase and rutile. While anatase displays a higher photocatalytic activity than rutile [66], it is well known that small amounts of rutile in anatase increase the photocatalytic efficiency of the material [67]. This increase in activity is caused by the mineral forms displaying different band gaps (3.2 and 3 eV for anatase and rutile, respectively [68]), which produce a heterojunction which increases photocatalytic activity, possibly by trapping electrons and preventing recombination and lowering the
For the annealing conditions at 700°C, a band gap of 3.16 eV was calculated using the Kubelka-Munk equation (Fig. S15). The effect of annealing time was also investigated, at 1.5 hours and 3 hours, respectively, with the latter displaying the highest degradation (Fig. S17).

Increasing the annealing temperature also increased the average crystal size, with values increasing from 19 to 48 nm with increasing annealing temperatures from 500 to 900 °C (Table S18 including rate constants). It is well-known that larger crystals increase recombination, thereby reducing photocatalytic activity [70], with the best performance observed for the samples annealed at 700°C, with an average crystal size of 34 nm. Similar results have been observed in the literature, with a sample with 35.7 nm average crystal size rutile samples out-performing anatase ones with a size of 19.1 nm [36]. In the annealing range 250-450 °C, phenol photocatalytic degradation was significantly lower (19 %) than at 700 °C. The XRD spectrum of the 450 °C sample did not present the sharp, high intensity peaks typical of a crystalline sample (shown in Figure S11). This suggests the oxide layer remained amorphous for annealing temperatures below 500 °C,

**Figure 4:** Effect of post-annealing temperature (500-900 °C) and rutile crystal phase ratio (vs anatase) in % on the photocatalytic activity of TiO₂ covered Ti wires for (a) carbamazepine (CBZ) and (b) phenol degradation with at 10 µM initial concentration over 1 hour. Error bars for removal data show standard deviation of three replicate experiments.

3.6. **Product formation from micropollutants**

The hydroxyl radical scavenger methanol (10 mM) was added during irradiation experiments to identify the degradation pathway [49],[71],[72]. For both micropollutants,
there was a stark decline in degradation (Fig. 5), indicating that the \*OH radical process is prevailing (complete degradation data in Table S20).

**Figure 5:** Photocatalytic degradation of carbamazepine (10 µM) and phenol (10 µM), using Methanol (10 mM) as a hydroxyl scavenger

The analysis of transformation products provided further indication of the underlying reaction pathways: For phenol, comparison with standards [73] confirmed that the main transformation products in the present work were catechol and hydroquinone, thus supporting the hypothesis that the main degradation pathway was via hydroxyl radical reactions [51], rather than absorption on to the photocatalyst surface. CBZ transformation products were detected using mass spectroscopy analysis and identified tentatively based on literature results [74, 75]. The three main degradation products found were hydroxyl carbamazepine (1), carbamazepine 10,11–epoxide (3) and acridine (5) (shown in Fig. 6). Products 1 and 3 have the same molecular mass so are grouped together. In addition, carbamazepine o-quinone (2) was produced (full preliminary degradation pathway shown in Fig. S19). Acridine (5) has been reported as a main transformation product [76], while hydroxyl carbamazepine and carbamazepine 10,11–epoxide are the primary products of the reaction between CBZ and \*OH.
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Figure 6: Preliminary degradation by products of carbamazepine; hydroxyl carbamazepine (1) (m/z: 253.0979), carbamazepine o-quinone (2) (m/z: 267.0771), carbamazepine 10,11-epoxide (3) (m/z: 253.0979) and acridine (5) (m/z: 180.08081). Their mass was determined using mass spectroscopy.

Mineralisation of organic matter was monitored via TOC removal. For phenol (210 μM), there was a 9% mineralisation via photolysis, which increased to 14% upon the addition of the TiO$_2$ catalysts within 7.5 hours of irradiation (shown in Table S20). Carbamazepine (90 μM) exhibited 11% mineralisation after 7.5 hours for both photolysis and UV/TiO$_2$. This highlights that both model contaminants are oxidatively transformed rather than mineralised.

4. Conclusions

In this work, a systematic study of the anodisation of titanium wires to produce TiO$_2$ photoactive nanostructures using fluoride-free electrolytes was conducted. NaCl was found to be too aggressive an electrolyte compared to potassium bromide (KBr). Optimisation of the anodisation process with addition of ethylene glycol (EG) to enhance viscosity showed that a KBr:EG (50:50 ratio, at 0.3M) electrolyte, coupled with post-annealing at 700°C for three hours, resulted in a uniform, stable and highly photoactive
TiO$_2$ coating on the Ti Wire. At these conditions, the TiO$_2$ is composed of 7% rutile and 93% anatase phases. Stability of the TiO$_2$ catalyst was confirmed with ICP-MS, with less than 10 µg/L of Ti leaching into solution, irrespective light or dark conditions. The catalyst retained photocatalytic performance during four repeat experiments, indicating longer-term stability. Based on quenching experiments and transformation product analysis model contaminants reacted most likely via hydroxyl radical induced degradation pathways, but without complete mineralisation. This work has shown that use of fluoride-free electrolytes can produce stable photoactive immobilised TiO$_2$ on Ti wires, which opens the way for a more sustainable titania photocatalyst production on diverse surface topographies.

Acknowledgements

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4.4 Supporting information

Photocatalytic immobilised TiO$_2$ nanowires via fluoride-free anodization

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<th>Caption</th>
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<td>Table S2</td>
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<td>Scanning electron microscopy of TiO₂ before and after use</td>
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<td>Figure S15</td>
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<td>S10</td>
</tr>
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<td>S11</td>
</tr>
<tr>
<td>Figure S18</td>
<td>Preliminary suggested CBZ transformation pathway</td>
<td>S12</td>
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<td>Table S19</td>
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<td>S13</td>
</tr>
<tr>
<td>Table S20</td>
<td>Total organic carbon (TOC) of micropollutants (carbamazepine and Phenol) under UV and UV/TiO₂</td>
<td>S13</td>
</tr>
<tr>
<td>Table S21</td>
<td>Ti anodisation studies using different electrolytes followed by photocatalytic experiments.</td>
<td>S14</td>
</tr>
</tbody>
</table>
Figure S1. Photocatalytic reactor

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/z [g/mol]</th>
<th>Retention time/ minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>110.11</td>
<td>1.41</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>110.11</td>
<td>1.92</td>
</tr>
<tr>
<td>Catechol</td>
<td>110.11</td>
<td>2.55</td>
</tr>
<tr>
<td>Phenol</td>
<td>94.11</td>
<td>4.85</td>
</tr>
<tr>
<td>Benzoquinone</td>
<td>108.09</td>
<td>2.21</td>
</tr>
</tbody>
</table>

Table S2. Phenol, including transformation times with HPLC retention time

Table S3. Identified carbamazepine transformation products

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydroxyl Carbamazepine</td>
<td>253.0979</td>
</tr>
<tr>
<td>2</td>
<td>Carbamazepine o-quinone</td>
<td>267.0771</td>
</tr>
<tr>
<td>3</td>
<td>Carbamazepine 10,11-epoxide</td>
<td>253.0979</td>
</tr>
</tbody>
</table>
Figure S4. Photocatalytic degradation of carbamazepine and phenol (both 10 µM) using a TiO$_2$ wire anodized at: 0, -5 and -10 °C over one hour in a tubular photocatalytic reactor.

Figure S5. Scanning electron microscopy (SEM) images of TiO$_2$ nanostructures on Ti wire, using KBr:EG (50:50 ratio, at 0.3 M) A.) before (unused) B.) after irradiation experiments.
Figure S6. XPS of spectra of TiO$_2$ nanocrystals: a) global, b) bromide, c) carbon, d) potassium, e) titanium and f) oxygen.
**Table S7.** XPS atomic concentration of TiO$_2$ nanocrystals

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
<th>% Atomic concentration</th>
<th>Total % Atomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br 3d</td>
<td>67.98</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.65</td>
<td>3.01</td>
<td>6.12</td>
</tr>
<tr>
<td></td>
<td>288.61</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>285.96</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>K 2p</td>
<td>292.66</td>
<td>2.98</td>
<td>4.47</td>
</tr>
<tr>
<td></td>
<td>295.43</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>396.08</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.28</td>
<td>63.05</td>
<td>63.05</td>
</tr>
<tr>
<td>Ti 2p</td>
<td>458.08</td>
<td>25.85</td>
<td>25.85</td>
</tr>
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</table>

**Figure S8.** TEM micrograph of TiO$_2$ nanocrystals (removed from support), including D-spacing of 0.3525 nm
Text S9. Particle size was calculated using software, SightX, by averaging the mean particle size in one sample over 40 different particles. The mean was found to be 29.67 nm with a $S_d$ of 11.32 nm.

Figure S10. The electron diffraction (SAED) pattern of TiO$_2$
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Figure S11. XRD spectra for as-produced TiO₂ (no annealing), 1 hour anodization (annealed at 700°C), TiO₂ annealed at 900°C, 800°C, 700°C, 600°C, 500°C and 450°C (all annealed for 3 hours) and a Ti wire. Key anatase and rutile peaks at 25.3 and 27.5 degrees respectively.
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**Figure S12.** Long term degradation of carbamazepine and phenol (both 10 μM) using TiO$_2$ as photocatalyst

**Table S13.** Ti levels measured by Inductively coupled plasma mass spectrometry (ICP-MS) for a Ti wire and a TiO$_2$ wire.

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>UV</th>
<th>Dark</th>
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<tbody>
<tr>
<td></td>
<td>Ti [μg/L]</td>
<td>[TiO$_2$ μg/L]</td>
</tr>
<tr>
<td>Wash off</td>
<td>1.8</td>
<td>44.8</td>
</tr>
<tr>
<td>0</td>
<td>2.3</td>
<td>4.2</td>
</tr>
<tr>
<td>15</td>
<td>4.6</td>
<td>4.2</td>
</tr>
<tr>
<td>30</td>
<td>4.7</td>
<td>3.0</td>
</tr>
<tr>
<td>45</td>
<td>7.2</td>
<td>2.8</td>
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<tr>
<td>60</td>
<td>3.6</td>
<td>3.0</td>
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Figure S14. Reusability of a TiO$_2$ wire over five uses (1 hour each use) to degrade phenol (10 µM).

Figure S15. Diffuse reflectance spectra of the TiO$_2$ a) F(R) versus wavelength b) modified Kubelka-Munk function, F(R)hv$^{1/2}$, against energy of the absorbed light.
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Table S17. Relationship between annealing temperature, ratio of rutile to anatase in sample, crystal size, micropollutant degradation and rate constant.

