



<http://researchspace.auckland.ac.nz>

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the [Library Thesis Consent Form](#) and [Deposit Licence](#).

Note : Masters Theses

The digital copy of a masters thesis is as submitted for examination and contains no corrections. The print copy, usually available in the University Library, may contain corrections made by hand, which have been requested by the supervisor.

Characterisation of Semi-Conductor Zinc Oxide (ZnO) thin films as Photocatalysts

Arshid Mahmood Ali

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, the University of Auckland, 2011.

Abstract

The objective of this project was to study the suitability of nanostructured ZnO thin films as efficient photocatalysts and to characterise any issues that may be involved in the scale-up of photocatalytic systems based on these types of immobilised nanostructure ZnO thin films. In particular, this study involved fabricating and then evaluating the effectiveness of a range of nanostructured zinc oxide (ZnO) thin films with different structures and chemistries (i.e. undoped and doped) as photocatalysts, and thereafter to systematically relate: the initial and reacted surface morphology; photocatalytic activity in terms of reaction rate; reaction intermediates and products; and liquid phase and solid phase reaction mechanisms under both limited and rich oxygen conditions at two different UV irradiation wavelengths (254nm and 340nm). These nanostructured thin films (i.e. undoped ZnO; nitrogen doped ZnO – N:ZnO; cobalt doped ZnO – Co:ZnO) were produced using an innovative combination of magnetron sputtered surfaces and hydrothermal solution deposition that allows the morphology, porosity and thickness to be controlled by varying the composition and processing conditions. SEM, UV-Vis, HPLC, LC-MS, AAS and XRD were used to study the changes in thin film morphology, Methylene Blue (MB) degradation and its reaction intermediates, the presence of Zn metal in the reaction fluid, if any, and crystallinity before and after the photocatalytic reaction respectively.

Undoped ZnO thin films: Results showed a clear relationship between surface morphology (and the related thin film preparation method) and photocatalytic activity for the ZnO thin film supported catalysts: the tallest, most aligned structure had the highest photocatalytic activity, whilst the smallest, least aligned structure had the lowest. Thus, the MB degradation rate was the fastest for the ZnO thin film (S2-MS) with a uniform arrayed structure. Adding oxygen made the films more stable: in oxygen-limited conditions, SEM and atomic absorption spectroscopy indicated zinc leaching had occurred. Furthermore, with additional oxygen the zinc leaching was minimised under the same reaction conditions. It is thought that this additional oxygen is either minimising the release of, or replacing lost ZnO lattice oxygens, indicating that this ZnO photocatalytic oxidation could be occurring via a Mars van Krevelen type redox mechanism.

There was also a significant difference in MB degradation rates, as well as reaction intermediate formation and destruction rates, correlated to the morphologies and crystallinity at both UV wavelengths, with the highest reaction rates at 340nm. Reaction analysis indicates that there is a competition between two different photocatalytic mechanisms: conventional photocatalysed radical oxidation and lattice oxygen-driven oxidation. The dominant reaction mechanism depends on the thin film morphology, crystallinity, availability of oxidant and the wavelength of the incident UV. The surface-photocatalysed radical formation was predominant for more aligned, highly crystalline, morphologies, where there was plentiful oxygen and UV irradiation at 340nm. Lattice oxygen photodegradation was predominant for the less aligned, more amorphous morphologies and UV irradiation at 254nm.

Doped (Co:ZnO) thin films: Results showed that cobalt dopant increases the photo-stability of the corresponding undoped thin films under oxygen-limited conditions – increasing with the increased dopant concentration. This increased stability of Co:ZnO nanostructure thin films comes with a price, however: the photocatalytic activity and concomitant degradation of MB and its azo dyes reaction intermediates is in general lowered, compared to the undoped ZnO thin films. At higher dopant concentrations, under oxygen-rich conditions and with UV irradiation at 254nm and 340nm, the MB degradation most likely occurs via a conventional photocatalytic reaction mechanism and/or via charge transfer of the MB into Azure B (AB) with the absence of Mars van Krevelen type mechanism (because of the increased lattice stability). At lower dopant concentrations under oxygen-limited conditions with UV irradiation at 254nm and 340nm, the Mars van Krevelen type reaction mechanism is probably the main mechanism propagating the oxidation of MB.

Overall, the undoped morphologies were more photocatalytically active compared to the doped morphologies. In general, this work has shown that several different solid and liquid phase photocatalytic reaction mechanisms govern the photocatalytic degradation of azo dyes such as MB on nanostructured ZnO thin films, and that surface morphology, crystallinity, lack or presence of oxygen, and the dopant concentration are the key parameters governing the overall photocatalytic activity and the activation of these different solid and liquid photocatalytic reaction mechanisms.

Acknowledgements

I would like to express my special thanks to Dr. Darrell Patterson, without whom I would not have carried out this research. His constant intellectual stimulation kept me motivated, and made me understand both how to cope with and enjoy top level research. I am grateful for the encouragement, support, many initial ideas and productive criticism. Indeed, I have been blessed with such a dynamic, dedicated, and highly organised person who allowed me to inculcate some invaluable attributes towards my grooming as a professional researcher. I have been kept equally provoked with invaluable counselling and advice from Dr. Emma Patterson; I am really indebted to her for all the knowledge and technical expertise.

I owe much gratitude to Prof. Wei GaO and his research group to allow me to use their facilities to accomplish this task; without their support it would not have been possible to carry on this study – including Dr. Chongwen Zou, Dr. Xiao Dong Yan, Ray Chen and Nadiah K. Zaman. I am delighted to take this opportunity to express my vote of thanks to all laboratory technicians – including Allan Clendinning, Peter Buchanan, Muhammad Shahmim, Raymond Hoffman, and Laura Liang, for all their help and support. I also owe a special thanks to Mrs Catherine Hobbis, Paul Butler and Dr Alec Asadov for their support in SEM, LC-MS and XRD analysis.

I also extend my sincere gratitude to my family and friends for their unconditional support, encouragement, affection and love, especially my father and mother: my father who taught me how to believe in myself and my mother for her indebted care and love. Truly without them I would not have achieved this milestone.

