Titanium-oxide Nanomaterials:
Synthesis, Characterization and
Selective Photocatalysis

Ainikalkannath Lazar Manoj
ADDENDUM

Page 4, line 6: Photocatalysis can be defined as

"change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance – the photocatalyst – that absorbs light and is involved in the chemical transformation of the reaction partners." [Braslavsky, S. E.; Braun, A. M.; Cassano, A. E.; Emeline, A. V.; Litter, M. I.; Palmisano, L.; Parnon, V. N.; Serpone, N., Glossary of terms used in photocatalysis and radiation catalysis (IUPAC recommendations 2011) 2011, doi:10.1351/PAC-REC-09-09-36]

Page 7, Figure 2: Figure caption

Figure 2. Photocatalytic generation of hydroxyl radicals in aqueous solution by UV light irradiated NTO.

Page 9, line 6: please read ‘negligible’ as ‘small’

Page 9, line 17: please read “1+K_{eq}C_{eq} + \sum_{i=1}^{n} ... is negligible” as “K_{eq}C_{eq} + \sum_{i=1}^{n} ... is small”

Page 10, equations 5-9

[h^+] is the concentration of holes generated on TiO$_2$ by the absorption of light, $k_{13}$ and $k_{3}$ are the forward and backward rate constants for the reaction of holes with water to form hydroxyl radicals, respectively.

Page 16, Figure 4: Figure caption

Figure 4. Creation of additional band (N2p) in NTO by nitrogen doping.

Page 18, Table 3: Table caption

Table 3. Recent (last five-year) examples of metal-and non-metal-doped NTO photocatalysis.

Page 20, Figure 6: Figure caption

Figure 6. (a) Schematic of the boron-doped diamond (BDD) anodic oxidation- and photocatalysis- coupled reactor and (b) comparison of degradation performance in different experimental systems used for the degradation of X-3B dye.
Copyright Notices

Notice 1

Under the Copyright Act 1968, this thesis must be used only under the normal conditions of scholarly fair dealing. In particular no results or conclusions should be extracted from it, nor should it be copied or closely paraphrased in whole or in part without the written consent of the author. Proper written acknowledgement should be made for any assistance obtained from this thesis.
Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>i</td>
</tr>
<tr>
<td>General Declaration</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iv</td>
</tr>
<tr>
<td>Thesis at a Glance</td>
<td>v</td>
</tr>
<tr>
<td>Aims of the Project</td>
<td>vii</td>
</tr>
<tr>
<td>Chapter 1. Introduction</td>
<td></td>
</tr>
<tr>
<td>1.1. Photocatalytic Water Treatment by Titanium dioxide: Recent Updates</td>
<td>3</td>
</tr>
<tr>
<td>Declaration for Publication 1.2.</td>
<td>32</td>
</tr>
<tr>
<td>1.2. Achieving Selectivity in TiO₂-based Photocatalysis</td>
<td>34</td>
</tr>
<tr>
<td>Declaration for Publication 1.1.</td>
<td>1</td>
</tr>
<tr>
<td>Chapter 2 Selective Photocatalysis</td>
<td></td>
</tr>
<tr>
<td>2.1. Selective Adsorption and Photocatalysis of Low-temperature Base-modified Anatase Nanocrystal</td>
<td>47</td>
</tr>
<tr>
<td>Declaration for Publication 2.2.</td>
<td>58</td>
</tr>
<tr>
<td>2.2. Understanding the Chemistry of TiO₂ Colloidal Systems: Preferential Adsorption and Selective Photocatalytic Degradation</td>
<td>60</td>
</tr>
<tr>
<td>3.1. Introduction</td>
<td>85</td>
</tr>
<tr>
<td>3.2. Experimental</td>
<td>86</td>
</tr>
</tbody>
</table>
3.2.1. Low-temperature sol-gel synthesis of anatase TiO$_2$ precursor 86
3.2.2. Near-ambient synthesis of potassium titanate nanostructures 86
3.2.3. Characterization 87
   3.2.3.1. Powder X-ray diffraction 87
   3.2.3.2. Nitrogen sorption analysis 87
   3.2.3.3. $\zeta$- potential analysis 88
   3.2.3.4. Scanning electron microscopy (SEM) 88
3.3. Results and discussion 89
   3.3.1. Powder X-ray diffraction 89
   3.3.2. Nitrogen sorption 91
   3.3.3. $\zeta$ – potential 94
   3.3.4. Scanning Electron Microscopy (SEM) 94
      3.3.4.1. Mechanism of nanorod formation 101
   3.3.5. Effect of KOH concentration 102
      3.3.5.1. Powder X-ray diffraction 102
3.4. Conclusions 104
3.5. References 105

Chapter 4. Selective Adsorption of Cationic Methylene Blue Dye by Negatively Surface Charged Potassium Titanate 106
4.1. Introduction 106
4.2. Experimental 107
   4.2.1. Adsorption studies 107
   4.2.2. Photocatalytic experiments 107
4.3. Results and discussion 107
   4.3.1. Selective adsorption 107
   4.3.2. Selective photocatalysis 109
4.4. Conclusion 112
4.5. References 113

Chapter 5. Conclusions and Future Works 114
Appendix: Nanostructured Thin Films as Functional Coatings 117
Abstract

The side effects of some recent scientific advances challenge the well-being of our planet. Water contamination, one of these side effects, from industrial effluents is a major source of fresh water pollution. Semiconductor photocatalysis, which operates under ultraviolet or visible light irradiation, is a well proven approach to water de-contamination. Among the various available semiconductor photocatalysts, nanocrystalline titanium-oxides are unique in their activity, stability and biocompatibility. Consequently titanium-oxide mediated photocatalytic mineralization of organic pollutants in aqueous solution has become a well established research area.

Titanium-oxides are mostly exploited as non-selective photocatalysts in degrading water contaminants, mainly organic compounds. However, selective degradation has the advantage of being able to allow the recovery of valuable desired compounds from waste water while degrading the rest. This thesis is about the synthesis, characterization and selective adsorption and degradation properties of titanium dioxide and potassium titanate nanostructures. A low-temperature sol-gel method followed by a pH controlled precipitation technique was adopted for the synthesis of titanium dioxide photocatalysts with tailored surface charge. Potassium titanate was derived by the alkali (KOH) treatment of titanium dioxide nanoparticles under near-ambient experimental conditions. These nanomaterials were tested for their selective adsorption and photocatalytic properties with a cationic and an anionic dye. The origin of the selective adsorption and photocatalytic ability of the synthesized titanium-oxide samples was found to be due to the synergistic effects of surface charge and crystallinity.
PART A: General Declaration

Monash University

Declaration for thesis based or partially based on conjointly published or unpublished work

General Declaration

In accordance with Monash University Doctorate Regulation 17 Doctor of Philosophy and Research Master’s regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes [1] original paper published in peer reviewed journals and [3] unpublished publications. The core theme of the thesis is [Titanium-oxide nanomaterials: synthesis, characterization and selective photocatalysis]. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the [SASE, Gippsland and School of Chemistry, Clayton, Monash] under the supervision of [Prof Douglas R. MacFarlane and A/Prof Walid A. Daoud].

[The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.]

In the case of [1.1, 1.2, 2.1, and 2.2] my contribution to the work involved the following:

<table>
<thead>
<tr>
<th>Thesis chapter</th>
<th>Publication title</th>
<th>Publication status</th>
<th>Nature and extent of candidate’s contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Photocatalytic Water Treatment by Titanium dioxide: Recent Updates</td>
<td>Revision submitted in Catalysts</td>
<td>Development of idea, structuring and preparation of the manuscript (90%)</td>
</tr>
<tr>
<td>1</td>
<td>Achieving Selectivity in TiO$_2$-Based Photocatalysis</td>
<td>Accepted in RSC Advances</td>
<td>Development of idea, structuring and preparation</td>
</tr>
<tr>
<td>2</td>
<td>Selective Adsorption and Photocatalysis of Low-Temperature Base-Modified Anatase Nanocrystals</td>
<td>Published in RSC Advances</td>
<td>Development and execution of the idea, interpretation of the results, and the manuscript preparation (80%)</td>
</tr>
<tr>
<td>2</td>
<td>Understanding the Chemistry of TiO$_2$ Colloidal Systems: Preferential Adsorption and Selective Photocatalysis</td>
<td>Submitted</td>
<td>Development and execution of the idea, interpretation of the results, and the manuscript preparation (80%)</td>
</tr>
</tbody>
</table>

I have renumbered sections of submitted paper in order to generate a consistent presentation within the thesis.

Signed: ........................................

Date: …05/12/2012…
Acknowledgements

I would like to convey my gratitude to my supervisors Prof Douglas R. MacFarlane and A/Prof Walid A. Daoud for their constant support and excellent guidance throughout my doctoral research. I am thankful to Ms Irene Hall (Research & Graduate Studies Officer), Dr Wendy Wright (Honours and Postgraduate Studies Coordinator) and Ms Margo Dundek (Safety Officer) for their sincere efforts to create a pleasant research atmosphere.

I acknowledge Dr Vincent Verheyen, Ms Alicia Reynolds, Dr Wing Sze Tung, Mr Kamran Khajepour, Dr Jianfeng Xue, Ms Lorena Lopez, Mr Santhosh S. Nair, Dr Adam Best, Dr Pradeepan Periyat, Dr Suzanne Neville, Mr Kalim Kashif, Mr Mohammad Barati, Dr Michael Danquah, and Mr Dominic Agyei for their assistance in my PhD studies. Many thanks to all members of SASE, Gippsland, and Doug’s research group for their immense support for my studies. I acknowledge the Monash Centre for Electron Microscopy (MCEM) for their facilities. I am thankful to the Monash Graduate School and Gippsland Campus for the financial support.