<table>
<thead>
<tr>
<th>Annealing temp/°C</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Average crystal size/nm</th>
<th>[CBZ]₀</th>
<th>Rate constant/ x 10⁻⁴ s⁻¹ (CBZ)</th>
<th>[Phenol]₀</th>
<th>Rate constant/ x 10⁻⁴ s⁻¹ (Phenol)</th>
</tr>
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<tr>
<td>500</td>
<td>0</td>
<td>19.06</td>
<td>0.83 (±0.04)</td>
<td>0.48</td>
<td>0.62 (±0.05)</td>
<td>1.29</td>
<td></td>
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<tr>
<td>600</td>
<td>0.03</td>
<td>22.24</td>
<td>0.84 (±0.01)</td>
<td>0.47</td>
<td>0.61 (±0.05)</td>
<td>1.29</td>
<td></td>
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<tr>
<td>700</td>
<td>0.08</td>
<td>33.71</td>
<td>0.83 (±0.02)</td>
<td>0.51</td>
<td>0.60 (±0.02)</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.73</td>
<td>37.51</td>
<td>0.95 (±0.03)</td>
<td>0.15</td>
<td>0.71 (±0.1)</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>3.52</td>
<td>48.33</td>
<td>0.99 (±0.001)</td>
<td>0.002</td>
<td>0.76 (±0.04)</td>
<td>0.75</td>
<td></td>
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</table>

Figure S16. The impact upon of preparation steps upon photocatalytic performance, including annealing time and anodization time.
Figure S18. Suggested CBZ transformation pathway
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**Table S19.** Rate constants and degradation of micropollutants under a) photolysis b) Ti wire and UV c) TiO$_2$ (annealed at 700 °C) d) TiO$_2$ (+ MeOH)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>[CBZ]$_t$</th>
<th>Rate constant/ [Phenol]$_t$</th>
<th>Rate constant/ x 10$^{-4}$ s$^{-1}$ (CBZ)</th>
<th>x 10$^{-4}$ s$^{-1}$ (Phenol)</th>
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<tbody>
<tr>
<td>UV</td>
<td>0.98 (± 0.01)</td>
<td>0.06</td>
<td>0.79 (± 0.05)</td>
<td>0.56</td>
</tr>
<tr>
<td>Ti</td>
<td>0.96 (±0.004)</td>
<td>0.10</td>
<td>0.75 (±0.01)</td>
<td>0.80</td>
</tr>
<tr>
<td>TiO$_2$ (700 °C)</td>
<td>0.83(±0.02)</td>
<td>0.51</td>
<td>0.61(±0.01)</td>
<td>1.34</td>
</tr>
<tr>
<td>TiO$_2$ (+ MeOH)</td>
<td>0.99 (±0.01)</td>
<td>0.028</td>
<td>0.81 (±0.02)</td>
<td>0.62</td>
</tr>
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</table>

**Table S20.** Total organic carbon (TOC) of micropollutants (carbamazepine and phenol) under UV and UV/TiO$_2$.

<table>
<thead>
<tr>
<th>Time/Minutes</th>
<th>Carbamazepine Carbon mg/L</th>
<th>Phenol Carbon mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV</td>
<td>UV + TiO$_2$</td>
</tr>
<tr>
<td>0</td>
<td>16.2</td>
<td>16.11</td>
</tr>
<tr>
<td>90</td>
<td>15.77</td>
<td>14.96</td>
</tr>
<tr>
<td>180</td>
<td>15.4</td>
<td>14.73</td>
</tr>
<tr>
<td>270</td>
<td>16.32</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>-</td>
<td>15.35</td>
</tr>
<tr>
<td>370</td>
<td>-</td>
<td>14.54</td>
</tr>
<tr>
<td>383</td>
<td>15.55</td>
<td>-</td>
</tr>
<tr>
<td>450</td>
<td>14.35</td>
<td>14.47</td>
</tr>
</tbody>
</table>
Table S21: Ti anodisation studies using different electrolytes followed by photocatalytic experiments.

<table>
<thead>
<tr>
<th>Morphology of TiO$_2$</th>
<th>Electrolyte</th>
<th>Ti Support</th>
<th>Compound tested</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanotubes</td>
<td>Fluoride-based</td>
<td>Wire</td>
<td>Methyl orange</td>
<td>[1]</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>Fluoride-based</td>
<td>Foil</td>
<td>Methyl orange</td>
<td>[2]</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>Chloride-based</td>
<td>Foil</td>
<td>Formaldehyde</td>
<td>[3]</td>
</tr>
<tr>
<td>Nanocuboids</td>
<td>Bromide-based</td>
<td>Wire</td>
<td>Phenol and carbamazepine</td>
<td>This work</td>
</tr>
</tbody>
</table>

References

   https://pubs.acs.org/doi/10.1021/es8031049

   https://doi.org/10.1016/j.apcatb.2009.12.003

   https://doi.org/10.3390/nano10010128
4.5 Additional Commentary

This section acts to expand upon certain aspects of the submitted manuscript (section 4.3) as well as the wider research carried out on the material, which were not included in the submitted manuscript. This includes: wire resistance & surface area (section 4.5.1), photocatalytic effect of anatase: rutile ratio (4.5.2), Effect of pH and gas on photocatalytic activity (4.5.3), nitrogen doping of TiO$_2$ (4.5.4).

4.5.1 Wire resistance & Surface Area

As discussed in section 4.3, titanium has a much higher resistance compared to other metals such as zinc, silver, tungsten (39 in comparison to 5.5, 1.6 and $4.8 \times 10^{-8}$ Ω.m at 273 K$^1$), thus titanium is much less conductive. Conductivity is temperature dependent, and at reduced temperatures, resistance can be related to resistivity via equation 4.6:

$$R = \frac{\rho L}{A}$$  \hspace{1cm} 4.6

R= resistance (Ω.m) $\rho$ = resistivity (Ω) L = Length (m) A= cross section (m$^2$)

This equation relates directly to the wire system and demonstrates that the electrical resistance is greater for longer and thinner wires, in comparison to short wires with larger cross sectional areas. In this study, the wire demonstrated higher surface area to that of the film, thus reduction in resistance during anodization. The difference in nanostructures produced, can be attributed to the difference in length and cross sectional areas of the Ti material used as well as the different anodization rigs used. Expanding on the impact of temperature on anodization. Decreasing temperature (down to 4 °C) has been found did to alter nanostructures formed during anodization of TiO$_2$, but can reduce the growth rate and allowed for higher potentials to be used, which led to nucleation density as well as more homogeneous and denser coverage on the surface.$^2$ This is similar to what was found in this study.

A key physical property of photocatalysis is surface area of the active photocatalyst layer (discussed in 1.4.2 & 1.4.3), with a larger surface area resulting in increased active sites for pollutants to absorb on to the material surface for photodegradation.$^3$ However, it was not possible to use the conventional method of Brunauer-Emmett Teller (BET) theory, which utilises the absorption of gas molecules upon a solid surface, to determine specific
surface area of the material (m²). The immobilised sample would not fit in the equipment, and to remove the oxide layer from the support would not provide an accurate surface area value. Other methods used included SEM, where the sample was sealed in resin and an attempt made to measure the oxide layer formed upon the metal core. However, the oxide layer separated and was inhomogeneous across the sample, thus was unable to provide an accurate reading of oxide layer thickness.

Another method investigated to quantify the surface area was based on a well-known electrochemical method. The method used in this study was based on measuring the current response to a reversible redox reaction between [Fe(CN)6]⁴⁺/[Fe(CN)6]³⁺ (using 5 mM Potassium ferricyanide and 0.1 M KCl as electrolyte) over various scan rates and sweeping voltages to produce a cyclic voltammetry (CV) plot. At higher scanner rate, the diffusion layer is reduced leading to higher current observed. The peak current is proportional to the square root of the scan rate. This relationship forms the foundation of the Randles-Sevcik equation, shown in equation 4.7⁴.⁵, to calculate the surface area:

\[ i_p = 0.446nFAC^0\left(\frac{nFvD_o}{RT}\right)^{1/2} \]  

Where \( i_p \) is equal to the peak current (A), the scan rate is \( v \) (V s⁻¹), \( n \) represents the number of electrons transferred in the redox event, \( F \) is Faradays constant (96485.332 C mol⁻¹), \( C^0 \) is the bulk concentration of the analyte (mol cm⁻³), \( R \) is the molar gar constant (8.3144598 m² kg s⁻² K⁻¹ mol⁻¹), \( T \) is temperature (K) and \( D \) is the diffusion constant of the oxidised analyte (cm² s⁻¹). However, this method is dependent on the conducting nature of the material, and considering the high resistance of titanium especially after post annealing, this method was unsuccessful. Other potential methods which could be used to determine the surface area of the oxide layer are outlined in further work (section 4.6).

Further examination into the effect of surface area on photocatalysis activity, was based on the surface area of the metal wire core (rather than the oxide nanostructures). Previously it has been shown that an anodized TiO₂ 0.25 mm wire displayed higher degradation of methyl orange compared to a 0.5 mm wire (13% higher using the thinner wire, compared to the thicker wire).⁶ Similarly, our own experiments showed that a 0.81 mm wire exhibited better degradation of phenol compared to a 0.25 mm wire (Figure 4.7).
Figure 4.7: Comparison of photocatalytic degradation of phenol (10 μM) using anodized TiO$_2$ wire; 0.25 mm and 0.81 mm diameter.

However, when photocatalytic degradation per wire surface area is considered, the thinner wire (0.25 mm) demonstrates higher photocatalytic activity per area in comparison to the thicker wire (0.81 mm), with 19.11 %/cm$^2$ and 7.80 %/cm$^2$ degradation over the same irradiation time respectively. However, it should be noted that the 0.25 mm wire was very fragile and brittle to handle, and thus inappropriate to study further. A Ti wire of 0.5 mm should have increased durability compared to the 0.25 mm wire, as well as the benefit of higher photocatalytic activity per area in comparison to the thicker 0.81 mm titanium wire.

4.5.2 Photocatalytic Effect of Anatase: Rutile ratio

As demonstrated in section 4.3, the ratio of anatase to rutile in the TiO$_2$ material could be correlated to the photocatalytic activity of the sample. The third TiO$_2$ crystal phase, brookite, was not detected in any synthesised sample. The most effective photocatalyst, including reproducibility, was produced by post-annealing at 700 °C, which contained a mix of both anatase and rutile.
Similarly, Degussa P25 TiO$_2$ is used as a benchmark for TiO$_2$ photocatalytic activity due to its high activity, composed of an rutile to anatase ratio of 1:4.$^8$ It is important to note that an increase in photodegradation activity using TiO$_2$ with mixed anatase and rutile phases, is caused by the increase in populations of heterojunction, not due to some cooperative effects of their individual photochemical properties and this can be tailored by annealing.$^9,^{10}$ Complete understanding of why the phase mixture increases photocatalytic activity is not known. As suggested in section 4.3, the mixture is producing a heterojunction and another possibility is that after the Fermi level alignment, the conduction band edge of rutile should be lower than that of anatase, resulting in favourable conditions for electron transfer from anatase to rutile (as shown in Figure 4.8).$^9$

![Proposed band alignment between valence and conduction bands in anatase/rutile. The flow electrons (holes) in the conduction band (valence band) are represented by yellow dots.](image)

**Figure 4.8:** Proposed band alignment between valence and conduction bands in anatase/rutile. The flow electrons (holes) in the conduction band (valence band) are represented by yellow dots. [Image adapted from Sokol et al.$^{11}$]

The impact of altering the ratio of anatase to rutile in Degussa P25 by annealing has been investigated previously.$^9$ It was found the highest photocatalytic activity is found with a mixture of anatase and rutile, with 83 % anatase in the TiO$_2$ nanoparticles (produced at 250 °C), followed by samples containing anatase (%) of 46 and 32, where there is a large population of hetero-junctions between the two TiO$_2$ phases. Regarding immobilised TiO$_2$ photocatalyst, it has been found that a calcination temperature of 600 °C, gave the phase content of 71.9 % anatase and 28.1 % rutile, which gave the best photocatalytic
activity in comparison to purely anatase samples or majority rutile samples. However, it should be noted that the ratio of anatase to rutile in a sample will impact other properties of the material such as particle size and surface area, which will also significantly effect photocatalysis activity. Therefore, photocatalysis active is not purely dependent on the hetero-junction formed between the anatase and rutile phases.

4.5.3 Methanol as an Hydroxyl Radical Scavenger

In section 4.3, methanol was used as a hydroxyl radical scavenger to determine the key degradation mechanism. Methanol is a moderate hydroxyl scavenger, with a second order rate constant of $9.7 \times 10^8$ L mol$^{-1}$ s$^{-1}$, which is similar to the well-studied scavenger tert-butanol ($6.0 \times 10^8$ L mol$^{-1}$ s$^{-1}$). Methanol has been used as a hydroxyl radical scavenger in previous studies. However, there have also been examples of methanol acting as a hole (second order rate constant of $2.6 \times 10^6$ L mol$^{-1}$ s$^{-1}$) and hydroxyl radical scavenger, thus there can be much mixed interpretation of the degradation pathway effected. In section 4.3, as well as using methanol as a radical scavenger, the transformation products were measured to investigate the degradation pathway taking place. It was found that the free bound hydroxyl radicals transformation products, catechol and hydroquinone, were mainly produced. This supports the hypothesis that the main degradation pathway was via hydroxyl radical reactions. These results could be confirmed with further investigation using, solely hydroxyl radical scavengers such as dimethyl sulfoxide (DMSO) and specific hole scavengers such as formic acid.