Table of Contents

Abstract.....	ii
Acknowledgements.....	iv
List of Figures.....	xii
List of Tables.....	xxiii
Nomenclature.....	xxvi
1 Introduction.....	1
1.1 Project Objectives.....	2
1.2 Outline of Thesis.....	3
2 Literature Review.....	4
2.1 Wastewater Treatment and Advanced Oxidation.....	4
2.2 Photocatalysis.....	4
2.2.1 Introduction to Photocatalysis.....	4
2.2.2 Advantages of Photocatalysis.....	6
2.2.3 Disadvantages of Photocatalysis.....	7
2.3 Homogeneous vs. Heterogeneous Photocatalysis.....	7
2.3.1 Homogeneous Photocatalysis.....	7
2.3.2 Heterogeneous Photocatalysis.....	7
2.4 The Conventional Mechanism of Photocatalysis.....	8
2.5 Photocatalytic Properties of Semiconductors.....	14
2.6 ZnO as Photocatalyst.....	15
2.7 Factors Affecting Photocatalysis.....	16
2.7.1 Suspended Versus Supported (Immobilised) Photocatalysts.....	16
2.7.2 Catalyst Concentration/Catalyst Loading.....	17
2.7.3 Effect of pH.....	18

2.7.4	Effect of UV Light Intensity and Wavelength.....	21
2.7.4.1	Effect of light intensity	23
2.7.4.2	Effect of UV wavelength.....	24
2.7.4.3	Overall implications of intensity and wavelength on photocatalytic activity/reaction rate.....	24
2.7.5	The Effect of Photocatalyst Type: Preparation Technique/Method	25
2.7.6	The effect of Surface Morphology.....	27
2.7.6.1	ZnO (Powder) as photocatalyst	27
2.7.6.2	ZnO thin films	28
2.7.7	Effect of Crystallinity	29
2.7.8	Effect of Dissolved Oxidant.....	30
2.7.8.1	Effect of dissolved oxygen	30
2.7.8.2	Effect of H ₂ O ₂	31
2.7.8.3	Effect of ozone.....	32
2.7.8.4	Overall effect of oxidant.....	32
2.7.9	The Effect of Mass Transfer	32
2.8	Photocatalytic Reactors.....	35
2.8.1	Classification of Photoreactor on the Basis of the State of the Catalyst.....	35
2.8.1.1	Slurry reactor	36
2.8.1.2	Immobilised reactor	39
2.8.2	Classification of Photoreactor on the Basis of Type of Illumination.....	43
2.8.3	Classification of Photoreactors on the Basis of Position of the Irradiation Source	44
2.9	Increasing Photocatalytic Activity – the Effect of Doping.....	46
2.9.1	Types of Dopant:.....	46
2.9.1.1	Cationic doping.....	46
2.9.1.2	Anionic doping	46
2.9.2	Impact of Dopant on the Semiconductors.....	47

2.9.3	Doped ZnO Photocatalytic Materials.....	48
2.9.4	Nitrogen-doped ZnO (N:ZnO).....	49
2.9.4.1	Nitrogen doping methods	49
2.9.4.2	Effect of N ₂ dopant on band gap and photocatalysis.....	50
2.9.4.3	Effect of doped nitrogen concentration on photocatalysis	50
2.9.4.4	Effect of N ₂ doping on morphology	51
2.9.4.5	Effect of N ₂ doping on crystallinity.....	51
2.9.5	Cobalt-doped ZnO (Co:ZnO).....	51
2.9.5.1	Methods used for Co:ZnO	52
2.9.5.2	Effect of Co dopant on band gap and photocatalysis	52
2.9.5.3	Effect of Co dopant type and concentration on Co:ZnO	52
2.9.5.4	Effect of Co dopant on surface morphology	53
2.9.5.5	Effect of Co doping on crystallinity	53
2.10	Kinetic Modelling	54
2.11	Implications of the Literature.....	56
3	Materials and Methods.....	58
3.1	Materials	58
3.2	Photocatalytic Experiments	58
3.2.1	Photocatalytic Reaction Vessel.....	58
3.2.2	Reaction Conditions for Initial Trial Experiments.....	59
3.2.3	Reaction Conditions for Second, Third, and Last Phase of Experiments.....	60
3.2.3.1	Reaction conditions for experiments under both oxygen-limited and rich conditions	60
3.2.3.1.1	Reaction under oxygen-limited conditions	60
3.2.3.1.2	Reaction under oxygen-rich conditions.....	61
3.3	Preparation of Undoped and Doped ZnO Nanostructured Thin Films	62
3.3.1	Preparation of Undoped Nanostructured ZnO Thin Films	62

3.3.2	Nitrogen-doped ZnO (N:ZnO) Thin Films	63
3.3.2.1	N:ZnO thin films preparation using dopant N ₂ gas	63
3.3.2.2	N:ZnO thin films preparation using TEA as nitrogen source.....	64
3.3.3	Preparation of Cobalt-Doped Nano Structure Zinc Oxide Thin Films (Co:ZnO). 67	
3.4	Analytical Techniques	68
3.4.1	UV-Visible Spectrophotometer (UV-Vis).....	68
3.4.2	High Performance Liquid Chromatography (HPLC)	69
3.4.3	Liquid Chromatography and Mass Spectroscopy (LC-MS)	69
3.4.4	Scanning Electron Microscopy	70
3.4.5	X-ray Diffractometer	70
3.4.6	Atomic Absorption Spectroscopy	70
4	The Effect of Morphology on Undoped ZnO Photocatalysed Reaction Rate, Film Stability and Implications to the Photocatalytic Mechanism	72
4.1	Introduction.....	72
4.2	Data Treatment and Kinetic Analysis	73
4.3	Relationships with Surface Morphologies and Thin Film Preparations	74
4.3.1	Morphology Before Reaction	74
4.3.2	Morphology after Reaction under Limited Oxygen Conditions	77
4.3.3	Morphology after Reaction under Oxygen-rich Conditions	82
4.4	Mass Transfer Limitation Studies	86
4.5	Relationships with Photocatalytic Activity (Reaction Rate)	89
4.5.1	Reaction Kinetics	89
4.5.2	Oxygen-limited Conditions.....	89
4.5.3	Oxygen-rich Conditions.....	91
4.6	Reuseability of the Thin Films.....	93
4.6.1	Oxygen-limited Conditions.....	94
4.6.2	Oxygen-rich Conditions.....	99