I would like to thank Dr Raksh Vir Jasra, my MTech supervisor, and my friends at CSMCRI, Bhavnagar, Gujrat, India, where I started my early research career. I remember my all teachers, friends, and relatives, with a thankful heart.

My parents are the happiest persons for this occasion and I deeply appreciate their sacrifice, prayers and blessings. I dedicate this thesis to them. My beloved wife, Hancy, deserves special thanks for her precious support and encouragement. Above all, thanks to GOD ALMIGHTY, who strengthen me in all situations.

Manoj A. Lazar
This thesis contains five chapters and the contents of each chapter are given below:

**Chapter 1. Introduction**

1.1. **Publication: Photocatalytic Water Treatment by Titanium dioxide: Recent Updates**

Titanium dioxide (TiO$_2$) is a versatile semiconductor photocatalyst for the photocatalytic mineralization of aqueous pollutants in UV/Vis light. Active research is going on in the mechanism and kinetics of photocatalytic degradation using TiO$_2$, immobilization, doping, photocatalytic reactors, and coupling of TiO$_2$ photocatalysis with other treatment technologies. Titanium-oxides are mostly exploited as non-selective photocatalysts in degrading water contaminants, mainly organic compounds. However, selective degradation has the advantage of being able to allow the recovery of valuable desired compounds from waste water while degrading the rest. Therefore *Selective photocatalysis* using titanium dioxide needs more exploration.

Recent progress in photocatalytic water treatment using TiO$_2$ is discussed in the review article entitled “Photocatalytic Water Treatment by Titanium dioxide: Recent Updates”.

1.2. **Publication: Achieving Selectivity in TiO$_2$-based Photocatalysis**

Different techniques have been reported to achieve the selective formation of valuable products and selective degradation of compounds using titanium-oxide nanomaterials. Some of these techniques involve complex and expensive synthesis methods and their application in real systems is therefore questionable.

More detail about selective photocatalysis by using TiO$_2$ is described in the review article entitled “Achieving Selectivity in TiO$_2$-based Photocatalysis,” accepted for publication in *RSC Advances*.
Chapter 2. Selective Photocatalysis

2.1. Publication: Selective Adsorption and Photocatalysis of Low-temperature Base-modified Anatase Nanocrystals

Titanium dioxide nanocrystals with positive and negative surface charge are synthesized and characterized. Synergistic effects of their surface charge and moderate crystallinity are successfully demonstrated for the preferential adsorption and selective degradation of methyl orange (anionic) and methylene blue (cationic) dyes.

The results of this study have been published in the paper entitled “Selective Adsorption and Photocatalysis of Low-temperature Base-modified Anatase Nanocrystals,” RSC Adv. 2012, 2, 447–452.

2.2. Publication: Understanding the Chemistry of TiO$_2$ Colloidal Systems: Preferential Adsorption and Selective Photocatalytic Degradation

This work concerns the systematic formation of titanium dioxide nanoparticles with tailored surface charge and an understanding of the chemistry of titanium dioxide colloidal systems in achieving selective photocatalysis.

The details of these investigations are described in the manuscript entitled “Understanding the Chemistry of TiO$_2$ Colloidal Systems: Preferential Adsorption and Selective Photocatalytic Degradation” (Submitted)


This chapter details the near-ambient synthesis of potassium titanate nanorods from low-temperature sol-gel derived titanium dioxide aliquots nanoparticles. Potassium titanate nanorod formation is monitored and a new mechanism of rod formation is proposed.
Chapter 4. Selective Adsorption of Cationic Methylene Blue Dye by Negatively Surface Charged Potassium Titanate

Chapter 4 illustrates the selective adsorption properties of potassium titanate nanorods. Potassium titanate samples are tested for their selective adsorption of methylene-blue dye from aqueous solution.

Chapter 5. Conclusions and Future Works

Chapter five summarises the findings of this doctoral project and also discusses the future of surface charged titanium-oxide nanostructures.

Aims of the Project

- Investigation of the properties of low-temperature derived titanium dioxide nanoparticles.

- Demonstration of a simple strategy, based on colloidal chemistry, for the synthesis of titanium dioxide nanoparticles with tailored surface charge.

- To study the scope of low-temperature synthesised titanium dioxide photocatalysts for the selective adsorption and selective degradation of charged pollutants.

- Design of ambient experimental conditions for the conversion of titanium dioxide into potassium titanate.

- Examination of morphological transformation of titanium dioxide nanoparticles to potassium titanate nanorods.

- Testing of potassium titanate nanomaterials for the selective adsorption selective adsorption and selective degradation of charged pollutants.
Monash University

Declaration for Thesis Publication 1.1

Declaration by candidate

In the case of Publication 1.1, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development of idea, structuring and preparation of the manuscript</td>
<td>90</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaji Varghese</td>
<td>Involved in preparing one part of the manuscript</td>
<td></td>
</tr>
<tr>
<td>Santhosh S. Nair</td>
<td>Involved in preparing one part of the manuscript</td>
<td>5</td>
</tr>
</tbody>
</table>

Candidate’s Signature

05/12/12

Declaration by co-authors

The undersigned hereby certify that:

(1) the above declaration correctly reflects the nature and extent of the candidate’s contribution to this work, and the nature of the contribution of each of the co-authors.

(2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
(3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
(4) there are no other authors of the publication according to these criteria;
(5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
(6) the original data are stored at the following location(s) and will be held for at least five years from the date indicated below:

<table>
<thead>
<tr>
<th>Location(s)</th>
<th>SASE, Gippsland Campus, Monash, Churchill, VIC-3842, Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signature 1</td>
<td><img src="signature1.png" alt="Signature" /> 05/12/12</td>
</tr>
<tr>
<td>Signature 2</td>
<td><img src="signature2.png" alt="Signature" /> 05/12/12</td>
</tr>
</tbody>
</table>
Photocatalytic Water Treatment by Titanium dioxide: Recent Updates

Manoj A. Lazar 1,2,a, Shaji Varghese 3 and Santhosh S. Nair 1,2

1 School of Applied Sciences and Engineering, Monash University, Churchill VIC, 3842, Australia.
E-Mails: manoj.ainikalkannath@monash.edu (ML), santhosh.nair@monash.edu (SN)
2 School of Chemistry, Monash University, Clayton VIC, 3800, Australia.
3 Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Complesso Universitario
Monsserrato, CA, Italy
E-Mail: shajivarg@gmail.com

* Author to whom correspondence should be addressed; E-Mail: manoj.ainikalkannath@monash.edu,
manojlazar2005@gmail.com(MAL); Tel.: +61 3 990 26411; Fax: +61 3 990 26738.

Received: / Accepted: / Published:

Abstract: Photocatalytic water treatment using nanocrystalline titanium dioxide (NTO) is a well-known advanced oxidation process (AOP) for environmental remediation. With the in situ generation of electron-hole pairs upon irradiation with light, NTO can mineralize a wide range of organic compounds into harmless end products such as carbon dioxide, water, and inorganic ions. Photocatalytic degradation kinetics of pollutants by NTO is a topic of debate and the mostly reporting Langmuir-Hinshelwood kinetics must accompanied with proper experimental evidences. Different NTO morphologies or surface treatments on NTO can increase the photocatalytic efficiency in degradation reactions. Wisely designed photocatalytic reactors can decrease energy consumption or can avoid post-separation stages in photocatalytic water treatment processes. Doping NTO with metals or non-metals can reduce the band gap of the doped catalyst, enabling light absorption in the visible region. Coupling NTO photocatalysis with other water-treatment technologies can be more beneficial, especially in large-scale treatments. This review describes recent developments in the field of photocatalytic water treatment using NTO.

Keywords: titanium dioxide; advanced oxidation process; photocatalysis; water treatment; degradation; Langmuir-Hinshelwood kinetics; photocatalytic reactor; doping.
1. Introduction

Realizing the importance of keeping our planet clean, researchers are actively working for eco-friendly alternative technologies for all areas of daily life. Sustainable energy production and pollutant destruction are two of the areas in which intense research is being carried out. Semiconductor-mediated photocatalysis is a well-established technique for pollutant degradation and hydrogen (clean fuel) production by water splitting. Photocatalysis can be defined as a “catalytic reaction involving the production of a catalyst by absorption of light” [1]. The appropriate positioning of valence (VB) and conduction (CB) bands in semiconductors (Figure 1a) makes them suitable materials for the absorption of light and photocatalytic action. Nanocrystalline titanium dioxide (NTO) is a multifunctional semiconductor photocatalyst that can be an energy catalyst (in water splitting to produce hydrogen fuel), an environmental catalyst (in water and air purification), or an electron transport medium in dye-sensitized solar cells (Figure 1b) [2-5]. Compared to other available semiconductor photocatalysts, NTO is unique in its chemical and biological inertness, photostability (i.e., not prone to photoanodic corrosion), and low cost of production [6]. Photocatalytic water and air purification using NTO is a predominant advanced oxidation process (AOP) because of its efficiency and eco-friendliness. Homogeneous photo-Fenton technique is another efficient AOP for the oxidation of water contaminants [7,8]. However, the photo-Fenton process requires the use of ferrous sulfate (FeSO₄) and hydrogen peroxide (H₂O₂). For example, in the photo-Fenton oxidation of catechol, H₂O₂ (2000 mg L⁻¹) and FeSO₄ (500 mg L⁻¹) were used in the experiment that reported the highest activity [7]. In contrast, NTO photocatalysis may not require any additional reagents beyond the NTO catalyst.