4.5.4 Effect of pH and gas upon photocatalytic degradation

As discussed in section 1.4.3 process parameters such as temperature and dissolved oxygen concentration can have a large impact upon the photocatalytic efficiency of a material and system. Regarding pH, this will alter the surface charge of the photocatalyst material, thus the attraction or repulsion between the material and pollutant. The effect of pH (5-8) on the photocatalytic degradation of micropollutants was examined. Preliminary results in this study using phosphate buffered solutions, showed pH did affect the photocatalytic behaviour of the material, resulting in different optimum conditions for carbamazepine and phenol (shown in Figure 4.9). Carbamazepine (CBZ) was found to have highest degradation at pH 7 in this study, and lowest at unbuffered solution. Multiple examples have shown that CBZ degrades fastest using TiO$_2$ at lower pH (3) and is least
effective under high pH (11).\textsuperscript{21,22} However is has also been suggested that CBZ photodegradation using TiO\textsubscript{2} can be increased under high pH (10 compared to 2.5), due to decreased electrostatic repulsion between the negatively charged TiO\textsubscript{2} and protonated CBZ.\textsuperscript{23} Whereas, phenol displayed highest degradation at unbuffered, and lowest at pH 7. Previously it has been shown that phenol degradation via TiO\textsubscript{2} photocatalyst is fastest under low pH,\textsuperscript{24} possibly due to the strong electrostatic attraction between phenol and TiO\textsubscript{2}.\textsuperscript{25}

Our preliminary results do not correlate with the literature, this could be due to many factors. The buffered solutions were made using phosphate salts, which have been shown to adsorb strongly to the TiO\textsubscript{2} surface and reduce hydroxyl radical production\textsuperscript{26} which will effect photocatalytic activity depending on the phosphate salt concentration. The effect of pH upon photocatalysis is complex (discussed in section 1.4.3) and will require thorough further investigation to determine the impact in this system.

\textbf{Figure 4.9:} Preliminary effect of pH (5-8) including unbuffered, upon the photocatalytic degradation of carbamazepine and phenol.

Dissolved oxygen is another key photocatalysis parameter, which was highlighted in the previous chapter (section 3.3), that can result in a change in behaviour of the material and photocatalytic degradation of the material. Oxygen can act as an electron acceptor,\textsuperscript{27} and led to increase oxygen radical formation, while nitrogen hinders photocatalytic activity by purging the system of oxygen, needed to produce hydroxyl radicals. As shown in Figure 4.10, like pH, the addition of a gas to the process produced opposite effects for carbamazepine and phenol.
Regarding, carbamazepine both the addition of oxygen and nitrogen increased degradation (to 54% and 42% respectively, compared to 28% at atmospheric conditions). This could be due to the additional gas aiding mass transfer in the system. Whereas, phenol degradation was fastest under atmospheric conditions (41%), and the addition of a gas reduced photocatalytic activity: oxygen (35 %) > Compressed air (33%) > Nitrogen (17 %). There are also examples of the TiO2, especially rutile, effectively photo-reducing substrates such as Ag⁺ and CCl4.28 The mechanism of degradation, photo-oxidation or photo-reduction, is very substrate specific. This would explain the differences seen between the degradation of carbamazepine, where nitrogen caused an increase in degradation, and phenol where nitrogen caused a decrease in degradation. These preliminary results do not clearly define the impact of gas influent upon photocatalytic activity. Both the effect of pH and gases upon photocatalytic activity should be further investigated, to determine a clear effect.

4.5.5 Nitrogen – Doping TiO2
As discussed in section 1.5.9, nitrogen doping (n-doping) allows for the TiO2 photocatalyst to absorb also into the visible light spectrum and therefore, may increase the efficiency of a TiO2 material which could be used within the solar spectrum or require less energy intensive lamps. Multiple methods for N-doing have been previously discussed in sections 1.5.9, but the three most suitable methods for this process were identified to be; one-step anodization, two-step anodization and finally a one-step
4.5 Additional Commentary

anodization followed by soaking in nitrogen rich solution. Preliminary results in this study found that it was only possible to N-dope the TiO$_2$ wire photocatalyst using the two-step anodization method, with urea as the nitrogen precursor (XPS characterisation shown in figure 4.11). There are two pathways of incorporating nitrogen into the TiO$_2$ structure; interstitial, the addition of nitrogen into the TiO$_2$ lattice and forming TiO$_2$N$_x$, and substitutional, which replaces oxygen in the lattice with nitrogen. These two pathways can be differentiated using XPS, where interstitial produces a peak at 400 eV and substitutional at ~ 396 eV.$^{29}$

![Figure 4.11: X-ray spectroscopy (XPS) of nitrogen incorporation TiO$_2$ via a two-step anodization process, using urea as a precursor.](image)

Both one-step anodization step and the soaking method were unsuccessful in doping the TiO$_2$ with nitrogen. One-step anodization produces a random pore arrangement and has been shown to successfully work many times, however over longer periods of time (> 2 hours) or with the use of ammonium fluoride.$^{30,31}$ A two-step anodization method conventionally is used to produce highly self-ordered nanostructures.$^{32}$ However, further investigation is required to determine what effect N-doping had on the TiO$_2$ nanostructures in this study.

This study used urea, which is a widely researched and mild nitrogen precursor, to dope the TiO$_2$ material as a proof on concept. However, there are other nitrogen precursors
which might be more effective in a one-step anodization process. Previously nitrogen precursors to produce N-doped titania via anodization have included; diethylenetriamine, triethylamine, ethylenediamine and urea. All these samples were photocatalytic active under visible light (\ (> 420\ nm\) ), with nitrogen context (\ (%)\ ) positively correlated with increased photocatalytic degradation of model pollutant, methylene blue.

### 4.5.6 Benchmark for comparison of photoactivity

As discussed in this chapter, and highlighted in section 4.3, it is possible to produce a photoactive TiO$_2$ layer using mild electrolytes such as NaCl and KBr, rather than the hazardous fluoride based electrolytes usually used. A comparison of other degradation studies using fluoride and chloride based electrolyte is giving in Table S21, in section 4.4 However, it is difficult to provide a clear comparison due to many contrasting parameters such as model pollutant, reactor design, catalyst support area and anodisation methods. Therefore, it would be beneficial in further study to include a benchmark for photoactivity under the same reaction conditions described in section 4.3. This could include self-aligned titania nanotubes anodised in commonly used fluoride electrolyte such as NH$_4$F$^{12,33}$ or HF.$^{34,35}$ Another method could be to deposit Evonik Aeroixde P25 particles, the benchmark for photocatalysis, onto a wire support using depositions methods such as chemical vapour deposition$^{36,37}$ (discussed further in section 1.5.3).
4.6 Chapter Conclusions and Further Work

The development of a fluoride-free anodization for a TiO$_2$ wire was investigated. Sodium chloride was found to be an unsuitable electrolyte because it caused severe corrosion of the parental support material. Thus, potassium bromide to oxidise Ti and etch TiO$_2$ with ethylene glycol (to increase viscosity) were used to produce a homogenous titanium dioxide layer, made up of nanocuboid structures. The anodization parameters could be optimised further by determining the effect of electrolyte concentration, which has been shown to relate to particle size, thus could be used to tailor surface area and photocatalytic efficiency.\textsuperscript{38} Preliminary results in this study suggested that thinner wires (0.25 mm diameter in comparison to 0.81 mm), have a higher photocatalytic activity per cm$^2$, however the thinner wire was too brittle, thus a 0.5 mm wire could be the optimum diameter to investigate. As well as continuing the work on wires, further investigation could be carried out on using multiple wires together\textsuperscript{6} or using a titanium mesh\textsuperscript{39} to increase surface contact with treatment solution.

A thorough investigation of the photocatalytic behaviour of fluoride-free anodized TiO$_2$ has not been previously investigated. This study demonstrated the photocatalytic ability of the material, as well as confirming stability, reproducibility and reusability. It was found that annealing temperature could be used to tailor the photocatalytic activity of the material, which would in turn alter the ratio of anatase to rutile in the mixture. The highest photocatalytic activity at 700 °C, which contained 7 % rutile and 9 3% anatase. Further investigation could explore the effect of annealing temperature in small intervals after 700 °C, to determine at which point the activity starts to decrease. It was not possible to determine the specific surface area of the oxide layer produced in this study, which could have translated to photocatalytic activity. This could be approached using a method to absorb heavy metals (or less hazardous salts in the same oxidation state) to absorb onto the TiO$_2$ catalyst surface, thus producing a calibration curve between absorption and surface area. However it should be noted that TiO$_2$ measurements are less precise in comparison to ZnO.\textsuperscript{40,41}

All photocatalytic experiments were carried out in ultrapure water using model pollutants, carbamazepine and phenol, with the key by-products and pathways identified, as well as confirming these undergo transformation rather than mineralisation. Further research should use different water matrices such as ground water and treated wastewater.\textsuperscript{42,43} The
Chapter 4: Photocatalytic immobilised TiO$_2$ nanostructures

role of hydroxyl radicals has been defined in this system as the main degradation pathway, but other experiments into the role of the h$^+$, e$^-$ and superoxide scavengers would also increase understanding of the system.$^{44}$ As well as examine thoroughly the role of pH and additional gases to the reaction solution, to determine the impact upon photocatalysis activity.

Preliminary results suggest the nitrogen doping of TiO$_2$ is possible using a two-step anodization process, further investigation could be carried out into one-step anodization using other nitrogen precursors$^{32}$ or by longer immersion experiments (2 - 10 hours instead of 1 hour tested in this study).$^{45,46}$ In addition, the effect of calcination temperature on nitrogen incorporation could be investigated, as this has been shown to reduce the incorporation of nitrogen.$^{47,48}$ Once the optimisation of this method has been carried out then, the photocatalytic activity of the N-doped TiO$_2$ nanowires can be investigated using model pollutants. Previously it has been demonstrated that the addition of nitrogen to TiO$_2$ nanoparticles increased the degradation of phenol from 15% to 47%.$^{49}$
4.7 References


Chapter 4: Photocatalytic immobilised TiO$_2$ nanostructures


Chapter 4: Photocatalytic immobilised TiO₂ nanostructures


Chapter 5

Photocatalytic Activity of Titania Nanoparticles Produced via Membrane Emulsification-Precipitation

Part of the work presented in this chapter has been published to Industrial + Engineering Chemistry Research in April 2020.

5.1 Context

This chapter will discuss the photocatalytic activity and application of Titanium (IV) dioxide (TiO$_2$) nanoparticles to degrade phenol in a batch reactor under UV and Visible/UV conditions. The nanoparticles (NPs) used for photocatalytic experiments were developed and produced by Dr Maria Medina-Llamas (discussed in the Continuous production of titania nanoparticles via membrane emulsification – precipitation, Manuscript S1 and in the thesis, “High throughput manufacturing of nanoparticles by membrane emulsification-precipitation processes”). The aim of this study was to determine the photocatalytic ability of five different types of TiO$_2$ and TiO$_2$-Nitrogen NPs (four developed via membrane emulsification-precipitation and commercial TiO$_2$ Degussa P25 nanopowder), as well as determine the impact of the nitrogen doping of the TiO$_2$ upon photocatalytic effectiveness under both UV and visible-UV conditions. This chapter is divided into six different sections; chapter context (section 5.1), method and materials (5.2), photocatalytic activity (5.3) and chapter conclusions & further work (5.4). Bibliography (5.5) and supporting information for the chapter is provided in section 5.6.

5.2 Materials & Method

The following experiments were conducted to meet with the aims and objectives:

- Establish UV filter solutions for use with the medium pressure lamp (mercury for energy efficiency), to minimise the wavelengths below 400 nm and to compare UV and UV-Vis for excitation of the nanoparticles.
- Prepare NPs for use in photocatalytic reactor.
- Determine photocatalytic activity under different UV and visible light conditions and relate the activity to the NPs physical properties.