4.7	Comparison between S2-MS, ZnO MS films and ZnO Powder.....	103
4.8	Effect of Model compound MB Concentration on Photocatalytic Activity	105
4.9	Summary	111
5	A More Detailed Investigation of Conventional versus Lattice Photocatalysed Reactions at both 254nm and 340nm.....	112
5.1	Introduction.....	112
5.2	Morphologies before Reaction.....	112
5.2.1	Morphologies after Reaction upon UV Irradiation of 254nm	114
5.2.1.1	Morphologies after reaction under oxygen-limited conditions	114
5.2.1.2	Morphologies after reaction under oxygen-rich conditions	116
5.2.2	Morphologies after Reaction upon UV Irradiation of 340nm	117
5.3	Reaction Intermediates and Product Analysis.	120
5.3.1	Species Identification.....	120
5.3.2	Reactions with Irradiation at 254nm.....	120
5.3.3	Reactions with Irradiation at 340nm.....	124
5.4	Proposed Reaction Mechanism.....	128
5.5	Summary	133
6	Doped Nanostructured ZnO Thin Films: Impact Of Dopant On Photocatalytic Activity, Reaction Mechanism and Stability	135
6.1	Introduction.....	135
6.2	Impact of Dopant on Surface Morphologies.....	135
6.2.1	Nitrogen-doped Zinc Oxide (N:ZnO) Nanostructured Thin Films.....	135
6.2.1.1	N:ZnO thin film morphologies obtained by using N ₂ gas as nitrogen source	136
6.2.1.2	N:ZnO thin films morphologies obtained by using TEA as an N ₂ source	138
6.2.1.2.1	Morphologies obtained at high concentration of TEA with pH control	139
6.2.1.2.2	Morphologies obtained at low concentration of TEA with pH control	142

6.2.1.2.3	Morphologies obtained at high and low concentrations of TEA without pH control	144
6.2.2	Cobalt-doped Nanostructured ZnO (Co:ZnO) Thin Films	146
6.2.2.1	Comparison of cobalt-doped and undoped ZnO nanostructure	146
6.2.2.1.1	Variation of Co:S1-MS morphology with Co concentration	147
6.2.2.1.2	Variation of Co:S1-CG morphology with Co concentration	148
6.2.2.1.3	Variation of Co:S2-MS and Co:S2-CG morphology with Co concentration	150
6.2.2.1.4	Overall morphology comparison between all doped and undoped films	152
6.2.2.2	Comparison of crystal planes and dopant concentration	153
6.2.2.2.1	Comparison of XRD analysis between doped and undoped films	153
6.2.2.2.1	Comparison of dopant concentration	155
6.2.2.3	Cobalt-doped ZnO nanostructure and pH	158
6.2.2.3.1	Effect of pH on the morphologies of Co:S1-MS and Co:S1-CG	158
6.2.2.3.2	Effect of pH on the morphologies of Co:S2-MS and Co:S2-CG	159
6.3	Impact of Photocatalytic Reactions on Cobalt-Doped Nanostructured Zinc Oxide (Co:ZnO) Thin Films	160
6.3.1	Morphologies after Reaction upon UV Irradiation at 254nm	161
6.3.1.1	Under oxygen-limited conditions	161
6.3.1.2	Under oxygen-rich conditions	162
6.3.2	Morphologies after Reaction upon UV Irradiation at 340nm	167
6.3.3	XRD Analysis of All Cobalt-Doped Thin Films	167
6.4	Doped Surface Morphologies and Photocatalytic Activity Relationship	170
6.4.1	Photocatalytic Activity, Reaction Rate and Reaction Kinetics	170
6.4.2	Photocatalytic Activity and Reaction Intermediate Kinetics under UV Irradiation of 254nm	170
6.4.2.1	Oxygen-limited conditions	170

6.4.2.2	Oxygen-rich conditions	179
6.4.2.3	Overall implications of Co doping on the photocatalytic reaction mechanism at 254nm	183
6.4.3	Photocatalytic Activity and Reaction Intermediate Kinetics under UV irradiation 340nm.....	186
6.5	Impact of Dopant on Reaction Mechanism(S).....	189
6.6	Summary.....	191
7	Conclusions and Future Work	194
7.1	Conclusions.....	194
7.1.1	Undoped Nanostructured ZnO Thin Films, Photocatalytic Activity and Reaction Mechanism.....	194
7.1.2	Impact of Dopant on Nanostructured ZnO Thin Films, Photocatalytic Activity and Reaction Mechanism.....	195
7.2	Implications for Industrial Applications	197
7.3	Future Work.....	197
	Appendix A: Control Experiments	199
	Appendix B: Reproducibility and effect on of nanostructured ZnO thin films morphologies under UV irradiation of 340nm.....	205
	Appendix C: Reaction Intermediate analysis by using LC-MS.....	207
	Appendix D: Band Gap Calculations.....	221
	Appendix E	223
	References.....	250

List of Figures

Figure 2.1: The general conventional mechanism of the photocatalysis. [Reproduced from N. Daneshvar <i>et al.</i> 2004].	9
Figure 2.2: Secondary reactions with activated oxygen species in the photo-electrochemical mechanism. [Reproduced from Hoffmann <i>et al.</i> [45]].	13
Figure 2.3: Pourbaix diagram for Zn .[Reproduced from [78]].	19
Figure 2.4: Dissolution of ZnO films in aqueous solutions at different pH level: (a) within 24 h; (b) after 24 h and 1 week. [Taken from Han <i>et al.</i> [83]].	21
Figure 2.5: Explanation of mass transfer in supported metal oxide photocatalyst.	33
Figure 2.6: Schematic diagram of the integrated photo-reactor-membrane UF system. [Reproduced from Lasa <i>et al.</i> [138]].	36
Figure 2.7: Taylor vortex reactor in operation. [Reproduced from Lasa <i>et al.</i> [138]].	36
Figure 2.8: Plug flow annular reactor. [Reproduced from Biard <i>et al.</i> [139]].	37
Figure 2.9: Experimental Up-Flow system; 1: glass jacket reactor; 2: UV lamp; 3: tank; 4: solution; 5: centrifugal pump; 6: cryostat of circulation water; 7: quartz jacket; 8: water inlet; 9: water outlet; 10: flow meter; 11: valve; 12: bypass; 13: air pump. [Reproduced from Merabet <i>et al.</i> [140]].	37
Figure 2.10: Swirl Flow Reactor. [Reproduced from Ray <i>et al.</i> [141]].	38
Figure 2.11: Turbulent slurry photocatalytic reactor for hydrogen production. [Reproduced from Xiaowei <i>et al.</i> [142]].	38
Figure 2.12: Open dish illumination arrangement. A, Pyrex glass dish; B, TiO ₂ coated sand; C, solution; D, peristaltic pump; E, 100 W medium pressure mercury lamp. [Reproduced from Matthews <i>et al.</i> [149]]	39
Figure 2.13: Schematic representation of the Falling Film Reactor. [Reproduced from Lasa <i>et al.</i> [138]]	40
Figure 2.14: Schematic representation of the optical-fibre bundled array photocatalytic reactor system. [Reproduced from Lasa <i>et al.</i> [138]]	41
Figure 2.15: Schematic representation of a multiple tube reactor. [Reproduced from Lasa <i>et al.</i> [138]]	41
Figure 2.16: Annular packed-bed reactor. [Reproduced from Lasa <i>et al.</i> [138]]	42