**Figure 1.** (a) VB and CB positions in metals, semiconductors, and insulators.  
(b) Tree diagram showing applications of TiO₂.
The spectrum of compounds that are susceptible to the destructive power of NTO photocatalysis is remarkable, comprising families of dyes, pesticides, herbicides, pharmaceuticals, cosmetics, phenolic compounds, toxins, and more. Recent examples of compounds photocatalytically degraded by NTO are given in Table 1. It is obvious from the table that researchers are focused on the photocatalytic degradation of real pollutant systems, such as cosmetics and pharmaceutical wastewaters [9,10], paper mill wastewater [11], grey water [12], and municipal wastewater [13]. Cheaper sources of TiO\textsubscript{2}, such as bulk-synthesized TiO\textsubscript{2} pigment [14] and iron-containing industrial TiO\textsubscript{2} by-products [15], have been explored for the photocatalytic degradation of phenol and humic acids. Interestingly, their activities were found to be comparable with those of the commercially available Degussa P25 TiO\textsubscript{2} photocatalyst, the benchmark TiO\textsubscript{2} photocatalyst for all applications. A report by Kim et al. describes the successful, elegant, and simultaneous use of NTO as both an energy and an environmental photocatalyst [16]. Their surface-fluorinated and -platinized NTO catalyst generated hydrogen gas when degrading 4-chlorophenol and bisphenol compounds. The selective degradation of contaminants is another promising area in photocatalytic water treatment. Selective degradation could be useful for mixtures of highly toxic pollutants in low concentrations and less harmful compounds in higher concentrations [17,18]. The former can be degraded by means of NTO photocatalysis, whereas the latter can be removed by less-expensive biological wastewater treatments [18]. In addition, valuable compounds must be recovered from wastewater; selective photocatalysis can be a useful tool. Recently, one of the authors reported the complete selective degradation of methyl orange and methylene blue dyes by base-modified nanocrystalline anatase (the most active form of TiO\textsubscript{2}) photocatalysts [19]. Among the two sol-gel-derived anatase photocatalysts, TSC60, with positive surface charge, selectively adsorbed and degraded the anionic dye methyl orange. In contrast, the second catalyst, TA60, with negative surface charge, showed selective adsorption of the cationic dye methylene blue, followed by its degradation, from an aqueous mixture containing methyl orange and methylene blue dyes.

2. Mechanism and kinetics

Photocatalytic destruction of pollutants in aqueous solutions using NTO is facilitated mainly by a series of hydroxylations reactions initiated by hydroxyl radicals (•OH) [20-26]. Possible modes of •OH generation during NTO photocatalysis are shown in Figure 2. Upon UV light illumination, electron-hole pairs are formed in the NTO semiconductor photocatalyst. Holes are positive charges, which when in contact with water molecules, produce •OH and H\textsuperscript{+} ions. Electrons react with dissolved oxygen to form superoxide ions (O\textsubscript{2}\textsuperscript{-}), which react with water molecules to produce hydroxide ions (OH\textsuperscript{-}) and peroxide radicals (•OOH). Peroxide radicals combine with H\textsuperscript{+} ions to form •OH and OH\textsuperscript{-}, and holes oxidize OH\textsuperscript{-} to •OH. Thus, all species eventually facilitate the formation of •OH, and these radicals attack the pollutants present in the aqueous solution. Medina et al. reported [20] the formation of 51 stable intermediates in the photocatalytic degradation of the mosquito repellent N,N-diethyl-m-toluamide (DEET) using titanium dioxide under simulated solar light. Using a technique that coupled high-performance liquid chromatography with high-resolution mass spectrometry, they also identified several isomeric species. The degradation of DEET began with •OH-mediated mono- and polyhydroxylation reactions, followed by the oxidation
Table 1. Recent examples of pollutants photocatalytically degraded by NTO.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Photocatalytic system</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dyes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive violet 5</td>
<td>UV/Anatase powder (Sigma Aldrich)</td>
<td>[27]</td>
</tr>
<tr>
<td>Blue 9, Red 51&amp; Yellow 23</td>
<td>Solar/TiO₂ (Degussa P25)</td>
<td>[28]</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>UV/TiO₂ on glass</td>
<td>[29]</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>UV/TiO₂ (Merck) on volcanic ash</td>
<td>[30]</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>UV/TiO₂ bilayer</td>
<td>[31]</td>
</tr>
<tr>
<td><strong>Pesticides &amp; herbicides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organophosphate &amp; Phosphonoglycine</td>
<td>UV/TiO₂ immobilized on silica gel</td>
<td>[32]</td>
</tr>
<tr>
<td>Azimsulfuron</td>
<td>UV/TiO₂ coated on glass rings</td>
<td>[33]</td>
</tr>
<tr>
<td>Swp residues</td>
<td>Simulated sunlight/TiO₂ (Degussa P25)</td>
<td>[34]</td>
</tr>
<tr>
<td><strong>Pharmaceuticals &amp; cosmetics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrocoagulation &amp; UV/TiO₂/H₂O₂</td>
<td>Solar/TiO₂ (six commercial samples)/H₂O₂</td>
<td>[42]</td>
</tr>
<tr>
<td>UV/TiO₂ (Aeroxide P25)</td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>TiO₂/Fe₃O₄ &amp; TiO₂/SiO₂/Fe₃O₄</td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>Benzylparaben</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[39]</td>
</tr>
<tr>
<td><strong>Drugs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxolinic acid</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[40]</td>
</tr>
<tr>
<td>Atenolol &amp; propranolol</td>
<td>UV/Commercial TiO₂</td>
<td>[41]</td>
</tr>
<tr>
<td>Ciprofloxacin, ofloxacin, norfloxacin &amp; erofloxacin</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[43]</td>
</tr>
<tr>
<td>Lamivudine</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[44]</td>
</tr>
<tr>
<td>Oxytetracycline</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[45]</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N,N-diethyl-m-toluamide (Insect repellent)</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[20,46]</td>
</tr>
<tr>
<td>β-naphthol</td>
<td>UV/TiO₂-SiO₂</td>
<td>[47]</td>
</tr>
<tr>
<td>15 emerging contaminants</td>
<td>Solar UV/TiO₂ coated on glass spheres</td>
<td>[48]</td>
</tr>
<tr>
<td>Grey water</td>
<td>UV/TiO₂ (Aeroxide P25)</td>
<td>[12]</td>
</tr>
<tr>
<td>Microcystins (Cyanotoxin)</td>
<td>UV/TiO₂ film</td>
<td>[49,50]</td>
</tr>
<tr>
<td></td>
<td>UV/Doped TiO₂</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>UV/ Nitrogen doped TiO₂</td>
<td>[52]</td>
</tr>
<tr>
<td><strong>Lipid vesicles &amp; E. coli cells</strong></td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[53]</td>
</tr>
<tr>
<td><strong>Bacterial colony</strong></td>
<td>UV/TiO₂ on titanium beads</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td>UV/TiO₂-coated bio-film</td>
<td>[55]</td>
</tr>
<tr>
<td><strong>Paper mill wastewater</strong></td>
<td>Solar/TiO₂</td>
<td>[11]</td>
</tr>
<tr>
<td><strong>Endocrine disrupting compounds</strong></td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>[56]</td>
</tr>
<tr>
<td><strong>Municipal waste water</strong></td>
<td>Solar/sol-gel TiO₂ &amp; Degussa P25</td>
<td>[13]</td>
</tr>
<tr>
<td><strong>Contaminated soil</strong></td>
<td>Plasma/TiO₂ ((Degussa P25)</td>
<td>[57]</td>
</tr>
</tbody>
</table>
and ring-opening reactions of intermediates. All the identified intermediates underwent complete mineralization after 4 h irradiation. The •OH-initiated photocatalytic oxidation of quinolones [21], i.e., flumequine and nalidixic acid, using NTO under solar light passed through fourteen stable intermediates that were identified using liquid chromatography-time of flight-mass spectrometry. In another example, five hydroxylated intermediates (Scheme 1) were identified in the degradation of a pesticide, carbofuran [22]. The role of •OH in the initiation of this photocatalytic degradation was confirmed by the knowledge of carbofuran adsorption on P25 catalyst and by conduction of the experiments using a non-aqueous solvent, acetonitrile. Carbofuran showed a negligible adsorption (~1%) on Degussa P25 TiO₂ catalyst. The absence of adsorption eliminates the possibility of the direct oxidation of carbofuran by surface-generated holes [22], which is considered to be a minor secondary reaction in NTO photocatalytic degradation [25,26] on TiO₂ catalysts under UV illumination. When this experiment was conducted in the non-aqueous solvent, acetonitrile, total inhibition of carbofuran degradation was observed [22], due to the low production of •OH in acetonitrile. These findings show that the photocatalytic degradation of aqueous pollutants is initiated mainly by •OH attack. However, An et al. reported [25] secondary mechanistic pathways for the photocatalytic degradation of the antiviral drug lamivudine by UV-irradiated NTO. These secondary pathways originated from photogenerated holes on NTO, which caused the initial oxidation of the lamivudine adsorbed on the NTO surface (Scheme 1). It is important to note that these secondary degradation pathways initiated by photogenerated holes were minor side reactions; the major degradation pathway of lamivudine was through •OH attack.
Scheme 1. Photocatalytic degradation pathways of (a) carbofuran and (b) lamivudine (Reproduced from [22] and [25] respectively, copyright (2011), with permission from Elsevier).