All chemicals and organic solvents were purchased from major supplies, unless otherwise stated. Titanium (IV) dioxide P25 nanopowder was purchased from Aldrich and had a particle diameter of 21 nm. Ultrapure water was supplied from a PURELAB®, ELGA LabWater purification system (18.2 MΩ cm) and used un-buffered. The particles photocatalytic activity was determined using a Peschl Ultraviolet slurry photocatalytic reactor (PhotoLAB, B400-700 Basic Batch-L) (shown in Figure 5.1) using either a low pressure (novaLIGHT LP30x, 2.7 emission at 254 nm) (UV) or medium pressure visible-UV (novaLIGHT TQ150 HG, 150 W broad band UV-visible emission spectrum) mercury
Heraeus Noblelight lamps (emission spectrum in Figure S2 and S3). The photocatalyst particles (0.07 – 0.14 g/L, with a particle diameter of 10.6 -11.4 nm) were suspended in 700 mL ultrapure water and sonicated for 24 hours prior to use and added to the photoreactor. Sonication was key to keep the photocatalyst nanoparticles in suspension and avoid a decrease in photocatalytic performance. Phenol stock solution was added to produce a 10 μM phenol solution to act as the model micropollutant. Experiments were conducted at 10°C and stirred. A sample was taken every six minutes for 60 minutes from the time of turning the UV lamp on. A sample was taken every 12 minutes for 120 minutes from the time of turning the visible-UV lamp on. These samples were then filtered with Durapore PVDF membrane 0.1 μm to remove photocatalyst particles. Samples were analysed via High Performance Liquid Chromatography (HPLC). HPLC was performed using a HPLC-UV Chromatograph (Agilent, series 1200) with a C-18 column (column Poroshell 120 EC-C18, 2.7 μm, 4.5 x 50mm). The conditions used were 20% MeCN and 80% 5mM phosphate buffer (1.5 mL H3PO4 in 1L UltraPure water), with a retention time of 10 minutes, flow rate of 0.5 mL/min and UV detection at 220 nm. When analysing the data, the rate of decay was calculated to be the gradient of the graph when decomposition began. Absorption and transmission spectra of the UV-filter solution, TiO2 nanoparticles (both in powder and in solution) was obtained by using a UV-Vis spectrophotometer (Cary 100).
When using the medium pressure lamp, a UV filter solution was used in the coolant circulating space between central lamp and the outer reactor chamber, to decrease the transmission of wavelengths below 370 nm the reaction solution absorbs. This UV filter was adapted from Wegelin et al., which consisted of 0.16 M NaNO$_2$ and 0.32 M NaNO$_3$, with a cut off at 370 nm. The original suggested coolant solution consisted of 0.05 M NaNO$_2$ and 0.25 M NaNO$_3$, however this concentration was increased to maximise absorption below 400 nm (shown in Figure 5.2).

**Figure 5.2:** The UV-visible absorption spectra of NaNO$_3$, NaNO$_2$ and composition mixtures. Sharp increase in absorption at 350 nm is due to experimental error caused by switching lamps in the UV-Vis spectrophotometer (Cary 100).

### 5.3 Photocatalytic Activity

For some experiments conducted in this study a different photoreactor with a stronger lamp had to be used (lamp emission spectrum in Figure S3). Initial experiments in this photoreactor using phenol and a broad-band medium pressure mercury lamp without filter solutions showed a very rapid degradation of phenol, resulting in complete degradation after 20 minutes (as shown in figure 5.3). The filter solution was used to reduce the UV emission from the medium pressure lamp, and the full photoprocess of the filter solution is described by Mack et al. The effectiveness of the UV filter coolant solution (0.16 M NaNO$_2$ and 0.32 M NaNO$_3$) in comparison to the suggested filter solution (0.05 M NaNO$_2$
and 0.25 M NaNO₃) and a unfiltered coolant solution, is shown in Figure 5.3, by the photolysis of phenol. The use of the suggested filter solution (0.05 M NaNO₂ and 0.25 M NaNO₃) resulted in complete degradation of 10 μM phenol after 108 minutes, therefore an increased concentration coolant was used (0.16 M NaNO₂ and 0.32 M NaNO₃) which results in 88% phenol degradation after 120 minutes. The concentration of nitrite and nitrate was not increased further, due to the toxicity and the staining nature of these compounds as well as the need to produce a large quantity of the coolant. Other examples of UV filter solutions include lead nitrate and sodium bromide⁴, however these were not used due to their hazardous nature and high concentrations required (3.16 M) respectively.² The nitrate (NO₃⁻)/nitrite (NO₂⁻) filter solution works best at UVA/B but served to attenuate some of the UVC-light (87% at 254 nm; 88% at 270 nm; 86% at 280 nm; 90% at 300nm [UVB]) responsible for direct photodegradation of phenol (absorption spectrum in Figure S1) in order to obtain a reasonable experimental time-scale for taking samples.

![Figure 5.3](image)

**Figure 5.3:** Ability of coolant solution (water, nitrite and nitrate) to filter UV wavelengths (below 400 nm), measured by degradation of phenol (10 μM) over two hours.

The reactor system is made of glass, so adsorption of phenol is unlikely to occur. During the initial experimental planning we also considered using a screen cooling mantle and other types of cooling solutions. However, the employed relatively weak nitrate/nitrite filter solution served the experimental purpose reasonably well. Also, this type of filter
solution is easy to dispose given that 5L of 1M or 2M concentration are needed because the filter solution runs through the cooling system of the reactor.

All UV experiments were carried out with 0.1 g TiO$_2$ nanoparticles per 700 mL reaction solution, and visible-UV experiments were conducted at 0.05 g/700 mL (0.14 g/L and 0.07 g/L respectively) due to limited amounts of photocatalyst available. Transmission spectra for the different photocatalyst concentrations indicated that there was little effect (< 10% difference) in light transmission (Figure 5.4), as a change in catalyst concentration can impact light transmission and scattering.

![Transmission spectra](image)

**Figure 5.4**: Impact of particle concentration (0.14 g/L and 0.07 g/L) upon transmission/%

The physical characteristics of the TiO$_2$ nanoparticles are shown in Table 5.1. The relationship between these physical properties, annealing temperature and photocatalytic activity were investigated in this study.
5.3 Photocatalytic activity

Table 5.1: Summary of physical properties of TiO$_2$ NPs and their annealing temperature; N-TiO$_2$ (nitrogen doped TiO$_2$) and TiO$_2$ (not doped).

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (at%)</th>
<th>C (at%)</th>
<th>Band Gap (eV)</th>
<th>Optical absorption threshold/nm</th>
<th>Surface Area/m$^2$ g$^{-1}$</th>
<th>Pore Volume/cm$^3$ g$^{-1}$</th>
<th>Pore size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (400°C)</td>
<td>-</td>
<td>18.2</td>
<td>2.76</td>
<td>449</td>
<td>89</td>
<td>0.102</td>
<td>3.40</td>
</tr>
<tr>
<td>N-TiO$_2$ (Dry)</td>
<td>4.61</td>
<td>7.44</td>
<td>3.39</td>
<td>366</td>
<td>468</td>
<td>0.168</td>
<td>2.91</td>
</tr>
<tr>
<td>N-TiO$_2$ (300°C)</td>
<td>0.87</td>
<td>20.0</td>
<td>2.05</td>
<td>604</td>
<td>351</td>
<td>0.157</td>
<td>3.02</td>
</tr>
<tr>
<td>N-TiO$_2$ (400°C)</td>
<td>0.40</td>
<td>18.9</td>
<td>2.23</td>
<td>555</td>
<td>208</td>
<td>0.238</td>
<td>3.44</td>
</tr>
<tr>
<td>P25 TiO$_2$</td>
<td>-</td>
<td>1.45</td>
<td>3.03</td>
<td>409</td>
<td>16</td>
<td>0.042</td>
<td>9.05</td>
</tr>
</tbody>
</table>

The nitrogen doping of TiO$_2$ NPs is shown in Table 5.1 by nitrogen context (%), which resulted in a band gap reduction and an increase in optical absorption threshold (nm). This should allow for the particles to be photoactive in a wider light spectrum.

It was found that with increasing annealing temperature reduced the band gap (eV) and leads to a reduction in nitrogen content, which is in agreement with the literature.$^{5,6}$ Increasing annealing temperature, also resulted in decreased surface area of the nanoparticles. This could be due to the bridges forming between the doped nitrogen, and the oxygen atoms present in the TiO$_2$ lattice, which help maintain a porous structure. However, with reducing nitrogen content, that structure is likely to collapse, leading to a reduced surface area (discussed further in manuscript S1 (section 5.6.1)). Annealing temperature has been shown to effect the degree of interstitial to substitutional, with increased temperature correlating with higher levels of interstitial nitrogen content.$^{7,8}$ However, it is unclear from the literature whether substitutional and interstitial cause the increase in photo activity.$^9$

No obvious relationship has found between annealing temperature and pore volume. The pore volume, or porosity, is the void spaces between the particles in contrast to the non-porous Degussa P25 TiO$_2$. If a sample demonstrates high porosity, this leads to a high surface area and high adsorptive capacity, which should result in increased photocatalytic
A positive correlation was found between pore size and increasing annealing temperature, which is in agreement with the literature.

Various studies have investigated the impact of physical material properties on photocatalytic activity. The most important parameters to influence the photocatalytic ability of TiO$_2$ were found to be the crystallinity of the material, and the ratio of anatase/rutile phases.

As can be seen in Figure 5.5, the results from UV were very similar so it was difficult to correlate any NPs characteristics with photocatalytic performance. There was very little difference between TiO$_2$ (400°C), N-doped TiO$_2$ (un-annealed) and N-doped TiO$_2$ (400°C annealed), all produced phenol degradation of 79 - 88%. Photolysis resulted in 87% degradation after 60 minutes, with all NPs increasing phenol degradation bar N-TiO$_2$ (300°C) which hindered it. It is expected that the un-annealed sample (N-TiO$_2$ (dry)) is not photoactive, however the least photocatalytic active sample investigated was N-TiO$_2$ (300°C). This is possibly due to the presence of organic residual impurities which act as hydroxyl scavengers, and are removed during calcination. It should also be noted that below 400°C calcination temperature the sample was not fully crystalline.

**Figure 5.5:** Photocatalytic degradation of phenol (10 μm) under UV-C conditions, using photolysis, Degussa P25 TiO$_2$, TiO$_2$ (400°C), N-TiO$_2$ (dry), N-TiO$_2$ (300°C) and N-TiO$_2$ (400°C), at 0.14 g/L during one hour.
To investigate the effectiveness of nitrogen doping, the TiO$_2$ NPs were investigated in the visible – UV spectrum (as shown in Figure 5.6). There was similar degradation for TiO$_2$ (400°C), N-doped TiO$_2$ (unannealed) and N-doped TiO$_2$ (300°C annealed), with phenol degradation at approximately 80-92% over two hours. The N-doped TiO$_2$ (400°C annealed) performed significantly better (100%) than TiO$_2$ (400°C), N-doped TiO$_2$ (unannealed) and N-doped TiO$_2$ (300°C annealed). In terms of VUV, there seems to be one clear trend with surface area and photocatalytic degradation. However the trend suggests increasing surface area, results in a reduced photocatalytic activity with the largest surface area particles (TiO$_2$ (400°C), N-doped TiO$_2$ (unannealed) and N-doped TiO$_2$ (300°C annealed), with 89, 468, 351 m$^2$ g$^{-1}$) producing the lowest degradation, while the best photocatalytic degradation was seen by P25 TiO$_2$ (surface area of 16 m$^2$ g$^{-1}$) and N-TiO$_2$ (400°C) (208 m$^2$ g$^{-1}$). It was expected that the larger surface area will lead to increased absorption onto the catalyst surface, and thus result increase degradation, however this was not demonstrated in this investigation.

![Photocatalytic degradation of phenol (10 μm) under UV-Visible conditions, using photolysis, Degussa P25 TiO$_2$, TiO$_2$ (400°C), N-TiO$_2$ (dry), N-TiO$_2$ (300°C) and N-TiO$_2$ (400°C), at 0.07 g/L during two hours.](image)

**Figure 5.6:** Photocatalytic degradation of phenol (10 μm) under UV-Visible conditions, using photolysis, Degussa P25 TiO$_2$, TiO$_2$ (400°C), N-TiO$_2$ (dry), N-TiO$_2$ (300°C) and N-TiO$_2$ (400°C), at 0.07 g/L during two hours.