Figure 2.17: Rotating disk reactor, (a) variable speed motor, (b) Pyrex reactor wall, (c) support disk,.....	42
Figure 2.18: Tube light Reactor (TLR). [Reproduced from Lasa <i>et al.</i> [138]].....	42
Figure 2.19: Various schemes illustrating the possible changes that might occur to the band gap electronic structure of anatase TiO ₂ on doping with various nonmetals: (a) band gap of pristine TiO ₂ ; (b) doped TiO ₂ with localized dopant levels near the VB and the CB; (c) band gap narrowing resulting from broadening of the VB; (d) localized dopant levels and electronic transitions to the CB; and (e) electronic transitions from localized levels near the VB to their corresponding excited states for Ti ³⁺ and F ⁺ centers. [Reproduced from Serpone [191]].....	48
Figure 3.1: Photo of the photo reactor illustrating the photoreactor set-up, showing the stainless steel enclosure with its concave reflector for the UV lamp, power supplies and magnetic stirrers.....	58
Figure 3.2: Schematic of the photoreactor set-up for experiments under oxygen-limited conditions.....	61
Figure 3.3: Schematic of the photoreactor set-up for experiments under oxygen-rich conditions.....	61
Figure 3.4: Preparation N:ZnO by using N ₂ gas as nitrogen dopant source: (A) N ₂ saturated Zn(NO) ₃ .6H ₂ O; (B) N ₂ saturated HMT; (C) Mixing of N ₂ saturated Zn(NO) ₃ .6H ₂ O and HMT under extensive supply of N ₂ ; (D) Magnified view of sealable glass jar.	64
Figure 3.5: Sealable glass jar.	68
Figure 4.1: Cross-sectional view of the surface morphologies of the different ZnO thin films before photocatalysis: (A) S1-MS; (B) S1-CG; (C) S2-MS (inset, an example of the large crystals that were sporadically present on the surface of the main structure); (D) S2-CG; (E) S3-MS; (F) S3-CG.	75
Figure 4.2: XRD analysis of all thin film morphologies after reaction under both oxygen-limited and rich conditions: (A) S1-MS; (B) S1-CG; (C) S2-MS; (D) S2-CG.	76
Figure 4.3: Comparison of the solution 1 (S1) derived ZnO thin film surface morphologies using SEM imaging before and after Methylene Blue photocatalysed degradation: (A)S1-MS (un-reacted); (B) S1-MS (reacted with limited O ₂); (C) S1-MS (reacted under O ₂ rich conditions); (D) S1-CG (un-reacted); (E) S1-CG (reacted with limited O ₂); (F)S1-CG (reacted under O ₂ rich conditions).	80

Figure 4.4: Concentration of Zn metal in the final reaction liquid as measured by atomic absorption spectroscopy (AAS) for the reactions photocatalysed by the ZnO thin film derived from solutions S1 and S2 on both clean glass slides (CG) and magnetron sputtered templates (MS).	81
Figure 4.5: Comparison of the solution 2 (S2) derived ZnO thin film surface morphologies using SEM imaging before and after Methylene Blue photocatalysed degradation: (A) S2-MS (un-reacted); (B) S2-MS (reacted with limited O ₂); (C) S2-MS (reacted under O ₂ rich conditions); (D) S2-CG (un-reacted); (E) S2-CG (reacted with limited O ₂); (F) S2-CG (reacted under O ₂ rich conditions).	82
Figure 4.6: Comparison of the solution 3 (S3) derived ZnO thin film surface morphologies from SEM imaging before and after Methylene Blue photocatalysed degradation: (A) S3-MS (un-reacted); (B) S3-MS (reacted with limited O ₂); (C) S3-MS (reacted under O ₂ rich conditions); (D) S3-CG (un-reacted); (E) S3-CG (reacted with limited O ₂); (F)S3-CG (reacted under O ₂ rich conditions).	84
Figure 4.7: Comparison of photocatalytic degradation of Methylene Blue solution at different mechanical stirring speeds.	88
Figure 4.8: Comparison of surface morphology of S1-MS under same reaction conditions at various mixing speeds. (A) 100rpm; (B) 200rpm; (C) 300rpm; (D) 400rpm.	88
Figure 4.9: Comparison of the degradation of Methylene Blue by the ZnO thin films derived from solutions S1, S2 and S3 under oxygen-limited conditions.....	90
Figure 4.10: Comparison of the degradation of Methylene Blue by the ZnO thin films derived from solutions S1, S2 and S3 under oxygen-rich conditions.....	91
Figure 4.11: XRD analysis of thin flm S2-MS.	93
Figure 4.12: Reusability and reproducibility of the ZnO thin films in the photocatalysed degradation of 5mg L ⁻¹ Methylene Blue under O ₂ limited conditions. (A) S1-MS; (B) S1-CG; (C) S2-MS; (D) S2-CG; (E) S3-MS; (F) S3-CG, where 1R denotes initial use of a film, and 2R and 3R denote the first and second reuse of the same film respectively.	95
Figure 4.13: SEM images of morphology S1-MS after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S1-MS first run (top view); (B) S1-MS first run (cross-sectional view); (C) S1-MS second run (top view); (D) S1-MS second run (cross-sectional view) under oxygen-limited conditions.....	96
Figure 4.14: SEM images of morphology S1-CG after first (1R) and second (2R) run; reproducibility and effect on morphology.(A) S1-CG first run (top view); (B) S1-CG	

first run (cross-sectional view); (C) S1-CG second run (top view); (D) S1-CG second run (cross-sectional view) under oxygen-limited conditions.....	96
Figure 4.15: SEM images of morphology S2-MS after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S2-MS first run (top view); (B) S2-MS first run (cross-sectional view); (C) S2-MS second run (top view); (D) S2-MS second run (cross-sectional view) under oxygen-limited conditions.....	97
Figure 4.16: SEM images of morphology S2-CG after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S2-CG first run (top view); (B) S2-CG first run (cross-sectional view); (C) S2-CG second run (top view); (D) S2-CG second run (cross-sectional view) under oxygen-limited conditions.....	97
Figure 4.17: Concentration of Zn metal in the final reaction liquid for the first run (1R) as measured by atomic absorption spectroscopy (AAS) for the reactions photocatalysed by the ZnO thin films derived from solutions S1 and S2 on both clean glass slides (CG) and magnetron sputtered templates (MS).	98
Figure 4.18: Concentration of Zn metal in the final reaction liquid for the second run (2R) as measured by atomic absorption spectroscopy (AAS) for the reactions photocatalysed by the ZnO thin films derived from solutions S1 and S2 on both clean glass slides (CG) and magnetron sputtered templates (MS).....	98
Figure 4.19: Reusability and reproducibility of the ZnO thin films in the photocatalysed degradation of 5mg L ⁻¹ Methylene Blue under O ₂ rich conditions, A) S1-MS; (B) S1-CG; (C) S2-MS; (D) S2-CG; (E) S3-MS; (F) S3-CG, where 1R denotes initial use of a film, and 2R and 3R denote the first and second reuse of the same film respectively.	100
Figure 4.20: SEM images of morphology S1-MS after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S1-MS first run (top view); (B) S1-MS first run (cross-sectional view); (C) S1-MS second run (top view); (D) S1-MS second run (cross-sectional view) under oxygen-rich conditions.....	101
Figure 4.21: SEM images of morphology S1-CG after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S1-CG first run (top view); (B) S1-CG first run (cross-sectional view); (C) S1-CG second run (top view); (D) S1-CG second run (cross-sectional view) under oxygen-rich conditions.....	101
Figure 4.22: SEM images of morphology S2-MS after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S2-MS first run (top view); (B) S2-MS first run (cross-sectional view); (C) S2-MS second run (top view); (D) S2-MS second run (cross-sectional view) under oxygen-rich conditions.....	102