The kinetics of the photocatalytic degradation of aqueous pollutants by NTO is still a subject of debate [58-60]. Several recent reports claim that it follows the Langmuir-Hinshelwood model (L-H model) of kinetics [21,22,25,26]. However, the validity of L-H model in photocatalytic degradation reactions could be a misconception or rather an easier way of interpretation [61]. Therefore reporting L-H model of kinetics in photocatalytic degradation without proper experimental evidences is dubious. The kinetic profile for the degradation of methylparaben, a bactericide and antimicrobial agent in
personal care products, by NTO photocatalysis has been reported to follow the L-H model, where the rate expression can be shown as follows [26].

\[
r = -\frac{dC}{dt} = k_{LH} \theta = k_{LH} \frac{K_L C_{eq}}{1 + K_L C_{eq}}
\]

(1)

where \(r\) is the reaction rate, \(k_{LH}\) is the apparent L-H rate constant, \(\theta\) is the surface coverage of methylparaben, \(K_L\) is the Langmuir adsorption constant, and \(C_{eq}\) is the equilibrium concentration. At low concentrations of methylparaben, \(K_L C_{eq} (K_L C_{eq} \ll 1)\) is negligible and equation (1) becomes a pseudo-first-order rate expression [26], as denoted below.

\[
r = -\frac{dC}{dt} = k_{LH} K_L C_{eq} = k_{app} C_{eq}
\]

(2)

Integrating equation (2)

\[
ln \frac{C_{eq}}{C} = k_{app} t + constant
\]

(3)

Equations (1)–(3) account for the adsorption of the reactant (methylparaben) only but do not consider the adsorption on NTO of any intermediates or products formed during the course of the degradation reaction. When the adsorption of intermediates or products must be considered [21], a modified rate equation results, as shown below.

\[
r = -\frac{dC}{dt} = k_{LH} K_L C_{eq} \frac{K_L C_{eq}}{1 + K_L C_{eq} + \sum_{i=1}^{n} K_i C_i (i = 1, n)}
\]

(4)

where \(K_i\) and \(C_i\) are the adsorption constant and concentration of intermediates at any given time, respectively. When the initial concentration of pollutants is very low, \(1 + K_L C_{eq} + \sum_{i=1}^{n} K_i C_i \ldots\) is negligible and the reaction follows pseudo first order kinetics, as shown in equations (2) and (3).

Sirtori et al. have reported that the photocatalytic degradation by NTO follows L-H kinetics at low pollutant concentrations and below the catalyst saturation level [21]. It deviates from the pseudo-first-order kinetics under several conditions. The NTO catalyst concentration and the light flux have been found to influence the degradation kinetics of methylparaben [26]. According to the L-H model, the photocatalytic degradation rate of methylparaben should increase with an increase in the NTO catalyst loading because of the additional available active sites (\(\theta\)) for adsorption. This was observed up to a certain catalyst loading (catalyst saturation), but above that limit, the experimental kinetics results did not fit the L-H model [26]. This was mainly ascribed to three reasons: at higher NTO loading, (i) deactivation of activated NTO could occur upon collision with ground state NTO catalysts, (ii) there is a higher possibility of agglomeration and sedimentation of NTO, and (iii) there is decreased light penetration through the reaction medium. UV light flux has been found to be an important influence on the degradation kinetics of methylparaben in aqueous medium [26]. At low UV light flux (1.2 ×
$10^{15}$ photons s$^{-1}$ cm$^{-2}$ $< \phi < 4.0 \times 10^{15}$ photons s$^{-1}$ cm$^{-2}$, methylparaben degradation followed L-H kinetics, where electron-hole pairs mainly resulted in chemical reactions rather than recombination. However, at intermediate UV light intensities (4.0 $\times$ $10^{15}$ photons s$^{-1}$ cm$^{-2}$ $< \phi < 5.8 \times 10^{15}$ photons s$^{-1}$ cm$^{-2}$), the methylparaben degradation rate varied as a functional order between zero and one. In this medium UV light region, the recombination of electron-hole pairs was predominant over degradation. The random selection of a particular concentration of the pollutant is not enough to study the dependence of rate on photon flow [61]. Concentration of the pollutant is also important as demonstrated by Serpone et al. [61] where the order of the photocatalytic reaction varied between zero (at low pollutant concentration) and one (at high pollutant concentration) in the same range of light irradiance. Therefore a complete study should focus on different concentrations of pollutant to know the dependence of light irradiance on the photocatalytic reaction rate.

Wang et al. posited a rate expression that was different from the conventional pseudo-first-order rate equation, to explain the kinetics of sulfosalicylic acid degradation in aqueous solution using NTO [58]. Their proposed rate equation considers factors such as the lifetime and concentration of $\cdot$OH, pH, and adsorption of intermediates on NTO. The rate equation can be represented as follows.

$$\frac{dC}{dt} = \frac{k_{+3}k_{4}\tau[h^+]}{k_{-3}[H^+]} \frac{K_aC_{eq}}{1 + \sum_{i=1}^{n} K_i C_i + K_a C_{eq}}$$

(5)

$$\frac{k_{+3}[h^+]}{k_{-3}[H^+]} = [\cdot OH]$$

(6)

where, $\tau$ is the lifetime of $\cdot$OH and $k_4$ is the rate constant for the reaction of $\cdot$OH with the adsorbed pollutant on NTO. $K_a$ and $K_i$ are the adsorption equilibrium constants of sulfosalicylic acid and the intermediates, respectively, and $C_{eq}$ and $C_i$ are their equilibrium concentrations. Adsorption of the identified intermediates of sulfosalicylic acid degradation on NTO was found to be insignificant [58]; hence, equation (5) can be simplified as

$$\frac{dC}{dt} = \frac{k_{+3}k_4\tau[h^+]}{k_{-3}[H^+]} \frac{K_aC_{eq}}{1 + K_aC_{eq}}$$

(7)

Integrating equation (7), we get

$$\ln\left(\frac{C_{eq}}{C}\right) + K_a(C_{eq} - C) = k_{app}t$$

(8)

$$k_{app} = \frac{k_{+3}k_4\tau[h^+]}{k_{-3}[H^+]} K_a$$

(9)

The order of the degradation reaction will then be determined by three different adsorption situations: (i) weak adsorption (\(K_a C_{eq} \ll 1\)), (ii) medium adsorption (\(0.1 < K_a C_{eq} < 10\)), and (iii) strong adsorption (\(K_a C_{eq} > 10\)) [58]. In the case of weak adsorption of the pollutant on NTO, equation (8) reduces to the pseudo-first-order expression, as shown in equation (3). Medium adsorption leads to
equation (8), which was observed in the case of sulfosalicylic acid degradation kinetics. In the case of strong adsorption, the rate is independent of $K_a$ and adsorption does not affect the rate of the reaction; here, the reaction will follow a zero-order kinetic model and the rate expression becomes

$$\ln \left( \frac{C_{eq}}{C} \right) = k_{app}$$  \hspace{1cm} (10)

Pace of photocatalytic degradation of a particular pollutant also depends on other factors such as alkalinity, and the presence of natural organic matter, [62] especially in real systems. Carbonate and bicarbonate ions, which are responsible for the alkalinity of water, have been found to decrease the rate of the photocatalytic degradation of microcystine-LR [62]. Also, the presence of humic acid and fulvic acid (natural organic matter) reduced the rate of microcystine-LR degradation [62].

3. Activity enhancement

Recent efforts to enhance the photocatalytic activity of NTO include the synthesis of mesoporous TiO$_2$ [63-73], the use of different TiO$_2$ morphologies (nanowires, nanotubes, and nanospheres) [74-77], reducing the agglomeration in NTO powders [78-80], and surface treatments of NTO [81-84]. Synthesis of mesoporous NTO is a means to achieve TiO$_2$ photocatalysts with improved photocatalytic activities. Some of the recently reported mesoporous TiO$_2$ photocatalysts exhibited superior photocatalytic activity than the bench mark Degussa P25 TiO$_2$ photocatalyst. TiO$_2$ photocatalysts with active [001] facets were derived hydrothermally by using ammonium fluoride [63] or mild sulfuric acid [64] capping agents and showed superior dye degradation activity in comparison with the Degussa P25. Mesoporous TiO$_2$ catalysts synthesized by using F127 triblock copolymer [65], polystyrene [66], and silica [67] (through etching and recalcination method) have been reported for the efficient degradation of methanol, methyl orange and rhodamine B pollutants, respectively. These synthesized mesoporous catalysts outperformed the commercially available Degussa P25 and Hombicat UV-100 [65] photocatalysts in their photocatalytic activity.

NTO nanowires obtained by the post-calcination of hydrothermally derived titanates were found to be more efficient than Degussa P25 in the degradation of humic acid [74] and Reactive Brilliant Blue X-BR [76]. These nanowires also caused less serious fouling than P25 in microfiltration membranes. In another study [75], NTO nanotubes obtained by the anodic oxidation of titanium metal plate were 25–40% more efficient than the nanoparticle-based experimental system for the degradation of rhodamine B. Anatase submicroparticles consisting of NTO nanorods (20–30 nm in diameter) with thorn-like shells have been reported [77]. This morphology resulted in multiple reflections of the incident light, and the catalyst was found to be equally comparable with P25 in the degradation of methylene blue dye solution under UV irradiation.