For both cases, the commercial photocatalyst, Degussa P25 TiO$_2$, which was used as a benchmark for photocatalysis produced the fastest degradation. P25 TiO$_2$ particles are 21 nm in diameter, which are larger than the TiO$_2$ NPs produced in this case which are 13.4
nm for undoped and 11.4 unit for doped (the difference in size is a result of crossflow velocity during synthesis), and display a significantly smaller surface area (P25 is 16 m$^2$ g$^{-1}$) in comparison to (208 m$^2$ g$^{-1}$ for N-doped TiO$_2$ 400°C and 89 m$^2$ g$^{-1}$ for non-doped TiO$_2$ 400°C). This could be due to the P25 particles producing a much finer dispersion prior to PC reactions. During the PC reactions despite stirring, the synthesised NPs settled quickly. Also, it should be noted that Degussa P25 TiO$_2$ NPs are made up of both anatase and rutile crystal phases, while the synthesised NPs in this investigation only consisted of the anatase phase. As discussed in section 4.4.2, a mixture of anatase and rutile phases is beneficial to photocatalysis. Overall little correlation was found between physical properties tested and the photocatalytic behaviour of the particles (shown in Figure S4-S7). However, it should be noted that out of the particles synthesised in this investigation, the ones which displayed the largest surface area performed the best (TiO$_2$ 400 and N-TiO$_2$ 400°C) in both UV and visible-UV investigations.

The relationship between a materials physical properties and photocatalytic behaviour is complex. Previous studies have highlighted the offset between high surface area of particles, and the small particle size upon photocatalysis. Photocatalytic degradation relies on a combination of various parameters, such as surface area, band gap and porosity. Behnajady et al. enhanced photoactivity of synthesised TiO$_2$ NPs over commercial Degussa P25 NPs by increasing surface area and pore volume. Increasing calcination temperature was shown to reduce photocatalytic activity over 500°C, due to increased NP size leading to agglomeration of the NPs as well as leading to reduced pore volume. High calcination temperatures have been shown to reduce nitrogen doping in TiO$_2$ as the unstable nitrogen in the crystalline lattice will be oxidised, resulting in a reduced photoactivity. However, at low temperatures (< 200°C) absorbed water molecules on the catalyst surface limits the active sites. Thus, these conditions need to be optimised to produce the highest photocatalytic activity. At high calcination temperatures, there is also agglomeration of NPs, reducing surface area. A key synthesis parameter for photocatalysis, which was not investigated in this study, is pH. Madkour et al. found preparing TiO$_2$ NPs (via a hydrothermal route) at different pHs resulted in different properties. At high pH (7-10), the particles presented with a negative surface charge as

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1 It should be noted that P25 is reported to have a SSA of 50 m$^2$ g$^{-1}$, rather than 16 reported here.
5.3 Photocatalytic activity

well as increased surface area, thus increasing attraction between the particles and model pollutant leading to increased degradation. In the case of the positively charged surface (pH 1.6), electrostatic repulsion was dominant, leading to significantly reduced photocatalytic activity.
5.4 Chapter Conclusions & Further Work

The photocatalytic activity of four different TiO$_2$ nanoparticles (produced by membrane emulsification-precipitation) under UV and visible-UV light was investigated. In UV light, TiO$_2$ (400°C), N-doped TiO$_2$ (un-annealed) and N-doped TiO$_2$ (400°C annealed) produced similar degradation rates of phenol, most of the annealed NPs enhanced degradation in comparison to photolysis alone. Under visible-UV light, N-doped TiO$_2$ (400°C) performed significantly better than TiO$_2$ (400°C), N-doped TiO$_2$ (unannealed) and N-doped TiO$_2$ (300°C annealed). Thus, the nitrogen doping demonstrated the highest photocatalytic performance under UV-visible light conditions, of all the synthesised particles investigated. As no direct correlation could be found between physical properties of the TiO$_2$ NPs and photocatalytic activity, there must be an undetermined key parameter affecting their activity. Therefore, to understand the properties of the NPs further, Zeta potential should be measured to monitor surface charge and dynamic light scattering to determine the aggregation of the NPs.$^{20}$ This will determine if the aggregation of the particles is leading to flocculation and thus reducing the photocatalytic activity of the NPs.

Further work could also investigate the photocatalysis activity of TiO$_2$ NPs produced at higher (> 400°C) and lower (< 300°C) annealing temperature, to determine if any clear trend exists along the spectrum of temperatures. Other reaction parameters to be investigated include lowering catalyst concentration to define any differences between samples, as well as using compounds with higher photo-resistance such as primidone and carbamazepine to reduce the effect of photolysis.$^{21}$
5.5 References


5.6 Supporting Information


Figure S2. The UV emission spectrum for low pressure (novaLIGHT LP30s) lamp by Heraeus Noblelight
Figure S3. The visible/UV emission spectra for medium pressure (novalIGHT TQ150) lamp by Heraeus Noblelight
Figure S4. The correlation between photocatalytic degradation of phenol (10 μM) and: a) wavelength (nm), b) band gap (eV), c) pore size (nm) using photocatalytic particles (TiO$_2$ 400°C annealed, Nitrogen-doped TiO$_2$ unannealed, Nitrogen-doped TiO$_2$ 300°C annealed, Nitrogen-doped TiO$_2$ 400°C annealed and Degussa P25 TiO$_2$), under UV spectrum.
Figure S5. The correlation between photocatalytic degradation of phenol (10 μM) and: a) surface area (m$^2$ g$^{-1}$), b) pore volume (cm$^3$ g$^{-1}$) c) carbon content (C, at%) using photocatalytic particles (TiO$_2$ 400°C annealed, Nitrogen-doped TiO$_2$ unannealed, Nitrogen-doped TiO$_2$ 300°C annealed, Nitrogen-doped TiO$_2$ 400°C annealed and Degussa P25 TiO$_2$), under UV spectrum.
Figure S6. The correlation between photocatalytic degradation of phenol (10 μM) and: a) Nitrogen content (N, at %) b) wavelength (nm), c) pore volume (cm³ g⁻¹) using photocatalytic particles (TiO₂ 400°C annealed, Nitrogen-doped TiO₂ unannealed, Nitrogen-doped TiO₂ 300°C annealed, Nitrogen-doped TiO₂ 400°C annealed and Degussa P25 TiO₂), under visible-UV spectrum.
Figure S7. The correlation between photocatalytic degradation of phenol (10 μM) and: a) Band gap (eV), b) Surface area (m$^2$ g$^{-1}$), c) pore size (nm) using photocatalytic particles (TiO$_2$ 400°C annealed, Nitrogen-doped TiO$_2$ unannealed, Nitrogen-doped TiO$_2$ 300°C annealed, Nitrogen-doped TiO$_2$ 400°C annealed and Degussa P25 TiO$_2$), under visible-UV spectrum.
5.7 Appendix

Declaration
The work presented in the published paper was produced and written by Dr Maria Medina-Llamas with the exception of the following:

“Photoactivity of the produced TiO\textsubscript{2} nanoparticles” experimental data was produced, and the section written by Caitlin M. Taylor

Transmission electron microscopy data was collected by Dr Jing Ji

5.7.1 Published Manuscript

Continuous production of metal oxide nanoparticles via membrane emulsification - precipitation

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Keywords: membrane emulsification; nanoparticle synthesis; continuous manufacturing; photocatalysis

ABSTRACT: A continuous and scalable method to produce metal oxide nanoparticles (NPs) with control of both particle size and composition via membrane emulsification is reported for the first time using an oil-in-water emulsion and a tubular ceramic membrane ($D_{\text{pore}}=100$ nm). Using titania (TiO$_2$) NPs as a model material, a systematic investigation of different process parameters allowed minimising the emulsion droplet size, yielding a low droplet diameter to membrane pore diameter ratio of less than 3, compared to literature values of up to 10. After calcination, TiO$_2$ NPs as small as $10 \pm 2$ nm were obtained. The particles’ composition was changed via non-metal doping, with the incorporation of interstitial nitrogen and carbon in the TiO$_2$ lattice, confirmed by FTIR and XPS. The TiO$_2$ NPs showed to be active for the photocatalytic degradation of phenol under both UV and UV-visible light. Productivity calculations showed that it is possible to obtain $\sim 2$ kg of NPs per hour per meter squared of membrane, opening the way to the large-scale production of NPs with fine control over their size and composition.

1. INTRODUCTION

The large scale production of nanomaterials with tight control of desired properties remains the largest obstacle towards their more widespread use.$^1$ This is due to the fact that, at the nanoscale, both size and shape often determine function, e.g. as in the case of gold, which switches from an inert material to an active catalyst for particle sizes below 5-7 nm.$^2$ Surface chemistry and crystal structure also do affect properties, for instance the anatase phase of titania becomes more stable than rutile for particle sizes below $\sim 14$ nm.$^3$ However, conventional large-scale methods for materials manufacturing, including co-precipitation,$^4$ liquid-liquid interfacial reactions,$^5$ and emulsion-assisted synthesis,$^6$ do
not offer sufficiently tuned control to take advantage of the nanoparticles’ promising properties.\textsuperscript{7} In fact, nanomaterials currently used in industry, e.g. zinc oxide in sunscreens, tend to have very broad size and shape distributions.\textsuperscript{8} Other common methods, e.g. hydrothermal, solvothermal synthesis and thermal decomposition do offer a higher degree of uniformity in morphology but suffer from long reaction times and require moderate to high temperatures.\textsuperscript{9} Microwave-assisted synthesis results in the production of monodisperse NPs but is a difficult technology to scale-up due the limited penetration depth of the radiation into the reaction medium.\textsuperscript{10} In contrast to these technologies, many of the laboratory-scale methods that do offer fine control over the nanoparticles’ properties cannot be easily scaled-up due to high complexity and/or cost, e.g. physical vapour deposition.\textsuperscript{11} An ideal method would combine the best of both worlds, while also addressing manufacturing considerations, such as safe operation and waste minimisation.

Amongst the methods to produce NPs, liquid-liquid reactions at the interface of emulsions combine good morphology control with a relatively inexpensive process.\textsuperscript{12} Emulsions represent an appealing approach as a controlled amount of the reactant is confined within the emulsion’s droplet surrounded by surfactant molecules that prevent droplet coalescence. In turn, this results in a self-limited reaction, potentially leading to particles with low polydispersity.\textsuperscript{13} Hence, controlling the size of emulsion droplets and the amount of reactant in them, could allow controlling the size of the resulting NPs. However, emulsion size control in conventional emulsification methods, including rotor-stator, ultrasound systems and high-pressure homogenizers, is limited.\textsuperscript{14} These methods apply disruptive forces (cavitation, shear or turbulence) to break a coarse emulsion into finer droplets, requiring a high energy input of $10^6 - 10^8$ J m$^{-3}$, and lead to the production
of highly polydisperse emulsions.\textsuperscript{15} On the other hand, membrane emulsification (ME) allows the production of low polydispersity and even monodisperse emulsions,\textsuperscript{14} with lower energy requirements in the order of $10^3$ - $10^6$ J m$^{-3}$.\textsuperscript{15} Under this approach, the future dispersed phase is permeated through the pores of a membrane into a continuous phase under the driving force of a transmembrane pressure difference.\textsuperscript{16} The dispersed phase droplets will grow up at the edge of the pores and eventually detach due to a balance of forces between the shear stress produced by the continuous phase flow, the interfacial tension between the two immiscible phases and the transmembrane pressure. As the droplet is formed, the surfactant molecules in the continuous and the dispersed phases will diffuse to the \textit{water/oil} interface preventing coalescence. The characteristic feature of ME is the linear relationship between the average membrane pore diameter and the average droplet diameter:\textsuperscript{17}

\begin{equation}
D_d = cD_p
\end{equation}

where $D_d$ is the average droplet diameter, $D_p$ is the average membrane pore diameter and $c$ is a proportionality constant related to the membrane material. Typical values for $c$ are up to 10 for Shirasu Porous Glass (SPG) membranes, and can go up to 50 for other types of membranes.\textsuperscript{18} These values can be seen as a measure of the quality of the ME process, depending on process parameters (e.g. shear), physical and chemical properties (e.g. interfacial tension) and the regularity of the membrane pore structure.\textsuperscript{14} In particular for the latter, the narrower the membrane’s pore size distribution, the narrower the emulsion’s droplet size distribution. The authors have shown that anodic alumina membranes with very narrow pore size distribution can produce \textit{oil-in-water} emulsions with droplets in the nanometre range and $c$ values as low as 2-3.\textsuperscript{19,20} According to Darcy’s Law, there is a positive relationship between the flux of the dispersed phase and the transmembrane
pressure (TMP). The minimum TMP required to achieve the permeation of the dispersed phase through the pores of the membrane is called critical pressure ($P_{\text{crit}}$):

\[ P_{\text{crit}} = \frac{4\gamma}{D_p} \]  

(2)

where $\gamma$ is the interfacial tension, which can be controlled via the addition of surfactants in the continuous and/or the dispersed phases. The emulsion droplet size is the result of a balance between the transmembrane pressure and the shear generated by the flow of the continuous phase.\(^{21}\) As the average pore size of a membrane decreases, it is essential to lower the interfacial tension to avoid an increase in $P_{\text{crit}}$, which, in turn, would require a significant increase in the continuous phase flow velocity,\(^{22}\) resulting in a decrease in the emulsification’s productivity, i.e. the amount of dispersed phase in the continuous phase.\(^{20}\)

ME in batch process configuration has been successfully employed for the production of both polymeric\(^{23}\) and inorganic NPs. The latter include Ag, SiO$_2$, ZnO$_2$, TiO$_2$, and SiO$_2$ NPs.\(^{24-26}\) However, all the above relied on the use of water-in-oil emulsions, employing hydrophobized ceramic membranes. This approach not only requires the extra step of hydrophobising the membranes but, more importantly, produces large amounts of organic waste. As such, these methods have not yet seen any large-scale use. On the other hand, using oil-in-water emulsions would address both issues, provided suitable metalorganic precursors for the synthesis of NPs can be identified. In fact, this method has been extensively used to create polymer nanoparticles,\(^{27,28}\) though not for metal oxide ones. Recently, the authors have demonstrated the production of hematite NPs using an oil-in-water emulsion in a semi-continuous process, using a ME stirred-cell setup.\(^{29}\)
In the present work, the continuous production of titania nanoparticles, as a model material, using *oil-in-water* emulsions in a ME setup in a crossflow configuration is reported for the first time. Doping of the NPs during the synthesis process is also demonstrated as well as their use to degrade a model pollutant via photocatalysis.