Figure 4.23: SEM images of morphology S2-CG after first (1R) and second run (2R); reproducibility and effect on morphology.(A) S2-CG first run (top view); (B) S2-CG first run (cross sectional view); (C) S2-CG second run (top view); (D) S2-CG second run (cross sectional view) under oxygen-rich conditions.102

Figure 4.24: Comparison between photocatalytic activity of MS films (S2-MS, ZnO MS) to ZnO powder under both oxygen-limited and oxygen-rich conditions..... 103

Figure 4.25: The effect of photocatalytic reaction of Methylene Blue on the top surface morphology of the MS films using SEM imaging: (A) MS only; (B) MS film reacted under oxygen-limited conditions O₂; (C) MS film reacted under oxygen-rich conditions..... 104

Figure 4.26: Overall comparison of degradation of MB (5 and 10 mgL⁻¹) for the thin films derived from solution S1 and S2 under both oxygen-limited and oxygen-rich conditions..... 109

Figure 4.27: Concentration of Zn metal in the final reaction liquid as measured by atomic absorption spectroscopy (AAS) for the reactions(5mgL⁻¹ MB) photocatalysed by the ZnO thin film derived from solutions S1 and S2 on both clean glass slides (CG) and magnetron sputtered templates (MS)..... 110

Figure 4.28: Concentration of Zn metal in the final reaction liquid as measured by atomic absorption spectroscopy (AAS) for the reactions(10mgL⁻¹ MB) photocatalysed by the ZnO thin film derived from solutions S1 and S2 on both clean glass slides (CG) and magnetron sputtered templates (MS). 110

Figure 5.1: SEM cross-sectional views of surface morphologies of the different ZnO thin films on glass substrate before photocatalysis: A, S1-MS; B, S1-CG; C, S2-MS; D, S2-CG. 113

Figure 5.2: HPLC Chromatograms and SEM cross-sectional views of the thin films after the photocatalytic degradation of MB with UV irradiation of 254nm under oxygen-limited conditions: A, reaction intermediates from thin film S1-MS; B, reaction intermediates from thin film S1-CG; C, reaction intermediates from thin film S2-MS; D, reaction intermediates from thin film S2-CG; E, cross-sectional view of thin film S1-MS after reaction; F, cross-sectional view of thin film S1-CG after reaction; G, cross-sectional view of thin film S2-MS after reaction; H, cross-sectional view of thin film S2-CG after reaction. 115

Figure 5.3: HPLC Chromatograms and SEM cross-sectional views of the thin films after the photocatalytic degradation of MB with UV irradiation of 254nm under

oxygen-rich conditions: A, reaction intermediates from thin film S1-MS; B, reaction intermediates from thin film S1-CG; C, reaction intermediates from thin film S2-MS; D, reaction intermediates from thin film S2-CG; E, cross-sectional view of thin film S1-MS after reaction; F, cross-sectional view of thin film S1-CG after reaction; G, cross-sectional view of thin film S2-MS after reaction; H, cross-sectional view of thin film S2-CG after reaction. 116

Figure 5.4: HPLC Chromatograms and SEM cross-sectional views of the thin films after the photocatalytic degradation of MB with UV irradiation of 340nm under oxygen-rich conditions: A, reaction intermediates from thin film S1-MS; B, reaction intermediates from thin film S1-CG; C, reaction intermediates from thin film S2-MS; D, reaction intermediates from thin film S2-CG; E, cross-sectional view of thin film S1-MS after reaction; F, cross-sectional view of thin film S1-CG after reaction; G, cross-sectional view of thin film S2-MS after reaction; H, cross-sectional view of thin film S2-CG after reaction. 118

Figure 5.5: Comparison of the concentration of Zn metal in the final reaction liquid as measured by atomic absorption spectroscopy (AAS) for the reaction photocatalysed by the ZnO thin films under oxygen-rich conditions upon UV irradiation 254 and 340nm. 119

Figure 5.6: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by four different ZnO thin films upon UV irradiation at 254nm under oxygen-limited and oxygen-rich conditions, obtained by HPLC: A, S1-MS: oxygen-limited; B, S1-CG: oxygen-limited; C, S2-MS: oxygen-limited; D, S2-CG: oxygen-limited; E, S1-MS: oxygen-rich; F, S1-CG: oxygen-rich; G, S2-MS: oxygen-rich; H, S2-CG: oxygen-rich..... 122

Figure 5.7: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by four different ZnO thin films upon UV irradiation at 340nm under oxygen-rich conditions only, obtained by HPLC: A, S1-MS; B, S1-CG; C, S2-MS; D, S2-CG..... 125

Figure 5.8: Proposed methylene blue ZnO photocatalysed reaction mechanism for the thin films studied based on the identified intermediates and reaction profiles in this work. 130

Figure 5.9: Overall reaction mechanism for the photocatalytic degradation of methylene blue based on this work and literature. 131

Figure 5.10: Schematic representation of the initial stages of the proposed Mars Van Krevelen type ZnO photocatalysed methylene blue reaction mechanism: (a) under oxygen-limited conditions, (b) under oxygen-rich conditions..... 132

Figure 6.1: A: SEM image (top view) of nitrogen-doped nanostructured ZnO thin films N:S1-MS; B:EDX analysis at position P1(ZnO single crystal)..... 136

Figure 6.2: A: SEM image (top view) of N:S1-CG; B:EDX analysis at position P1(ZnO single crystal)..... 137

Figure 6.3: A: SEM image (top view) of N:S2-MS; B: EDX analysis at position P1(complex ZnO single crystal). 138

Figure 6.4: A: SEM image (top view) of N:S2-CG; B: EDX analysis at position P1(complex ZnO single crystal). 138