The agglomeration of NTO during its formation can reduce the dispersion of TiO$_2$ in aqueous suspensions, contributing to decreased photocatalytic activity. The agglomeration of TiO$_2$ can be minimized by changing the pH of the reaction mixture [79], adsorbing polyallylamine hydrochloride on the TiO$_2$ surface [79], adopting a flame hydrolysis synthesis route [80], or ball milling of the TiO$_2$ powder [78]. All attempts were successful in reducing the agglomeration of NTO in aqueous suspensions, but the photocatalytic activities were found to depend not only on agglomeration but also
on several other factors. Recently reported surface treatments include surface fluorination [82], high-energy electron beam treatment [83], modification with S-1-dodecyl-S’-(α,α’-dimethyl-α”-acetic acid) trithiocarbonate (DDAT) [84], and incorporation of a TiO₂ microsphere layer [81]. During the photooxidation of catechol and phenol, an electrochemical surface-fluorinated NTO electrode could reduce electron-hole recombination and also displace the oxidizable organic compounds and poisoning species from the surface [82]. This resulted in the superior performance of the fluorinated TiO₂ versus the bare TiO₂ electrode. In the high-energy electron beam treatment of NTO, the carbon content on the TiO₂ surface was increased by the burning of impurities already present on the catalyst [83]. This increased the hydrophilicity and the photocatalytic activity of the electron beam-treated TiO₂ in the degradation of methylene blue dye. Modifying NTO with DDAT caused a red shift in the absorbance of the modified catalyst through a ligand-to-metal charge transfer transition, which enhanced its visible light activity towards the degradation of 2,4-dichlorophenol, when compared to the as-prepared TiO₂ catalyst [84]. The formation of a TiO₂ microsphere layer over a nanostructured TiO₂ layer (deposited on Pyrex glass by spin coating) increased the contact area for methylene blue dye in aqueous solution, resulting in faster degradation kinetics [81].

4. Immobilization of TiO₂

Immobilization of TiO₂ on various substrates is an important research area with its photocatalytic water treatment applications [85]. The primary aim of doing so is to avoid the post separation difficulties associated with the powder form of the TiO₂ catalyst. However, there are several other advantages including higher surface area, superior adsorption properties [30,86,87], and increased surface hydroxyl groups or reduced charge recombination [88] are achievable in immobilized systems. Immobilization of TiO₂ can be done on powder/pellet substrates [30,86,87], soft/thin materials [55,89-94] or on rigid/thick substrates. Some of the recent examples of powder/pellet substrates include activated carbon [86], vermiculite (magnesium-aluminium silicates) [87], and volcanic ash [30]. Sedimentation of these TiO₂ immobilized systems could be easier than the TiO₂ catalyst alone systems, since they are heavier particles. TiO₂ immobilized on soft/thin substrates, normally referred as TiO₂ membrane or films, are applicable in ultra filtration and bacterial inactivation. Since they are immobilized with TiO₂, they can act as self cleaning surfaces. Recent examples of this category include TiO₂ immobilized on alumina (1.5 micron thick) [89-91], polyvinylidene difluoride [92], glass filter [93], cellulose fibres [94], and sponge [55]. Various immobilization techniques such as chemical vapour deposition [90,91], slip coating [89], dip coating [89], film casting [92], electrospinning [93,94] and dip-evaporation [55] has been employed to achieve immobilization of TiO₂ on soft/thin substrates.

Immobilization of TiO₂ on rigid substrates is mostly done on glass [31,33,88,95-99]. Main advantage with glass substrate is the transparency of the system even after the immobilization. This can allow the penetration of light which can result in improved photocatalysis. Dionysiou et al. [95] have reported a non-ionic surfactant (Tween20) templated self assembly pathway to immobilize TiO₂ on borosilicate glass by the dip coating technique. The use of surfactant resulted in a uniform and crack free TiO₂ surface with partially ordered mesoporosity to the calcined borosilicate glass TiO₂ films. Addition of Degussa P25 to the surfactant containing TiO₂ sol imparted a bimodal mesoporous structure to the
catalyst immobilized system which improved the structural integrity of the films [96]. The use of a non-ionic fluoro surfactant (Zonyl FS-300) instead of Tween 20, and the addition of ethylene diamine into the TiO₂ sol for dip coating; nitrogen and fluorine Co-doped visible light active TiO₂ coating on borosilicate glass was achieved (after calcination) [97]. Interestingly, the surface was found to be hydrophilic under both UV and visible (400-510 nm) light exposure while the undoped TiO₂ surface was hydrophilic only under UV light [98]. They could also achieve sulfur doped visible light active (after calcination) TiO₂ coating by adding sulfuric acid (sulfur precursor) and polyoxyethylene (80) sorbitan monoooleate surfactant (as pore directing agent) into the TiO₂ sol [99]. All these TiO₂ immobilized borosilicate glass systems were successfully tested for the photocatalytic degradation of creatinine [95,96], microcystines [97,99-101], and cyindrospermopsis [101] under UV/visible light irradiation.

The role of surface defects in the TiO₂ surface on the photocatalytic degradation mechanism is demonstrated by Zhuang et al [31]. They produced three TiO₂ immobilized systems (with normal surface, surface defects and with interface defects) on quartz by either using dip coating techniques alone or using both dip coating and cold plasma treatment techniques. The normal TiO₂ surface mainly promoted N-deethylation of rhodamine B dye while the TiO₂ surface with defects was very efficient for cyclorevision of RhB. The TiO₂ surface with interface defects showed both mechanisms and was found to be the best system for the rhodamine B dye degradation.

5. Photocatalytic reactors

Reactor design is an intense focus for photocatalytic water treatment. Here, reviewed photocatalytic reactors can be divided in to two categories, i.e., (i) lab-scale reactors [75,102-112], where the volume of reactant solution is <1 L, and (ii) pilot plant-scale reactors [45,113-117], where the reactor volume is >5 L. Recent innovations in lab-scale reactors include the use of energy-efficient UV/visible light emitting diodes (LEDs) as light sources [107-106], the design of rotating disc-type reactor models [75,107], the fabrication of NTO-immobilized catalytic beds [108,109], and post-separation/reuse of NTO powder catalysts [110-112]. LEDs are light sources that need less energy and, therefore, LED-based photocatalytic reactors are more energy-efficient systems. The combination of UV-LEDs and NTO powder [102], NTO nanotubes [103], or immobilized NTO [104,105] has been reported for the degradation of various dyes such as methyl orange, methylene blue, rhodamine B, and malachite green. The UV-LED photoreactor developed by Nickels et al. [105] was equipped with a microcirculating fluid pump (to keep the reactant solution constantly mixed) and an in-stream sensor unit (Figure 3). The sensor unit, an assembly of a liquid flow cell with transparent windows, an LED lamp, and a photodiode monitor, enabled the real-time evaluation of the decrease in the concentration of methyl orange dye. Other attributes of the reactor, such as its light weight, low production cost, and flexibility, make this design ideal for both laboratory and field work applications, as claimed by the authors. Visible LEDs with carbon-nitrogen co-doped NTO achieved the visible light degradation of bisphenol [106]. The reactor consisted of four strips of visible LEDs, i.e., white, green, blue, and yellow, which covered the wavelength range of 450 to 600 nm.
Rotating disc reactor design in NTO photocatalysis has several merits as first demonstrated by Dionysiou et al. [118,119]. A NTO-coated borosilicate rotating disc (diameter = 6 cm) was reported for the degradation of methyl orange dye [107]. The aqueous methyl orange solution film thickness on the disc was optimized by adjusting the flow rate of the reactant feed and the rotating speed of the disc. Zhang et al. designed a rotating disc reactor of TiO$_2$ nanotubes by the anodization of a Ti metal plate [75]. Half of the disc was always immersed in the bulk solution of the reactant rhodamine B dye, whereas the other half was exposed to air. They observed a faster degradation rate for rhodamine B dye on the air-exposed disc surface than in the bulk of the solution. This TiO$_2$ nanotube disc reactor was 20–25% more efficient than the TiO$_2$ nanoparticle-coated disc system.

Recently reported immobilized catalytic bed designs include a NTO-coated pebble bed photocatalytic reactor [108] and an ETS-10 (Engelhard titanium silicate 10)-coated optic fiber reactor [109]. The former consisted of a Perplex$^\text{TM}$ sheet onto which NTO-coated pebbles were affixed [108]. The arrangement of the pebbles was such that the pebbles in one row formed an equilateral triangle with the pebbles in the next row. Keeping the reactor in a horizontal position, textile dye solution (0.66 L) was degraded under sunlight irradiation. In the other example, the ETS-10-coated optic fiber reactor showed 4–5 times greater quantum efficiency than an ETS-10 slurry reactor in degrading methylene blue dye solution under UV light illumination [109]. The reactor consisted of optical fibers, uniformly coated with ETS-10, inserted in an acrylic cylinder.

Post separation of NTO powder catalysts in slurry reactors is one of the major challenges in photocatalytic water treatment. Toward this end, Kim et al. [110] reported a reactor design in which the P25 powder catalyst could be separated from the treated water by a submerged microfiltration membrane. They used this reactor system in conjunction with reverse osmosis for the photocatalytic treatment of seawater samples. In another reactor design, Suryaman et al. [111] achieved the natural sedimentation of the P25 powder catalyst after phenol degradation in pipe water. Treated water overflowed from the separation tank, whereas the P25 catalyst settled at the bottom of the separation.
Table 2. Examples of large-scale photocatalytic reactors.