2. MATERIALS AND METHODS

2.1. Membrane Emulsification Apparatus. Figure 1 shows a schematic of the ME rig, using a tubular ceramic membrane in a crossflow configuration. A picture of the ME rig can be found in Figure S1. The ME rig includes a continuous phase tank with a temperature controller (Grant). The dispersed phase was kept in a stainless-steel cylinder and was fed into the emulsification module using filtered compressed air via a two-stage pressure regulator (Swagelok). A pulse-less gear pump (Ismatec MPC-Z) was used to feed the continuous phase into the membrane’s bore. The membrane module and the ceramic membranes were purchased from Inopor. The tubular membranes are made of $\alpha$-Al$_2$O$_3$ with average pore size of 100 nm (see Table 1 and Figure S2 for details).

**Table 1.** Characteristics of membranes according to the manufacturer, Fraunhofer IKTS.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer diameter/mm</td>
<td>10 mm</td>
</tr>
<tr>
<td>Substrate</td>
<td>$\alpha$-Al$_2$O$<em>3$, $d</em>{50} = 3$ μm</td>
</tr>
<tr>
<td>Inner diameter/mm</td>
<td>7 mm</td>
</tr>
<tr>
<td>Membrane</td>
<td>$\alpha$-Al$_2$O$<em>3$, $d</em>{50} = 100$ nm</td>
</tr>
<tr>
<td>Membrane length/mm</td>
<td>250 mm</td>
</tr>
<tr>
<td>Filtration area/m$^2$</td>
<td>$5.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Prior to the emulsification, the $\alpha$-Al$_2$O$_3$ membranes were pre-soaked in the continuous phase using a sonication bath for 20 minutes. The membrane was installed in the module and the continuous phase crossflow velocity set. Next, the dispersed phase was delivered to the membrane module after extraction of air from the interior of the membrane module.
The dispersed phase pressure was then gradually increased until it reached the desired value. Then, the as-produced emulsion was collected in a glass container, discarding the start-up material. The performance of the ME rig was evaluated in terms of average emulsion droplet size and size distribution when parameters like crossflow velocity and transmembrane pressure were varied.

![Schematic of the membrane emulsification – precipitation apparatus.](image)

**Figure 1.** Schematic of the membrane emulsification – precipitation apparatus.

### 2.2. Synthesis of titanium oxide nanoparticles.

To produce TiO$_2$ NPs, titanium (IV) 2-ethylhexanoate, Ti(C$_8$H$_{15}$O$_2$)$_4$, Ti(EH)$_4$, was used as precursor and purchased from Alfa Aesar. Diocyl sulfosuccinate, commonly named docusate, (C$_{20}$H$_{37}$NaO$_7$S) was selected as surfactant in the dispersed phase due to its hydrophobic nature. Therefore, the dispersed phase consisted of 105 ml of a 33 % v/v Ti(EH)$_4$ in 1 % wt. diocyl sulfosuccinate in hexane. The continuous phase was a 2 % wt. sodium dodecyl sulfate (SDS) in DI Water. The resultant emulsion was collected in a glass container were NH$_4$OH was added dropwise using a pump, with a 10 % molar excess of NH$_4$OH based on the stoichiometric amount of Ti(EH)$_4$ added in the dispersed phase. The as-produced NPs were kept in a
gentle agitation for 24 h. After the synthesis, the NPs were immediately washed using four consecutive cycles of centrifugation and sonication in ethanol and water to remove any residual trace of the solvents used in the synthesis. Later the NPs were dried at 70 °C for 24 h and then calcined at different temperatures (200, 300 and 400 °C) using a heating ramp of 5 °C/min and 1 hour of dwell.

Non-metal doped TiO$_2$ NPs where produced using a similar procedure as the one described above with the addition of 8 g NH$_4$NO$_3$ prior to the addition of NH$_4$OH. The NPs were kept in a gentle agitation for 24 h. Finally, the NPs were dried and calcined using the same protocol as the undoped TiO$_2$ NPs. Titanium (IV) dioxide P25 nanopowder was purchased from Aldrich, with an average particle diameter of 21 nm, and used as a benchmark photocatalyst.

**2.3. Characterization.** TEM (JEOL-JEM-2100 Plus) was used to characterize the TiO$_2$ NPs. ImageJ was used to perform statistical image analysis of TEM micrographs to calculate average particle size. XRD diffraction patterns were obtained using a Bruker D8-Advance. A Raman spectrometer was used to characterize the samples (InVia, Reinshaw). The droplet size distribution of the emulsions was analysed by DLS with a detection angle of 173° (Zetasizer Nano-ZS, Malvern Instruments). The interfacial tension of the dispersed phase/continuous phase were measured using a goniometer (Dataphysics OCA20) based on the pendant drop method. The band gap of the TiO$_2$ NPs was obtained by measuring the reflection spectra using a UV-vis spectrophotometer (Cary 100). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific K-alpha+ spectrometer. Samples were analysed using a micro-focused monochromatic Al x-ray source (72 W) over an area of approximately 400 micrometres. Data was recorded at pass energies of 150 eV for survey scans and 40 eV for high
resolution scan with 1 eV and 0.1 eV step sizes respectively. Charge neutralisation of the sample was achieved using a combination of both low energy electrons and argon ions. Data analysis was performed in CasaXPS using a Shirley type background and Scofield cross sections, with an energy dependence of -0.6. The specific surface area and pore size distribution were characterized by analysing the N\textsubscript{2} adsorption and desorption isotherms obtained at 77 K using a micromeritics 3Flex equipment. Prior to these measurements, the TiO\textsubscript{2} NPs were degassed 23 °C for 300 min, after having reached a vacuum level of 0.067 mbar. The surface area of the materials was calculated using the Brunauer–Emmett–Teller (BET) equation, and pore-size distributions were determined using the Barrett–Joyner–Halenda (BJH) formula from the desorption branch.

2.4. Photocatalytic Activity. The photocatalytic activity (PCA) of TiO\textsubscript{2} NPs was investigated using a Peschl Ultraviolet photoreactor (PhotoLAB, B400-700 Basic Batch-L) equipped with either low pressure (novaLIGHT LP30x, 2.7 W emission at 254 nm) or medium pressure (novaLIGHT TQ150 HG, 150 W broad band UV-visible emission spectrum) mercury lamps, both Heraeus Noblelight. Photocatalytic experiments were conducted with 0.1 g (low pressure lamp) and 0.05 g (medium pressure lamp) of TiO\textsubscript{2} NPs dispersed in 700 mL (determined by reactor size) ultrapure water (MilliQ), respectively. 10 μM phenol was added as model pollutant. During irradiation the solution was magnetically stirred and maintained at 10 °C. For the medium pressure lamp, emission at wavelengths below 370 nm was minimised by using an aqueous nitrite/nitrate filter solution of 11 g/L NaNO\textsubscript{2} and 27 g/L NaNO\textsubscript{3} as the cooling solution circulating in the annulus between the central lamp and the outer reactor chamber.\textsuperscript{31} Ten samples at equidistant time intervals were taken for 60 minutes and 120 minutes for low pressure lamp and medium pressure lamp experiments, respectively. Subsequently, samples were
filtered with Durapore PVDF 0.1 μm membrane filters, stored at 4 °C and analysed within 24 h via High Performance Liquid Chromatography (HPLC). HPLC was performed with an Agilent, series 1100 machine with a Poroshell 120 EC-C18, 2.7 μm, 4.5 x 50 mm column. Isocratic conditions used for phenol detection were 15 % acetonitrile and 85 % 5 mM phosphoric acid (pH 2.4), flow rate of 0.5 mL/min and UV detection at 220 nm, at 8 minutes retention time.

3. RESULTS AND DISCUSSION

3.1. Oil-in-water emulsion production. Interfacial tension measurements (IFT) of the hexane/water system were carried for different surfactant concentrations (SDS) in the continuous phase (Figure 2a). SDS was selected as it has fast adsorption kinetics due to its low molecular weight (288 g/mol). In addition, the anionic nature of the SDS produces a faster detachment of the droplet, due to the electrostatic repulsion between the sulphate anion and the negatively charged functional groups at the membrane surface. The latter provides a net negative charge in the dispersed phase droplet, reducing droplet coalescence. The results in Figure 2a show that for concentrations higher than 0.5 % wt. SDS, the equilibrium IFT has been reached (3.5 ± 0.4 mN/m).
However, a higher value of 2 % wt. SDS was selected, as previous reports using ceramic membranes with pores ranging from 0.1 to 0.8 µm use 2 % wt. SDS as optimal concentration under a wide range of surfactants.\textsuperscript{34, 35} Such higher value is needed to prevent coalescence: In ceramic membranes, emulsion polydispersity does not originate from the coalescence of the droplets after they are formed, but rather from coalescence when the droplets are being formed on the membrane surface.\textsuperscript{34} This is due to the droplet formation mechanism, with dispersed phase droplets forming in the voids between the small sintered alumina particles of which the membrane is made of (Figure S2).\textsuperscript{36} The small spacing between these voids requires a very fast reduction of the IFT to avoid droplet coalescence and prevent the dispersed phase from wetting the membrane surface when adjacent droplets are growing.\textsuperscript{32} This phenomenon will be further enhanced by the significantly smaller membrane pore size (100 nm) and higher porosity (0.45-0.55) of the membranes used here, compared to the SPG ones typically used in the literature.\textsuperscript{17} As such, an additional surfactant (dioctyl sulfosuccinate) was incorporated in the dispersed
phase, to obtain an even faster reduction of the IFT. This resulted in a further reduction to 0.70 ± 0.1 mN/m when 1 % wt. was added to the dispersed phase (Figure 2a).