Figure 6.5: A: SEM image (top view) of N1:S1-MS; B: EDX analysis at position P1 (X-shaped ZnO crystal); C: EDX analysis at position P2 (layer upon magnetron sputtered coating and small ZnO crystal) at high concentration of TEA with pH control..... 139

Figure 6.6: A:SEM image (top view) of N1:S1-CG; B:EDX analysis at position P1(regular ZnO crystal); C:EDX analysis at position P2(layer upon magnetron sputtered coating) at high concentration of TEA with pH control. 140

Figure 6.7: A: SEM image (top view) of N2:S2-MS; B: EDX analysis at position P1(cluster of ZnO crystal); C: EDX analysis at position P2(ZnO single crystal); D: EDX analysis of at position P3 (layer upon magnetron sputtered coating). 141

Figure 6.8: A: SEM image (cross-sectional) of N2:S2-MS; B: EDX analysis at position P1 (cluster of ZnO crystal); C: EDX analysis at position P2(complex ZnO single crystal)..... 141

Figure 6.9: A: SEM image (top view) of N3:S1-MS; B: EDX analysis at position P1 (cluster of small ZnO crystals); C: EDX analysis at position P2 (large ZnO crystal); D: EDX analysis at position (layer upon magnetron sputtered coating) at low concentration of TEA with pH control. 142

Figure 6.10: A: SEM image (top view) of N4:S2-MS; B: EDX analysis at position P1(cluster of ZnO crystal); C: EDX analysis at position P2(layer upon magnetron sputtered coating)..... 143

Figure 6.11: A: SEM image (top view) of N4:S2-CG; B: EDX analysis at position P1(ZnO jointed crystal); C: EDX analysis at position P2 (layer upon magnetron sputtered coating) at low concentration of TEA with pH control..... 143

Figure 6.12: A:SEM image (top view) of N5:S2-MS; B:EDX analysis at position P1(cluster of ZnO crystal); C:EDX analysis at position P2(layer upon magnetron sputtered coating) at high concentration of TEA without pH control.	144
Figure 6.13: A:SEM image (top view) of N5:S2-CG; B:EDX analysis at position P1(edged ZnO crystal); C:EDX analysis at position P2(layer upon magnetron sputtered coating) at high concentration of TEA without pH control.	145
Figure 6.14: A:SEM image (top view) of N6:S2-MS; B:EDX analysis at position P1(cluster of ZnO crystal); C:EDX analysis at position P2(flowery layer upon magnetron sputtered coating) at low concentration of TEA without pH control.	145
Figure 6.15: Cross-sectional SEM images of cobalt doped and un-doped ZnO nanostructured thin films. A: Un-doped S1-MS; B: Co5%:S1-MS, C: Co10%:S1-MS, D: Co15%:S1-MS and E: Co25%:S1-MS.	148
Figure 6.16: Cross-sectional SEM images of cobalt doped and un-doped ZnO nanostructured thin films. A: Un-doped S1-CG; B: Co5%:S1-CG, C: Co10%:S1-CG, D: Co15%:S1-CG and E: Co25%:S1-CG.....	150
Figure 6.17: Cross-sectional SEM images of cobalt doped and undoped ZnO nanostructured thin films. A: Undoped S2-MS; B: Co5%:S2-MS, C: Co10%:S2-MS, D: Co15%:S2-MS and E: Co25%:S2-MS.	151
Figure 6.18: Cross-sectional SEM images of cobalt doped and undoped ZnO nanostructured thin films. A: Undoped S2-CG; B: Co5%:S2-CG, C: Co10%:S2-CG, D: Co15%:S2-CG.	152
Figure 6.19: XRD comparison of undoped and cobalt-doped ZnO nanostructured thin films.	154
Figure 6.20: Cross-sectional SEM images of the cobalt doped ZnO nanostructured thin films. A: Co5%:S1-MS at pH=4, B: Co5%:S1-MS at pH=5, C: Co5%:S1-CG at pH=4 and D: Co5%:S1-CG at pH=5.	159
Figure 6.21: Cross-sectional SEM images of cobalt doped ZnO nanostructured thin films. A: Co5%:S2-MS at pH=6.5, B: Co5%:S2-MS at pH=7.5, C: Co5%:S2-CG at pH=6.5 and D: Co5%:S2-CG at pH=7.5.	160
Figure 6.22: Cross-sectional SEM images of cobalt-doped nanostructured ZnO thin films surface morphologies before and after reaction under oxygen-limited and rich conditions upon UV irradiation of 254nm. A: Co15%:S1-MS unreacted, B: Co15%:S1-MS reacted under O ₂ limited conditions, C: Co15%:S1-MS reacted under O ₂ rich conditions, D: Co10%:S1-MS unreacted, E: Co10%:S1-MS reacted under O ₂ limited	

conditions, F: Co10%:S1-MS reacted under O₂ rich conditions, G: Co5%:S1-MS unreacted, H: Co5%:S1-MS reacted under O₂ limited conditions, I: Co5%:S1-MS reacted under O₂ rich conditions.....163

Figure 6.23: Cross-sectional SEM images of cobalt-doped nanostructured ZnO thin films surface morphologies before and after reaction under oxygen-limited and rich conditions upon UV irradiation of 254nm. A: Co15%:S1-CG unreacted, B: Co15%:S1-CG reacted under O₂ limited conditions, C: Co15%:S1-CG reacted under O₂ rich conditions, D: Co10%:S1-CG unreacted, E: Co10%:S1-CG reacted under O₂ limited conditions, F: Co10%:S1-CG reacted under O₂ rich conditions, G: Co5%:S1-CG unreacted, H: Co5%:S1-CG reacted under O₂ limited conditions, I: Co5%:S1-CG reacted under O₂ rich conditions.....164

Figure 6.24: Cross-sectional SEM images of cobalt-doped nanostructured ZnO thin films surface morphologies before and after reaction under oxygen-limited and rich conditions upon UV irradiation of 254nm. A: Co25%:S2-MS unreacted, B: Co25%:S2-MS reacted under O₂ limited conditions, C: Co25%:S2-MS reacted under O₂ rich conditions, D: Co15%:S2-MS unreacted, E: Co15%:S2-MS reacted under O₂ limited conditions, F: Co15%:S2-MS reacted under O₂ rich conditions, G: Co10%:S2-MS unreacted, H: Co Co10%:S2-MS reacted under O₂ limited conditions, I: Co Co10%:S2-MS reacted under O₂ rich conditions, J: Co5%:S2-MS unreacted, K: Co5%:S2-MS reacted under O₂ limited conditions, L: Co5%:S2-MS reacted under O₂ rich conditions.165