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Experimental condition</th>
<th>Volume (L)</th>
<th>pollutant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound parabolic collector pilot-plant</td>
<td>0.2 g L(^{-1})/solar</td>
<td>22 &amp; 110</td>
<td>Cork boiling and bleaching waste water</td>
<td>[113]</td>
</tr>
<tr>
<td>Concentric parabolic concentrator pilot-plant</td>
<td>TiO(_2) coated paper (20 g m(^{-2}))/solar</td>
<td>16.2</td>
<td>Humic substances</td>
<td>[114]</td>
</tr>
<tr>
<td>Membrane pilot system</td>
<td>0.05 g L(^{-1})/UV</td>
<td>-</td>
<td>32 pharmaceuticals</td>
<td>[115]</td>
</tr>
<tr>
<td>Thin film fixed-bed reactor</td>
<td>TiO(_2) on the reactor walls/solar</td>
<td>-</td>
<td>Yellow Cibacron FN-2R</td>
<td>[116]</td>
</tr>
<tr>
<td>Tubular continuous flow pilot-plant</td>
<td>0.1 g L(^{-1})/solar</td>
<td>7</td>
<td>p-nitrophenol, naphthalene, dibenzothiophene</td>
<td>[117]</td>
</tr>
<tr>
<td>Compound parabolic collector pilot-plant</td>
<td>0.5 g L(^{-1})/solar</td>
<td>6</td>
<td>Oxytetracyclin</td>
<td>[45]</td>
</tr>
</tbody>
</table>

tank. The use of NTO pellets is another option to avoid post separation requirements in photocatalytic reactors. With a patented “drum reactor” design [112], McCullagh et al. reported the degradation of methylene blue dye solution by Hombikat TiO\(_2\) pellets. The reactor had three cylinders with paddles, which contained TiO\(_2\) pellets. Each cylinder was supplied with 36 W UV lamps and was connected to a 12 V motor to effect cylinder rotation.

Recently reported pilot plant photocatalytic reactors have mainly utilized natural sunlight as a light source [45,113,114,116,117]. However, an UV light-based pilot plant reactor has also been reported [115]. The use of NTO in powder [45,113,115,117] or immobilized forms [114,116] has also been examined. Table 2 depicts some recent examples of pilot plant photocatalytic reactors used for the degradation of various contaminants.

6. Doping

The band gaps (3–3.2 eV) of NTO semiconductors, which absorb from the UV region of the solar spectrum, are drawbacks in photocatalysis; only about 5% of sunlight comprises UV radiation. Modification of the band gap in NTO is, therefore, a well-studied research area. Modifications can be effected either in bulk or on the surface of TiO\(_2\) (Scheme 2). Surface modifications are usually achieved by anchoring colored inorganic semiconductors (for example, CdS and CdSe) [120] or organic dyes on the TiO\(_2\) surface [121], where they act as sensitizers. However, most of these sensitizers are susceptible to photocorrosion or degradation in aqueous solutions and are not suitable for photocatalytic water-treatment applications. Instead, they are good candidates for solar cell devices.
On the other hand, bulk modification is mainly effected by doping metals or non-metals into bulk NTO. The modified catalysts appear to be photo-stable in aqueous solution and can be used in photocatalytic water purification.

Scheme 2. Different methods of modification on NTO.

Doping NTO with metals and non-metals creates new energy levels between the VB and CB of TiO$_2$[122], which in turn reduces its band gap and helps the doped catalyst to absorb in the visible region (Figure 4). Recently, researchers have reported the successful doping of vanadium [123], iron [124], rhodium [51], palladium [125], and silver [126] metals, and carbon [106,127], nitrogen [52,97,106,122,125,128,129], sulfur [99,130], fluorine [97], and iodine [131] non-metals in NTO to achieve the visible light photocatalytic degradation of various chemicals and *Escherichia coli* in aqueous solution (Table 3). In all reports, except in silver doping, the visible light photocatalytic activity was mainly attributed to the associated red shift that originated from the creation of local bands between the VB and CB of NTO (Figure 4). Silver doping in P25 by a photoreduction method did not reduce the band gap of the doped catalyst, but superior photocatalytic degradation of oxalic acid was still observed, when compared to undoped P25, under artificial sunlight [126]. This was explained by the formation of silver oxalate, which absorbed from the visible region and was subsequently degraded.

Not all doping in NTO will exhibit positive effects, as reported in the cases of rhodium, carbon, and platinum doping. Rhodium doping afforded the highest activity for microcystin-LR degradation under visible light, followed by the carbon-doped catalyst [51]. In contrast, the platinum-doped NTO catalyst did not exhibit efficient visible light degradation because of the interference from chloride radicals generated by the homolytic cleavage of the platinum–chlorine bond in the platinum precursor. The synthetic route for the doped NTO catalyst also influences its activity. For example, hydrothermally derived vanadium-doped TiO$_2$ showed higher activity than its sol-gel-derived counterpart in the degradation of an aqueous solution of isobutanol [123]. The addition of ammonium fluoride during hydrothermal treatment caused further enhancement in the activity of doped catalyst. The higher crystallinity resulting from the hydrothermal treatment and the hydrophobic surface formation by
ammonium fluoride were responsible for these observations [123]. Heat treatment has a great influence in the characteristics and activity of doped NTO catalysts, especially in the case of nitrogen doping. Gohin et al. [129] observed a color change of anatase nanoparticles from slight yellow (at 500°C) to darkish green (above 650°C) at different nitridation temperatures using urea as a nitrogen source. The yellow color at 500°C resulted from the formation of localized N 2p states above the VB of TiO₂. However, the darkish green color change, observed above 650°C, was due to the reduction of Ti⁴⁺ in anatase to Ti³⁺ by ammonia (from the decomposition of the urea precursor). These Ti³⁺ species were found to have detrimental effects on photocatalytic activity because they can act as recombination centers. The sample nitridated at 500°C exhibited superior photocatalytic activity under visible light irradiation. However, whether Ti³⁺ in doped NTO can reduce [131] or increase [99,129] the electron-hole pair recombination is still open to debate. The selection of pollutants is very important in visible light-induced photocatalytic degradation using doped NTO catalysts [126,130]. For example, when 4-methoxyresorcinol, quinoline, and 1-(p-anisyl)neopentanol were subjected to visible light photocatalytic degradation with sulfur-doped TiO₂ (sol-gel method), only 4-methoxyresorcinol (at pH = 8.5) was destroyed [130]. The reason was the formation of a charge transfer complex (which absorbed the visible light) between 4-methoxyresorcinol and the catalyst, whereas quinoline and 1-(p-anisyl)neopentanol cannot form such charge transfer complexes. This limits the use of the abovementioned sulfur-doped TiO₂ catalyst in the degradation of compounds that cannot form charge transfer complexes. Other factors that influence the activity of the doped NTO catalyst include dopant concentration [125,127], the crystal phase of the NTO [128], and the intensity of light irradiance [106]. Doped NTO photocatalysts have also been reported for their photocatalytic activity with UV light irradiation in pollutant degradation [132,133], nitrate reduction, and in bacterial disinfection [134,135].

Even though doped NTO catalysts can operate in the visible region, several issues must be considered before their wide use in photocatalytic water treatment. The visible light photocatalytic activity in most of the bulk modified NTO is far lower than the activity of unmodified catalyst under UV irradiation [51,123,130]. In addition, NTO catalysts modified by metal/non-metal doping sometimes have poor activity under UV irradiation [51,123,130]. Here, the doped species could act as recombination centers. Leaching of the doped species is another problem [130], which is a serious concern, especially when the dopants are toxic metals. Furthermore, doping is never a guarantee of high photoreactivity in the doped NTO catalyst, since reactivity is a complex function of dopant concentration, distribution, energy levels in the TiO₂ lattice, d-electron configuration, and light intensity [136]. The choice of doped TiO₂ as a photocatalyst versus un-doped TiO₂ only depends on whether the requirement of low efficiency visible light activity outweighs the higher performance of photocatalysis under UV light [130]. Sometimes, even the smaller fraction of UV radiation in solar light can degrade selected pollutants effectively with unmodified NTO (Figure 5) [46].

7. Coupling with other treatment technologies.

Combining NTO photocatalysis with other oxidation techniques was found to be very effective in pollutant destruction. These technologies include electrocatalysis [35,137-139], sonocatalysis/Fenton process [140], biodegradation [141-145], and wetland technology [146]. The combination of NTO photocatalysis with any of these techniques can not only improve the total efficiency of the
degradation but also has the advantage of treating large quantities of wastewater (in real systems), especially with electrocatalysis, biodegradation, and wetland technology. Electrocoagulation (using an iron cathode/anode (12.50 cm × 2.50 cm × 0.10 cm) at a current density of 763 Am⁻² for 90 min) of an effluent from pharmaceutical and cosmetic companies removed the majority of the suspended particles, followed by further purification using NTO photocatalysis [35].

Table 3. Recent examples of metal- and non-metal-doped NTO photocatalysis.

<table>
<thead>
<tr>
<th>Doped catalyst</th>
<th>Synthesis route</th>
<th>Pollutant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium/TiO₂ (λ &gt; 430 nm)</td>
<td>sol–gel and hydrothermal</td>
<td>isobutanol</td>
<td>[123]</td>
</tr>
<tr>
<td>Iron/TiO₂ (λ &gt; 420 nm)</td>
<td>co-thermal hydrolysis</td>
<td>methyl orange</td>
<td>[124]</td>
</tr>
<tr>
<td>Rhodium/TiO₂ (visible light)</td>
<td></td>
<td>microcystin-LR</td>
<td>[51]</td>
</tr>
<tr>
<td>Silver/P25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>artificial solar light</td>
<td>photoreduction</td>
<td>oxalic acid</td>
<td>[126]</td>
</tr>
<tr>
<td>solar irradiation</td>
<td>electrospinning</td>
<td>E. coli</td>
<td>[93]</td>
</tr>
<tr>
<td>Sulfur/ TiO₂ (495 nm filter)</td>
<td>sol-gel</td>
<td>4-methoxyresorcinol, quinoline &amp;1-(p-anisyl) neopentanol</td>
<td>[130]</td>
</tr>
<tr>
<td>(λ &gt; 420 nm)</td>
<td>sol-gel, self assembly</td>
<td>microcystin-LR</td>
<td>[99]</td>
</tr>
<tr>
<td>Nitrogen/P25 (λ &gt; 420 nm)</td>
<td>milling</td>
<td>rhodamine B</td>
<td>[128]</td>
</tr>
<tr>
<td>Nitrogen/TiO₂ (λ = 390 &amp; 470 nm)</td>
<td></td>
<td>rhodamine 6 G</td>
<td>[129]</td>
</tr>
<tr>
<td>Solar and visible light</td>
<td>sol-gel</td>
<td>microcystin-LR</td>
<td>[52]</td>
</tr>
<tr>
<td>Carbon/TiO₂ (Artificial solar light)</td>
<td>high pressure heating</td>
<td>methylene blue</td>
<td>[127]</td>
</tr>
<tr>
<td>Iodine/TiO₂ (spectrum close to sunlight)</td>
<td>hydrothermal</td>
<td>phenol</td>
<td>[131]</td>
</tr>
<tr>
<td>Nitrogen-Palladium co-doped TiO₂ (visible light)</td>
<td>sol-gel</td>
<td>eosin yellow</td>
<td>[125]</td>
</tr>
<tr>
<td>Carbon-nitrogen co-doped TiO₂ (λ = 465, 523 &amp; 589 nm)</td>
<td>solvolothermal</td>
<td>bisphenol A</td>
<td>[106]</td>
</tr>
<tr>
<td>Fluorine-nitrogen co-doped TiO₂ (λ &gt; 420 nm)</td>
<td>sol-gel</td>
<td>microcystin-LR</td>
<td>[97]</td>
</tr>
</tbody>
</table>