With these surfactant conditions, the calculated critical pressure is 28 kPa (Eq. 2). Membrane emulsification experiments were carried out at two different transmembrane pressure values, which correspond to x2 and x3 times the critical pressure, respectively, for different crossflow velocities. The results in Figure 2b show a decrease in droplet size and narrowing of the droplet size distribution as the crossflow velocity increases for both transmembrane pressure values, with the sharpest decrease at the lowest shear stress, where a 52 % droplet size reduction is observed when the crossflow velocity is increased from 0.2 to 0.3 m/s. The latter behaviour is a consequence of the higher shear stress produced by the recirculation of the continuous phase producing an earlier droplet detachment.\(^{37}\) At higher values of the crossflow velocity the droplet size becomes independent of the shear stress, a trend previously reported for crossflow ME,\(^{17}\) and an effect of the inverse quadratic dependence of droplet diameter with wall shear stress.\(^{21}\) In addition, a positive relation is observed between the droplet size and the transmembrane pressure, due to an increase in the inertial force on the dispersed phase and resulting in the formation of larger droplets.\(^{22}\) Reported values of the optimum ratio of transmembrane pressure to capillary pressure are between 2.6 to 3.5.\(^{16}\) In addition, Figure 2c shows the ratio of the droplet size to pore size, \(c\), which is a common parameter to evaluate the performance of a ME setup under specific conditions. The \(c\) values of 2-3 obtained here for the highest crossflow velocities are indicative of the production of high quality emulsions (i.e. with narrow size distribution), compared to higher values reported in the literature for ceramic,\(^{38}\) and SPG membranes.\(^{17}\) This is further confirmed by evaluating the Euler number (\(Eu\)), defined as the ratio of pressure to inertial forces, the former
determined by the injection of the dispersed phase and the latter one by the crossflow velocity of the continuous phase, $v_c$:\textsuperscript{19}

$$Eu = \frac{\Delta P}{\rho_c v_c^2}$$  

(3)  

where $\rho_c$ is density of the continuous phase, $v_c$ is the crossflow velocity and $\Delta P$ is the transmembrane pressure. This dependence is shown in Figure 3a. For both transmembrane pressure values, a decrease in the $D_d/D_p$ ratio is observed when the Euler number decreases (due to its inverse relation with the crossflow velocity).

In a membrane emulsification setup operating in a crossflow configuration, the shear stress can be calculated from the correlation friction factor ($f$) as:\textsuperscript{21}

$$f = \frac{2\tau}{v_c^2 \rho_c} = \begin{cases} 
\frac{16}{Re} & Re < 500 \\
0.0792Re^{-1/4} & 500 \leq Re \leq 20000
\end{cases}$$  

(4)  

where $\tau$ is the shear stress and $Re$ is the Reynolds number. The former parameter allow estimating the average droplet size using the following droplet size estimation model:\textsuperscript{20}

$$\left[6k_x\pi^2 h^2 + \frac{4}{3}\pi r^3 (\rho_c - \rho_d)g\right]h = 2\pi \gamma r_p^2$$  

(5)

$$\frac{4}{3}\pi r^3 = \frac{\pi}{6} h(3r_p^2 + h^2)$$  

(6)

where $k_x$ is the wall correction factor, $h$ is droplet height, $r$ is the estimated radius droplet, $g$ is gravitational constant, $r_p$ is the pore radius and $\rho_d$ is the density of the dispersed phase, respectively. Figure 3b shows that the predicted droplet size values tend to converge at higher crossflow velocities, with an overestimation of 99 % at 0.6 m/s. While this number...
might seem large, the authors have previously shown that other droplet size estimation models available in the literature lead to overestimation of up to 600 %.  

Figure 3. a) Droplet diameter to pore diameter vs. Euler number for emulsions produced at two different transmembrane pressures and b) comparison between a droplet size estimation model from the literature and the experimental data for a emulsions prepared using a tubular ceramic membrane, \( D_p = 100 \text{ nm} \), 56 kPa. The Peng Lee model is described in ref.  

3.2. Production of TiO\(_2\) nanoparticles. TiO\(_2\) NPs were produced at three different crossflow velocities, 0.4, 0.5 and 0.6 m/s using a constant transmembrane pressure of 56 kPa. They are produced by a single emulsion mechanism, whereby the metalorganic precursor, Ti(EH)\(_4\), is solubilized in the dispersed phase droplets, with the surfactants acting as a protective layer to avoid droplet coalescence. The subsequent addition of \( \text{NH}_4\text{OH} \) to the emulsion and its diffusion to the core of each dispersed phase droplet lead to the formation of nanoparticles by intramicellar nucleation and particle growth mechanisms. As the concentration of the precursor is finite in the droplet, the reaction will terminate once it has all reacted. This leads to a narrow particle size distribution, provided the droplets, acting as a reactor, have a narrow size distribution themselves.
The resulting NPs were characterized by XRD and TEM after calcination at 400 °C. XRD diffraction patterns confirm the presence of anatase as the crystal phase (Figure S3a). The average crystal size was calculated using Scherrer equation using the highest intensity peak, facet (101), Table 2.

**Table 2.** Crystal size for TiO$_2$ NPs from XRD data as a function of crossflow velocity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crossflow velocity (m/s)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (400 °C)</td>
<td>0.4</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>9.7</td>
</tr>
<tr>
<td>N-TiO$_2$ (400 °C)</td>
<td>0.5</td>
<td>11.4</td>
</tr>
</tbody>
</table>

The results, showing a decrease in the crystal size as crossflow velocity increases, are due to the smaller amount of reactant in the emulsion droplet as the average droplet size decreases with increasing crossflow velocity (cfr. Figure 2b). Figure 4a and 4b show TEM micrographs of the doped ($\bar{D}_p = 12.8 \pm 2.6$ nm) and un-doped ($\bar{D}_p = 10.5 \pm 2.4$ nm) TiO$_2$ NPs synthetized at 0.5 m/s, with the results in good agreement with XRD. Figure 4c shows the particle size distribution from a statistical image analysis of TEM micrographs. An FFT analysis returned a d-spacing value of 0.35 nm which corresponds to anatase.
Further results, for both un-doped and doped samples, are here reported only for a crossflow velocity of 0.5 m/s.

**Figure 4.** TEM micrographs of a) doped and b) un-doped TiO$_2$ nanoparticles produced at a crossflow velocity of 0.5 m/s and calcined at 400 °C for 1 h. Average particle size for doped and un-doped NPs is $\bar{D}_p = 12.8 \pm 2.6$ nm and $\bar{D}_p = 10.5 \pm 2.4$ nm, respectively; c) particle size distribution from statistical image analysis of TEM micrographs.

The obtained NPs were calcined at different temperatures and further characterized. First, FT-IR was conducted to assess the incorporation of nitrogen in the TiO$_2$ when NH$_4$NO$_3$ was added (Figure S3b). A strong peak at 1383 cm$^{-1}$ is observed for the non-metal doped NPs (labelled as N-TiO$_2$) which has been attributed to the presence of nitrate groups.$^{41}$ The FT-IR spectrum of the N-TiO$_2$ show a decrease in the nitrogen content within the TiO$_2$ matrix as the calcination temperatures increases, with the highest concentration for the sample calcined at 200 °C, and only a small peak observed for the N-TiO$_2$ sample calcined at 400 °C. The same peak is absent from the un-doped sample, TiO$_2$ (400 °C). In addition, the peak observed around 540 cm$^{-1}$ is assigned to the stretching vibration of the Ti-O bond from the [TiO$_6$] octahedron,$^{42}$ while the peak at 1644 cm$^{-1}$ corresponds to the -OH bending vibration of absorbed water molecules. XPS analysis was conducted to investigate the composition and bonding of the TiO$_2$ and the N-TiO$_2$ NPs. The global
XPS profile for all the samples is shown in Figure 5a. The results show the successful incorporation of nitrogen and carbon within the TiO$_2$ matrix, both of which are well known non-metal doping elements.$^{43}$

For a further analysis, the chemical structure of the TiO$_2$ samples was examined in four specific areas of the XPS spectrum: In the first region from 280 to 292 eV, corresponding to the C $1s$ core level, a similar profile was observed for the four samples with a broad peak centred around 285 eV (Figure 5b): This can be de-convoluted in a main peak at 284.8 eV associated with carbon residue from SDS on the surface of the titanium oxide,$^{44}$ and a shoulder at 286.3 eV associated to carboxylic groups from the organometallic precursor.$^{45}$ No peak at 281.9 eV ascribed in the literature to C $1s$ core level from Ti-C, resulting from the substitution of O by C in the TiO$_2$ lattice,$^{46}$ was observed here. Figure 5.
5c shows the region corresponding to the N 1s core level for all the samples. The N-TiO₂ NPs have a distinctive peak close to 400 eV, assigned to interstitial nitrogen compounds in the form of NOx, NHx or chemisorbed N₂.⁴⁷ To further understand the nature of the nitrogen incorporation in the TiO₂ network, the Ti 2p₃/2 and 2p₁/2 core levels, located at 464 and 458 eV, respectively, were also investigated (Figure 5d). The peak separation for all the samples is ~5.7 eV, which indicates titanium atoms have +4 as oxidation state,⁴⁸ and confirms that nitrogen incorporation into the TiO₂ lattice is interstitial, as it did not cause a reduction in the oxidation state of titanium to Ti⁺³ (when N substitutes a O in the TiO₂ lattice, O-Ti-N). The concentration of nitrogen and carbon in the TiO₂ matrix has an inverse correlation with the calcination temperature (Table 3), results in good agreement with FT-IR experiments and the literature.⁴⁵

The optical properties of the TiO₂ NPs were evaluated by diffuse reflectance UV-Vis spectroscopy. The raw data % reflectance against wavelength can be found in Figure 6a, while Figure 6b shows the band gap, derived from extrapolation of the linear section of the modified Kulbelka-Munk function against energy. The values were 3.03 eV (409 nm) for a commercial TiO₂ NPs; 2.76 for the un-doped TiO₂ (400 °C) NPs; and 2.12, 2.05 and 2.23 eV, which correspond to 584, 604 and 555 nm for the N-TiO₂ NPs calcined at 200, 300 and 400 °C, respectively (Table 3). The experimental results indicate a reduction of up to 1.06 eV in the band gap due to the incorporation of N and C during the synthesis, in agreement with literature on non-metal doping of titania.⁴⁹
Chapter 5: Photocatalytic Activity of Titania Nanoparticles

Figure 6. Diffuse reflectance spectra of the TiO$_2$ and N-TiO$_2$ NPs a) F(R) versus wavelength b) modified Kubelka-Munk function, [F(R)hv]$^{1/2}$, against energy of the absorbed light.

The as-produced titania particles as well as those calcinated at 200 and 300 °C showed poor crystallinity, with distinct Raman peaks for anatase and rutile (Figure S4), with each phase confined into localized structures that are interconnected with each other in the framework. However, once the sample was calcined at 400 °C, with or without non-metal doping, only the peak for anatase was observed (Figure S4).

The surface area of the undoped and doped samples was also measured, showing an expected negative correlation between the surface area and the calcination temperature (Table 3). Interestingly, the surface area after calcination at 400 °C decreased 79 % for the undoped TiO$_2$ NPs, while a smaller decrease of 56 % was observed for the N-TiO$_2$ NPs. A possible explanation for the former behaviour is that interstitial non-metal doping agents helped reduce the collapse of the porous structure due to the formation of linkages between the non-metal doping agents and the oxygen atoms in the TiO$_2$ lattice. A similar trend was observed when nitrogen and sulphur were used as doping agents during the synthesis of TiO$_2$ NPs. The nitrogen adsorption-desorption isotherms of the TiO$_2$ NP
calcined at 400 °C can be found in Figure S5. Type IV isotherms are obtained, with the sharp decline in the desorption curve indicative of mesoporosity, while the hysteresis formed is a H2 type, which is an indicative of a non-uniform pore size.\textsuperscript{53}

### Table 3. Summary of physico-chemical properties of produced TiO\textsubscript{2} nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (at%)</th>
<th>C (at%)</th>
<th>Band gap (eV)</th>
<th>Optical abs. threshold (nm)</th>
<th>Surface area (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Pore volume (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>0.52</td>
<td>8.01</td>
<td>3.18</td>
<td>390</td>
<td>429</td>
<td>0.140</td>
<td>2.77</td>
</tr>
<tr>
<td>TiO\textsubscript{2} (400 °C)</td>
<td>n.d.</td>
<td>18.2</td>
<td>2.76</td>
<td>449</td>
<td>89</td>
<td>0.102</td>
<td>3.40</td>
</tr>
<tr>
<td>N-TiO\textsubscript{2}</td>
<td>4.61</td>
<td>7.44</td>
<td>3.39</td>
<td>366</td>
<td>468</td>
<td>0.168</td>
<td>2.91</td>
</tr>
<tr>
<td>N-TiO\textsubscript{2} (200 °C)</td>
<td>1.29</td>
<td>21.8</td>
<td>2.12</td>
<td>584</td>
<td>438</td>
<td>0.295</td>
<td>2.78</td>
</tr>
<tr>
<td>N-TiO\textsubscript{2} (300 °C)</td>
<td>0.87</td>
<td>20.0</td>
<td>2.05</td>
<td>604</td>
<td>351</td>
<td>0.157</td>
<td>3.02</td>
</tr>
<tr>
<td>N-TiO\textsubscript{2} (400 °C)</td>
<td>0.40</td>
<td>18.9</td>
<td>2.23</td>
<td>555</td>
<td>208</td>
<td>0.238</td>
<td>3.44</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>n.d.</td>
<td>1.45</td>
<td>3.03</td>
<td>409</td>
<td>16</td>
<td>0.042</td>
<td>9.05</td>
</tr>
</tbody>
</table>

n.d. = not detected

### 3.3. Photoactivity of the produced TiO\textsubscript{2} nanoparticles. Photocatalytic degradation experiments using phenol as a model pollutant were carried out for the TiO\textsubscript{2} and N-TiO\textsubscript{2} NPs and their performance compared to commercial TiO\textsubscript{2} NPs (P25). Figure 7a and Figure 7b show the % phenol degradation for each photocatalyst under UV and Visible light conditions, respectively.
Figure 7. Photocatalytic degradation of phenol under a) UV-C using a low-pressure lamp and b) UV-Visible medium pressure lamp (peak emissions 370 nm, 550 nm & 575 nm).