Figure 6.25: Cross-sectional SEM images of cobalt-doped nanostructured ZnO thin films surface morphologies before and after reaction under oxygen-limited and rich conditions upon UV irradiation of 254nm. A: Co15%:S2-CG unreacted, B: Co15%:S2-CG reacted under O₂ limited conditions, C: Co15%:S2-CG reacted under O₂ rich conditions, D: Co10%:S2-CG unreacted, E: Co10%:S2-CG reacted under O₂ limited conditions, F: Co10%:S2-CG reacted under O₂ rich conditions, G: Co5%:S2-CG unreacted, H: Co5%:S2-CG reacted under O₂ limited conditions, I: Co5%:S2-CG reacted under O₂ rich conditions.....166

Figure 6.26: Cross-sectional SEM images of cobalt-doped and undoped nanostructured ZnO thin films surface morphologies before and after reaction under oxygen-limited and rich conditions upon UV irradiation of 340nm. A: Co:S1-MS(15wt%) unreacted, B: Co:S1-MS(15wt%) reacted under O₂ limited conditions, C: Co:S1-MS(15wt%) reacted under O₂ rich conditions, D: Co:S2-MS(25wt%) unreacted, E: Co:S2-MS(25wt%)

reacted under O ₂ limited conditions, F: Co:S2-MS(25wt%) reacted under O ₂ rich conditions, G: Co:S2-MS(15wt%) unreacted, H: Co:S2-MS(15wt%) reacted under O ₂ limited conditions, I: Co:S2-MS(15wt%) reacted under O ₂ rich conditions.	168
Figure 6.27: Comparison of XRD analysis of photocatalytically reacted cobalt doped nanostructured ZnO thin films upon UV irradiation of 254nm and 340nm under both oxygen-limited and oxygen-rich conditions.	169
Figure 6.28: Overall comparison of photocatalytic degradation profiles of MB by using nanostructured Co:ZnO thin films under oxygen-limited conditions upon UV irradiation of 254nm. A: Co5%:ZnO thin films; B: Co10%:ZnO thin films; C: Co15%:ZnO thin films; D: Co25%:ZnO thin films.	173
Figure 6.29: Overall comparison of photocatalytic degradation profiles of MB by using undoped nanostructured Co:ZnO thin films under oxygen-limited and rich conditions upon UV irradiation of 254nm. A: undoped ZnO thin films under oxygen-limited conditions; B: undoped ZnO thin films under oxygen-rich conditions.	174
Figure 6.30: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by three different Co:S1-MS thin films upon UV irradiation at 254nm under both oxygen-limited and oxygen-rich conditions. A: Co5%:S1-MS under O ₂ limited conditions, B: Co5%:S1-MS under O ₂ rich conditions, C: Co10%:S1-MS under O ₂ limited conditions, D: Co10%:S1-MS under O ₂ rich conditions, E: Co15%:S1-MS under O ₂ limited conditions, F: Co15%:S1-MS under O ₂ rich conditions.	175
Figure 6.31: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by three different Co:S1-CG thin films upon UV irradiation at 254nm under both oxygen-limited and oxygen-rich conditions. A: Co5%:S1-CG under O ₂ limited conditions, B: Co5%:S1-CG under O ₂ rich conditions, C: Co10%:S1-CG under O ₂ limited conditions, D: Co10%:S1-CG under O ₂ rich conditions, E: Co15%:S1-CG under O ₂ limited conditions, F: Co15%:S1-CG under O ₂ rich conditions.	176
Figure 6.32: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by four different Co:S2-MS thin films upon UV irradiation at 254nm under both oxygen-limited and oxygen-rich conditions. A: Co5%:S2-MS under O ₂ limited conditions, B: Co5%:S2-MS under O ₂ rich conditions, C: Co10%:S2-MS under O ₂ limited conditions, D: Co10%:S2-MS under O ₂ rich conditions, E: Co15%:S2-MS under O ₂ limited conditions, F: Co15%:S2-MS under O ₂ rich conditions, G: Co25%:S2-MS under O ₂ limited conditions, H: Co25%:S2-MS under O ₂ rich conditions.	177

Figure 6.33: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by three different Co:S2-CG thin films upon UV irradiation at 254nm under both oxygen-limited and oxygen-rich conditions. A: Co5%:S2-CG under O₂ limited conditions, B: Co5%:S2-CG under O₂ rich conditions, C: Co10%:S2-CG under O₂ limited conditions, D: Co10%:S2-CG under O₂ rich conditions, E: Co15%:S2-CG under O₂ limited conditions, F: Co15%:S2-CG under O₂ rich conditions..... 178

Figure 6.34: Overall comparison of photocatalytic degradation profiles of MB by using nanostructured Co:ZnO thin films under oxygen-rich conditions upon UV irradiation of 254nm. A: Co:ZnO thin films at 5wt%; B: Co:ZnO thin films at 10wt%; C: Co:ZnO thin films at 15wt%; D: Co:ZnO thin films at 25wt%..... 180

Figure 6.35: Overall comparison of photocatalytic degradation profiles of MB by using nanostructured Co:ZnO thin films under oxygen-limited and rich conditions upon UV irradiation of 340nm. A: Co:ZnO thin films (Co15%:S1-MS, Co15%:S2-MS and Co25%:S2-MS) under oxygen-limited conditions; B: Co:ZnO thin films (Co15%:S1-MS, Co15%:S2-MS and Co25%:S2-MS) under oxygen-rich conditions..... 188

Figure 6.36: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by Co:S1-MS thin films upon UV irradiation at 340nm under both oxygen-limited and oxygen-rich conditions. A: Co15%:S1-MS under O₂ limited conditions, B: Co15%:S1-MS under O₂ rich conditions. 188

Figure 6.37: Reaction profile comparison of the reaction intermediates from methylene blue photocatalysed by two different Co:S2-MS thin films upon UV irradiation at 340nm under both oxygen-limited and oxygen-rich conditions. A: Co15%:S2-MS under O₂ limited conditions, B: Co15%:S2-MS under O₂ rich conditions, C: Co25%:S2-MS under O₂ limited conditions, D: Co25%:S2-MS under O₂ rich conditions..... 189