The effluent had an initial chemical oxygen demand (COD) value of 1753 mg L⁻¹, which was reduced to 160 mg L⁻¹ and 50 mg L⁻¹ after electrocoagulation and electrocoagulation/photocatalysis, respectively. Here, the electrocoagulation pre-treatment removed the suspended particles, and thus, the turbidity in the effluent. Thereby, the working load of the TiO₂ catalyst was reduced and the transparency of the medium was increased, such that UV radiation could pass through easily. In an another study, the synergetic effect of TiO₂ photocatalysis and boron-doped diamond (BDD) anodic oxidation improved the total organic carbon (TOC) reduction in the degradation of X-3B dye in an experimental set up, as shown in Figure 6a [137]. Figure 6b represents the efficiency (as a function of time) of different reaction systems employed in the decolorization of X-3B dye, in which the systems
using TiO₂ photocatalytic and BDD anodic oxidation showed the highest activities. The removal of bromate by reduction to bromide [138] and the degradation of chlortetracycline [139] in high efficiencies were also achieved by photoelectrocatalysis using Ti/TiO₂ as the photocathode and photoanode, respectively. Another example for the synergic effect of different AOPs is the combined ultrasound-, Fenton-, and TiO₂-photoassisted mineralization of bisphenol A [140]. By this combined approach, 93% dissolved organic carbon (DOC) removal was achieved, whereas DOC removals by the individual processes were 5, 6, and 22% for TiO₂ photocatalysis, ultrasound, and photo-Fenton, respectively [140]. Here, ultrasound eliminated the initial substrate and provided H₂O₂ for the photocatalytic reactions. TiO₂ photocatalysis and photo- Fenton treatments were mainly responsible for the total mineralization of the intermediates generated by the ultrasound technique.

Biological oxidation is one of the oldest techniques for water treatment. The combination of biological oxidation followed by NTO photocatalysis was employed (Figure 7a) for the mineralization of a mixture containing 2-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, and pentachlorophenol in tap water (total concentration was 100 mg L⁻¹, each component was 25 mg L⁻¹) [141]. The order of the treatments was very important, as the combined biological–photocatalytic treatment removed chlorophenols at a rate of 25.8 mg h⁻¹, whereas, for the combined photocatalytic–biological treatment, the removal rate was only 10.5 mg h⁻¹. Similar observations were reported for the degradation of dyes [142], cyproconazole [143], and a tetracycline/tylosin mixture [144], in which the TiO₂ photocatalytic pre-treatment eradicated the activity of biological oxidation. In this case, some of the intermediates generated during photocatalysis were not biodegradable. In contrast to the above observations, Chen et al. reported the feasibility of using NTO photocatalysis as a pre-treatment followed by the use of a constructed wetland [146]. In their experiment (Figure 7b), they initially treated domestic and agricultural wastewaters (COD was 36.2 ± 7.4) by TiO₂ (coated on α-alumina) photocatalysis before transfer to a bench-scale wetland system. With a hydraulic retention time of 2 days, they reduced the
Figure 6. (a) Schematic of the anodic oxidation- and photocatalysis-coupled reactor and (b) comparison of degradation performance in different experimental systems [137].
Figure 7. Schematic of the coupling of (a) biological [141] and (b) wetland treatment technologies [146] with photocatalysis.
levels of halomethanes and haloacetic acids below the maximum allowed contamination thresholds for drinking water. The intermediates generated by the photocatalytic treatment were biodegradable, which made the wetland treatment fruitful. However, they did not attempt the wetland pre-treatment followed by NTO photocatalysis. From these contrasting observations, we think that the order of treatment is crucial, and varies according to the nature of the contaminants.

8. Conclusions and future prospects

Photocatalytic water treatment by NTO is a hot topic of environmental research and a versatile technique for pollutant degradation. Having a long history of active investigation since the 1970s, photocatalytic water treatment by NTO still retains its importance in contemporary research. This is because of the unique properties of TiO₂, its ability to completely mineralize a wide spectrum of pollutants, its cheap operating costs, and simple experimental design. By reviewing recent developments in this area, the authors have arrived at the following conclusions.

A large number of individual compounds have been successfully tested for photocatalytic degradation by NTO, and researchers are now more focused on real systems, which is promising for the commercialization of the technology. Selective photocatalysis by NTO is a potential research area where researchers can find several opportunities.

Photocatalytic degradation of pollutants by NTO is mainly triggered by •OH radicals, along with the direct oxidation of adsorbed pollutants by surface-generated holes; however, the latter is a minor secondary degradation pathway. The kinetics of photocatalytic degradation by NTO was found to depend on catalyst loading, the extent of adsorption, and light intensity. However, several reports claim that it follows L-H reaction kinetics, especially below catalyst saturation. This is an area where more studies must be conducted in order to clarify the ambiguities in photocatalytic degradation kinetics.

Different NTO morphologies have been synthesized and found to be effective for the photocatalytic degradation of various compounds. Surface treatment of NTO is another option for increasing catalytic activity.

The design of photocatalytic reactors is a key area where intense research is in progress. An ideal photocatalytic reactor should be simple, energy efficient, less expensive to build and operate, and able to handle high wastewater volumes. Reactors operating with solar radiation or LEDs and reactor designs that do not require post separation of the catalyst hold great promise.

Doping NTO with metals and non-metals was investigated to achieve absorption from the visible region by reducing the band gap of the doped catalyst. However, the practicability of applying doped NTO catalysts in photocatalytic water treatment needs reconsideration because of the low catalytic activity of the doped NTO catalysts under visible light and because of the possibility of dopant leaching.
NTO photocatalysis in conjunction with other treatment technologies was explored by several groups. Coupling NTO photocatalysis with other technologies has great potential in large-scale water treatment, and further research is necessary.

Acknowledgments

This work was financially supported by Monash Research Graduate School (MRGS) and the Gippsland Campus, Monash. Manoj A. Lazar is grateful to Lane McDonald for the proof reading of the revisions.

References


© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.0/).
Monash University

Declaration for Publication 1.2.

Declaration by candidate

In the case of Publication 1.2., the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development of idea, structuring and preparation of the manuscript</td>
<td>90</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walid A. Daoud</td>
<td>Development of idea and correction of the manuscript</td>
<td></td>
</tr>
</tbody>
</table>

Candidate’s Signature

05/12/12

Declaration by co-authors

The undersigned hereby certify that:

(7) the above declaration correctly reflects the nature and extent of the candidate’s contribution to this work, and the nature of the contribution of each of the co-authors.

(8) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;

(9) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;

(10) there are no other authors of the publication according to these criteria;
(11) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and

(12) the original data are stored at the following location(s) and will be held for at least five years from the date indicated below:

<table>
<thead>
<tr>
<th>Location(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SASE, Gippsland Campus, Monash, Churchill, VIC-3842, Australia</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Signature 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

07/12/12
Achieving selectivity in TiO₂-based photocatalysis

Manoj A. Lazar* and Walid A. Daoud*\textsuperscript{a,b}

Received on XXX, XXX Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Nanocrystalline titanium dioxide (NTO) mediated photocatalysis is a powerful tool for the total mineralization of a wide range of organic compounds. UV light irradiated NTO has the ability to break down target compounds into final stage molecules, i.e. carbon dioxide (CO₂), water and other inorganic species. This process is commonly referred as 'total mineralization'. The 'total mineralization' power of NTO is usually greatest in aqueous environments, which has made it a superb candidate for photocatalytic water purification, where the target molecules are the contaminants or pollutants.

The ultimate destruction of an organic compound (pollutant) by NTO mediated photocatalysis is mainly the result of a series of hydroxyl reaction reactions. These hydroxyl reaction reactions are triggered by the hydroxyl radicals (OH) generated in the reaction medium as depicted in Fig. 1. Being a semiconductor of band gap (3.2 eV), NTO absorbs in the UV region of the electromagnetic spectrum, producing electron-hole pairs. The electron-hole pairs thus formed generate superoxide ions (O₂⁻), peroxy radicals (OOH), hydroxyl ions (OH⁻) and H⁺ ions upon contact with the surrounding water molecules and dissolved oxygen in the reaction mixture. All these species will finally end up forming hydroxyl radicals (OH⁻) (Fig. 1). Free radicals are highly unstable and are aggressive reactive species in chemical reactions. Here, the OH radicals attack the pollutants in a variety of ways, forming different oxygenated intermediates before eventually mineralizing them into CO₂ and water. NTO photocatalysis can thus render the pollutant completely harmless, without producing harmful by-products.