Under 254 nm UVC-light (Figure 7a) all materials except N-TiO$_2$ (300 °C), despite similar reflectance spectra, showed an increased removal for phenol compared to its direct photodegradation (80%). For experiments with the medium pressure lamp (Figure 7b), which employed a UV filter solution of NaNO$_2$/NaNO$_3$ to eliminate most light below 370 nm, all materials, including undoped TiO$_2$ NPs showed removal of phenol that was much higher, than its direct photodegradation (37%) under the same conditions. The photocatalytic activity of the undoped TiO$_2$ NPs in the visible range can be explained by the emission spectrum of the lamp used (novaLIGHT TQ150 HG) which has a wide range of wavelengths, from visible to the UV.  

Although the commercial titania did outperform the nanoparticles prepared here, the results in Figure 7 clearly demonstrate that continuous membrane emulsification can indeed produce TiO$_2$ NPs whose photocatalytic activity can be controlled via controlling the process parameters: Whereas the as-synthesized, undoped TiO$_2$ particles have no detectable photocatalytic activity, as expected, the same particles annealed at 400 °C, have high pseudo-first-order reaction rate constant ($k_{app}$) and reaction rate ($r_o$) in the UV
range (Table 4). In the visible range, the N-doped particles annealed at 400 °C, significantly outperform all other NPs, including those without nitrogen doping but annealed at the same temperature TiO$_2$ (400 °C), and those with nitrogen doping, but annealed at a lower temperature N-TiO$_2$ (300 °C). The stronger performance of the N-TiO$_2$ NPs when visible light is irradiated might be due to a combination of factors: First, the formation of highly crystalline NPs, as demonstrated by XRD and Raman experiments; second, the band gap reduction (cfr. Table 3) expands PCA to a wider wavelength spectrum; finally, a higher surface area which might facilitate the adsorption of reactants (Table 3). 

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV</th>
<th>UV-Visible</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{app}$</td>
<td>$r_o$</td>
</tr>
<tr>
<td></td>
<td>(1/min)</td>
<td>(µM/min g$_{cat}$)</td>
</tr>
<tr>
<td>TiO$_2$ (400 °C)</td>
<td>0.036</td>
<td>3.58</td>
</tr>
<tr>
<td>N-TiO$_2$</td>
<td>0.035</td>
<td>3.5</td>
</tr>
<tr>
<td>N-TiO$_2$ (300 °C)</td>
<td>0.017</td>
<td>1.7</td>
</tr>
<tr>
<td>N-TiO$_2$ (400 °C)</td>
<td>0.033</td>
<td>3.3</td>
</tr>
<tr>
<td>P25</td>
<td>0.224</td>
<td>22.3</td>
</tr>
</tbody>
</table>

**Table 4.** Photocatalytic rate constant ($k_{app}$) and reaction rate ($r_o$) of the TiO$_2$ NPs.

**3.4. Productivity and scale-up.** The productivity of the NPs production was calculated starting from the flow rate of the dispersed phase, the amount of titanium ions in the dispersed phase and the area of the porous section of the membrane. Assuming (i) that each droplet will convert into one titania NP, and (ii) 100% conversion of the titanium precursor to titania as per the reactions:
Chapter 5: Photocatalytic Activity of Titania Nanoparticles

\[ Ti(EH)_4 + 4NH_4OH \rightarrow Ti(OH)_4 + 4NH_4EH \]  
(7)

\[ Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \]  
(8)

the mass of titania NPs particles produced in one hour per square metre of membrane is \( \sim 2.8 \text{ kg h}^{-1} \text{ m}^2 \). Details of the calculations can be found in Table S1. Assuming there will be losses associated to fouling or agglomeration, a more conservative production rate of 2 kg of NPs per hour per \( \text{m}^2 \) of membrane is assumed here. Nonetheless, such a value for the production rate of NPs with the narrow size distribution shown here would open the way to the large-scale manufacturing of NPs with fine control over their properties. In terms of process scale-up, the washings and calcination steps employed here are routinely performed in continuous using conveyor-based systems, as done e.g. in the mining industry.\(^{57}\)

4. CONCLUSIONS

We report for the first time, the synthesis of TiO\(_2\) NPs, by producing oil-in-water emulsions in a continuous membrane emulsification setup. Titania was selected as a model material due to its large commercial use. Different crossflow velocities and transmembrane pressures were evaluated, resulting in a positive correlation between the droplet size and the pore size with proportionality constant values ranging from 2.3 to 5.8. In addition, a positive correlation was observed between dispersed phase droplet size and TiO\(_2\) particle size, with values ranging from 9.7 to 13.4 nm. Highly crystalline anatase NPs were produced after calcination at 400 °C. FT-IR and XPS results demonstrated the successful incorporation of interstitial nitrogen and carbon in the TiO\(_2\) lattice, resulting in a net reduction up to 1.06 eV in the band gap and thus the formation of TiO\(_2\) NPs with photocatalytic response in the UV-visible light spectrum. Based on the calculation of the
NPs production rate, this manufacturing method can produce up to 2 kg of NPs per hour per metre square of membrane. Taken together, these results open the way to using continuous membrane emulsification to produce titania nanoparticles with tight control over average size and photocatalytic activity and possibility of tailoring these properties to specific applications.

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The authors declare no competing financial interest.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Image of the membrane emulsification rig (Figure S1), cross section of the tubular alumina membrane (Figure S2), XRD and FT-IR of the TiO$_2$ NPs (Figure S3), Raman of the TiO$_2$ NPs (Figure S4), nitrogen adsorption-desorption isotherms (Figure S5) and productivity calculation for the ME setup (Table S1).

REFERENCES


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Chapter 6

Conclusions
Chapter 6: Conclusions

6.1 Context
This thesis has investigated the sustainable synthesis and activity of nanostructured photocatalysts, designed for micropollutant removal from wastewater. The work has focused on immobilized TiO$_2$ and ZnO photocatalysts, produced via the electrochemical method, anodization. This work has aimed to examine the effectiveness of a metal wire as an alternative to the conventional flat films (section 6.2), as a support for the photocatalysis. This includes the development of the synthesis method and material characterization (6.3). The materials photocatalytic activity was investigated by the degradation of model micropollutants (6.4), and further methods were examined to enhance the activity and stability of the photocatalytic material (6.5). Also investigated in this thesis, was the photoactivity of TiO$_2$ and nitrogen doped TiO$_2$ nanoparticles, and the correlation between their physical parameters and photoactivity (6.6).

6.2 Photocatalyst wire support
This thesis showed that both titanium and zinc wires could be effectively used as the support for an immobilized photocatalyst, where the titanium dioxide and zinc oxide respectively is anodized onto the surface. This required the development of an in-flow anodization rig, to reduce electrolyte use and not require the wire to be deformed. The wire in comparison to the conventional flat film, demonstrated higher surface area and reduced waste of material.

6.3 Synthesis conditions
Anodization conditions for ZnO have been investigated previously, however the change from Zn film to Zn wire, required changes to anodization conditions due to different physical properties of the material. Potassium bicarbonate was used to anodize a ZnO layer, however the pre-treatment of electro-polishing which is usually used to remove native oxide layers on metals was found to cause brittleness.

Regarding TiO$_2$, this usually requires hazardous anodization conditions involving fluoride based electrolytes upon flat films. This study investigated the use of mild anodization conditions, including chloride and bromide-based electrolytes with ethylene glycol as an additive. It was found that chloride electrolytes caused severe corrosion, but oxide layers could be produced using potassium bromide and ethylene glycol. Varying
6.4 Photocatalytic Activity and Key Parameters

the electrolyte composition altered the nanostructures which formed. Temperature was found to be another key reaction parameter, with optimum formation of the oxide layer at low temperatures (0 °C). In both cases, post-thermal annealing was found to be vital, while pre-thermal treatment increased the brittleness and fragility of both the titanium and zinc wire. The materials produced were characterized using a variety of techniques such as XRD, XPS and SEM, which showed ZnO to consist of nanowires and TiO₂ to consist of nanocuboids.

6.4 Photocatalysis activity and key parameters

The photocatalytic activity of the materials was investigated by monitoring the degradation rates of model micropollutants, carbamazepine and phenol, under the UV-C spectrum. An in-flow tubular photoreactor was developed to enhance irradiation conditions. The ZnO wire allowed for increased UV radiation onto the catalyst surface as well as increased mass transfer between the reaction solution and catalyst solution in comparison to flats films, which resulted in an increase in photocatalytic activity of 57% from 19% phenol degradation respectively. The anodization time was found not to impact the photocatalytic activity, despite producing different nanostructures.

The ratio of crystal phases; anatase to rutile in TiO₂ was dependent on the annealing temperature. The highest photocatalyst efficiency was found at 700 °C annealing temperature, with degradation rates of 83 % and 61 % for carbamazepine and phenol, respectively. The use of hydroxyl scavenger, methanol was used to determine the role of direct or indirect oxidation, which showed that indirect oxidation was the main pathway for pollutant degradation. Total organic carbon (TOC) measurements showed that the micropollutants were undergoing oxidative transformation rather than mineralization.

Another key parameter in the reactor was highlighted to be the flow rate of the system, which would affect the rate of absorption on to the catalyst surface and thus impact the rate of degradation.

6.5 Enhancing stability and activity

Zinc oxide is prone to photocorrosion leading to instability, which has prevented it being used widely. The addition of oxygen to the reservoir solution increased photocatalytic activity, reduced zinc leaching into solution and enhanced nanostructure growth. The
passing of current through the photocatalyst metal core was investigated to increase photocatalytic efficiency by minimizing electron/hole recombination, increasing potential direct oxidation as well as altering the wettability of the catalyst surface, however an increase in activity could not be shown. Preliminary results suggest a two-step anodization process could successfully dope TiO₂ with nitrogen, which can enhance the photoactivity of the material under the visible light. This process and the activity of the material needs to be examined further and optimized.

6.6 Photocatalytic activity of TiO₂ Nanoparticles
The photocatalytic activity of titania nanoparticles produced via membrane emulsification – precipitation was investigated as part of this thesis (chapter 5). The photocatalytic activity of five different nanoparticles (some of which were nitrogen doped); TiO₂ (400°C), Nitrogen-TiO₂ (dry), N-TiO₂ (300°C), N-TiO₂ (400°C) and commercial, Evonik Aeroxide P25 TiO₂, was examined under UV and visible-UV light. Under UV light, all synthesized nanoparticles presented similar phenol degradation rates, increasing in comparison to photolysis alone (apart from N-TiO₂ (300°C)). Under visible-UV light irradiation, the N-doped TiO₂ (400°C) performed the best, despite having the smallest surface area. There was no clear trend between physical properties and the photocatalytic behavior of the nanoparticles found in this study. There needs to be further investigation to determine the relationship between physical properties and the photocatalytic activity of these nanoparticles.

This thesis has demonstrated the viability and effectiveness of using an anodized wire for a photocatalyst. It has shown that TiO₂ and ZnO anodized wires can be produced using mild anodization conditions, and that synthesis parameters can be used to tailor the photoactivity of the material. The development of a tubular photoreactor demonstrated the efficiency of these wire photocatalyst over conventional flat films and highlighted how key reactions parameters can be used to enhance performance of photocatalytic materials.