List of Tables

Table 2.1: Band-Gap energies of semiconductors used for photocatalytic processes reproduced from Bhatkhande <i>et al.</i> 2002.....	15
Table 2.2: Types of UV radiation	22
Table 2.3: Comparison of slurry and immobilised photo-reactors reproduced from [138].....	43
Table 3.1: Summary of the initial parameters to study the photocatalytic activity. ..	59
Table 3.2: Reaction conditions for experiments under both oxygen-limited and rich conditions.....	60
Table 3.3: Un-doped ZnO thin film preparation conditions	63
Table 3.4: Nitrogen-doped nanostructure ZnO thin film (N:ZnO) preparation conditions by using N ₂ gas as nitrogen dopant source.....	64
Table 3.5: Nitrogen doped nanostructured ZnO thin film (N:ZnO) preparation conditions by using TEA as Nitrogen dopant source.....	66
Table 3.6: Cobalt-doped ZnO thin film preparation conditions.	67
Table 3.7: Summary of nanostructured ZnO thin films morphologies obtained at different cobalt (as dopant) concentration.	68
Table 3.8: HPLC gradient method used to resolve methylene blue and its reaction products.....	69
Table 4.1: Concentration of zinc in reaction solutions as determined by atomic absorption spectroscopy (AAS), summarised as total zinc concentration (Zn; ppb) and zinc concentration normalised by the original surface area of the thin film catalyst (Zn/S; ppb/m ²).	78
Table 4.2: pH of the reaction fluid throughout the reaction under oxygen-limited and rich conditions.....	83
Table 4.3: Summary of Reynold's Number and reaction rate constant(s) on a liquid volume basis (k_{app} ; s ⁻¹) and a UV exposed surface area (S) basis (k''_{app} , m ³ m ⁻² s ⁻¹) for the photocatalysed degradation of methylene blue.	87

Table 4.4: Summary of the 1 st order reaction rate constants on a liquid volume basis (k_{app} ; s ⁻¹) and a UV exposed surface area (S) basis (k''_{app} , m ³ m ⁻² s ⁻¹) for the photocatalysed degradation of 5 mg L ⁻¹ methylene blue.....	90
Table 4.5: Summary of 1 st order reaction rate constants on liquid volume basis (k_{app} ; s ⁻¹), UV exposed surface area (S) basis (k''_{app} , m ³ m ⁻² s ⁻¹) and mass of the catalyst basis (k'''_{app} , m ³ kg ⁻¹ s ⁻¹) for the photocatalysed degradation of 5 mg L ⁻¹ methylene blue.....	106
Table 4.6: Summary of I st order reaction rate constants on liquid volume basis (k_{app} ; s ⁻¹), UV exposed surface area (S) basis (k''_{app} , m ³ m ⁻² s ⁻¹) and mass of the catalyst basis (k'''_{app} , m ³ kg ⁻¹ s ⁻¹) for the photocatalysed degradation of 10 mg L ⁻¹ methylene blue.....	106
Table 4.7: Summary of % photocatalytic degradation for the photocatalysed degradation of 5 and 10 mg L ⁻¹ methylene blue under oxygen-limited conditions.	107
Table 4.8: Summary of % photocatalytic degradation for the photocatalysed degradation of 5 and 10 mg L ⁻¹ methylene blue under oxygen-rich conditions.....	107
Table 5.1: Summary of 1 st order reaction rate constant on liquid volume basis (k_{app} : s ⁻¹), catalyst mass basis (k'_{app} : m ³ kg ⁻¹ s ⁻¹) and a UV exposed surface area (S) basis (k''_{app} : m ³ m ⁻² s ⁻¹) for the photocatalysed degradation of 10 mg L ⁻¹ Methylene Blue under UV irradiation of 254nm.....	123
Table 5.2: Summary of 1 st order reaction rate constant on liquid volume basis (k_{app} : s ⁻¹), catalyst mass basis (k'_{app} : m ³ kg ⁻¹ s ⁻¹) and a UV exposed surface area (S) basis (k''_{app} : m ³ m ⁻² s ⁻¹) for the photocatalysed degradation of 10 mg L ⁻¹ Methylene Blue under UV irradiation of 340nm.....	126
Table 6.1: Comparison of Cobalt content in the Co:ZnO thin films at two different concentration of Co(NO) ₃ .6H ₂ O, derived from EDX analysis.....	156
Table 6.2: Comparison of Cobalt content in the Co:ZnO thin films at two different concentration of Co(NO) ₃ .6H ₂ O, derived from EDX analysis.....	157
Table 6.3: Summary of the 1st order reaction rate constants on mass of the catalyst (k'_{app}), UV exposed catalyst surface area (k''_{app}) and volume of the catalysts (k'''_{app}) basis for the photodegradation of 10 mg L ⁻¹ methylene blue by using cobalt-doped ZnO thin films under oxygen-limited conditions upon UV irradiation of 254nm...	184
Table 6.4: Summary of the I st order reaction rate constants on mass of the catalyst (k'_{app}), UV exposed catalyst surface area (k''_{app}) and volume of the catalysts (k'''_{app})	

basis for the photodegradation of 10 mg L⁻¹ methylene blue by using cobalt-doped ZnO thin films under oxygen-rich conditions upon UV irradiation of 254nm..... 184

Table 6.5: Summary of the 1st order reaction rate constants on mass of the catalyst (k'_{app}), UV exposed catalyst surface area (k''_{app}) and volume of the catalysts (k'''_{app}) basis for the photodegradation of 10 mg L⁻¹ methylene blue by using cobalt doped ZnO thin films under both oxygen-limited and rich conditions upon UV irradiation of 340nm..... 185

Nomenclature

ZnO	Zinc Oxide
N:ZnO	Nitrogen Doped Zinc Oxide
Co:ZnO	Cobalt Doped Zinc Oxide
MB	Methylene Blue
AB	Azure B
AC	Azure C
TH	Thionin
R , R'	Alkyl radicals
TEA	Triethyleneamine
HMT	Hexamethylenetetramine
TFA	Trifluoro Acetic Acid
MO	Metal Oxide
UV	Ultra Violet
HPLC	High Performance Liquid Chromatography
UV-Vis	Ultra Violet Visible Spectrophotometer
AAS	Atomic Absorption Spectroscopy
XRD	X-ray Diffraction
LC-MS	Liquid Chromatography-Mass Spectrometry
EDX	Energy Dispersive X-ray Spectroscopy
μmol/L	Micro Mole per Litre

mg L^{-1}	Milligram per Litre
Wt%	Weight per Cent
rpm	Revolution per Minute
mL	Millilitre
mm	Millimetre
μm	Micrometer
S	Exposed Surface Area
t	Time
N	Number of Moles
K	Adsorption Equilibrium Constant
V	Liquid Volume (m^3)
W	Mass of the Solid Catalyst (kg)
V_s	Volume of the solid catalyst (m^3)
k'_{app}	Apparent Reaction Rate Constant on Mass Basis ($\text{m}^3\text{kg}^{-1}\text{s}^{-1}$)
k''_{app}	Apparent Reaction Rate Constant on Area Basis ($\text{m}^3\text{m}^{-2}\text{s}^{-1}$)
k'''_{app}	Apparent Reaction Rate Constant on Volume Basis ($\text{m}^3\text{m}^{-3}\text{s}^{-1}$)