Selectivity in NTO photocatalysis

NTO is generally regarded as a non-selective photocatalyst in waste water treatment. A better assessment of its performance is that researchers have seldom paid attention to the selectivity, since their aim is usually to completely destroy contaminants in water. But selectivity is important when dealing with a mixture which contains compounds that we need to destroy and other compounds we need to recover. Or a mixture which contains highly toxic pollutants (in low concentrations) and comparatively less toxic substances (in high concentrations), where the latter pollutants can be removed by less expensive biological waste water treatments. Furthermore, if we can control and direct the formation of the desired oxygenated products, then photocatalysis could be one of the most economical and eco-friendly techniques to obtain valuable organic compounds. These ideas have led researchers to explore the feasibility of selectivity in NTO mediated photocatalysis.

Selective photocatalysis using NTO can mainly be divided into two categories, (i) selective degradation/mineralization: where one or more of the compounds in an aqueous mixture are mineralized selectively/preferentially over the other compounds present and (ii) selective formation: where a desired product is achieved, selectively, in high yields from the starting compound (reactant). In the second case, the reaction can take place either in aqueous solution or in organic solvents/liquid reactants, but the former case is much eco-friendlier. In most reported photocatalytic organic transformations using NTO, there is only one starting compound (reactant), not a mixture of reactants.

Both the selective degradation and selective formation in NTO photocatalysis are based on the same principle as shown in Fig. 1. But in selective formation, desorption of the desired product from
the catalyst surface takes place, thus stopping it from undergoing the further oxidation steps to total mineralization, whereas, in selective degradation, the adsorbed contaminant and its oxygenated intermediates stick onto the catalyst surface until they are finally completely mineralized. Selectivity in NTO photocatalysis is achieved through one or more of the following approaches: (i) attraction of the target/s towards the catalysts, (ii) adsorption of the target/s on the catalyst surface, (iii) desorption of the product/s from the catalyst surface, (iv) doping effect, (v) crystallinity of the NTO catalysts, and (vi) mineralization of the adsorbed species.

Attraction of the target/s towards the NTO catalyst is the main way of selecting compounds from a mixture, especially in selective degradation. Compounds that have strong attraction towards the catalyst will reach the catalyst surface and be adsorbed preferentially to other compounds. The factors which contribute to this stage are hydrophilic/hydrophobic environments, polarity of the molecules and other chemical interactions.

If there is more than one compound available for adsorption on the catalyst surface, then a second screening based on the size of the molecules can occur. Smaller molecules adsorb first and are degraded more readily than bigger molecules. In other cases, smaller molecules enter the pores and remain in a ‘protective environment’, whilst bigger molecules on the catalyst surface are preferentially degraded.

Here, degradation happens only on the catalyst surface, but not inside the pores. Desorption of the products (influenced by the hydrophilic/hydrophobic interactions and crystallite size of the NTO), moderate crystallinity of the NTO and doping effects (i.e. the chemical environment at the NTO surface) then determine whether the reaction will be selective formation or selective degradation. The mineralization stage of selective degradation is again influenced by the crystallinity of the NTO and also by the intensity of irradiation. If the catalyst is highly crystalline anatase (the most active form of TiO₂) then selectivity may not be achieved irrespective of the attraction and adsorption stages. This is because of the high activity arising from the well ordered crystal lattice of NTO. These factors are summarized in Scheme 1. A short review of the literature for each stage is given below.

All photocatalytic reactions discussed in this review have been carried out under UV irradiance, unless otherwise mentioned.

Attraction towards the catalyst

Hydrophilic/hydrophobic interactions

Hydrophobic attraction between the NTO and the target molecules can lead to selective adsorption of compounds containing bigger alkyl groups. Hydrophobic NTO surfaces can be achieved in mesoporous silica-NTO composites, or by grafting the NTO surface with organic chains such as n-ocetyl groups (Fig. 2). These TiO₂ catalysts could selectively degrade norpyrophylol (NLP) from an aqueous mixture of NLP and phenol (PL). A nanocomposite of Degussa P25 (which is a benchmark TiO₂ photocatalyst) incorporated into a surfactant templated mesoporous silica (MS-P25) selectively degraded phenols with longer alkyl side chains - NLP and heptylphenol - from an aqueous mixture containing NLP, heptylphenol, propylphenol and PL. The selectivity in degradation was further increased when a nanocomposite of n-ocetyl grafted P25 incorporated mesoporous silica (MS-P25oct) was used. The hydrophobic surfaces in MS-P25 and MS-P25oct caused the attraction of long alkyl chains (nonyl and heptyl) leading to their selective adsorption, followed by degradation. Bare P25 does not have a hydrophobic surface, so it degraded all phenols at more or less the same rate. In contrast with the above observations, Nakamura et al. have reported the formation of a more hydrophilic TiO₂ surface in a core shell P25-mesoporous silica nanocomposite (CMS-P25) compared to that of the bare P25. CMS-P25 selectively degraded PL and NLP from an aqueous mixture containing PL, NLP and nonane. This observation was...
attributed to the increased hydrophilicity of CMS-P25 in comparison with the bare P25 (which did not show any selectivity under the same experimental conditions). However it is unclear why MSP25 is hydrophobic while CMS-P25 is hydrophilic, since they have been derived using similar synthetic methods.

Electrostatic interactions

The surface charge on NTO helps it to attract compounds carrying opposite charges from solutions. This principle can be employed to achieve the selective degradation of cationic and anionic pollutants. The conventional way of doing this is by changing the pH of the reaction medium. The ‘zero point charge’ (pHpzc) of TiO₂ is in between pH = 6.1–6.3. Below this pH range TiO₂ adsorbs H⁺ ions and acquires a positive surface charge, whilst above this pH range it adsorbs OH⁻ and acquires a negative surface charge in aqueous solution.

This is the reason for the preferential degradation of 4-hydroxybenzoic acid (HBA) over benzamide (BAM) at pH < 6.4 (and vice versa at pH > 6.4) by P25 photocatalyst under simulated sunlight (300 nm < λ < 800 nm). Fluoride terminated hollow TiO₂ anatase microspheres (HTAS-F) with 20% [001] facets have been reported to preferentially degrade the anionic dye methyl orange (MO) from an aqueous mixture with the cationic dye methylene blue (MB). When HTAS-F underwent surface treatment with NaOH, the resultant catalyst (HTAS-OH) preferentially degraded MB over MO. The selectivity exhibited by HTAS-F towards MO adsorption and degradation was explained by the presence of [001] facets. In HTAS-OH, surface rehydroxylation” (during NaOH treatment of HTAS-F) was thought to cause the selective adsorption and degradation of the MB. However we strongly believe that the surface charge on HTAS-F and HTAS-OH has played a crucial role in this behaviour. Recently, we have reported the fully selective photocatalytic degradation of MO and MB dyes by base precipitated anatase nanocrystals. Our TiO₂ catalyst with positive surface charge (TSCO) showed selective adsorption of the anionic dye MO, whereas the TiO₂ catalyst with negative surface charge (TASO60) exhibited selective adsorption of the cationic dye MB, from an aqueous mixture of both dyes (Fig. 3). Each catalyst then completely degraded the selectively adsorbed dyes before beginning to degrade the other dye, thus displaying fully selective photocatalysis (Fig. 4). Incorporating P25 into Faujasite (FAU)-type zeolite (FAU-P25) yielded a selective photocatalyst which degraded cationic substrates such as rhodamine B (RB), anilinium (ANL) ion and tetramethylammonium (TMA) ion. Importantly, its activity towards anionic substrates such as reactive blue, benzene and dichloroacetate was poor. Attraction of the cationic species
towards the negatively charged FAU-P25 surface was the reason for this selectivity.5

**Chemical interactions**

Modification to NTO to render a different surface chemical environment than that of bare TiO₂ can be used to achieve selective photocatalysis. For example, in the presence of an arginine modified NTO (Arg-TiO₂), the reaction pathway of aqueous 4-nitrophenol (4NP) changed to yield 4-aminophenol, whereas the unmodified catalyst resulted in the total mineralization of 4NP.33 The amino acid, arginine, modification changed the surface charge which enhanced the reduction of 4NP to 4-aminophenol.34 When an aqueous mixture containing nitrobenzene (NB) and PL was tested for photocatalytic degradation, Arg-TiO₂ degraded only nitrobenzene whilst the bare TiO₂ degraded both compounds.35 The electron withdrawing effect of nitro groups (⁻NO₂) imparts an electron deficiency to the aromatic ring of NB, while there is no such an electron deficiency in the aromatic ring of PL. Also, the increased electron density on the -NO₂ group enables it to form hydrogen bonds with arginine.33 These two factors helped to increase the adsorption of NB on Arg-TiO₂.

Exploiting the affinity of β-cyclodextrin with different contaminants, Mukerji et al. have reported the preferential degradation of p-benzoquinone (PBQ) from its mixture with benzene in 1:1 (v/v) water-propanol solvent.32,33 They used three different catalyst coatings (A, B and C) on silicon wafers as shown in Fig. 5a. Among them, type C formulation showed a rate of degradation of PBQ 4.23 times higher than that for benzene.32 In type C, triloaded β-cyclodextrin molecules anchored on alternatively (with TiO₂) positioned gold stripes act as ‘molecular recognition sites’ (MRS) for PBQ (Fig. 5b).34 PBQ then diffuses from the MRS to the photocatalytic sites in the

*Fig. 3* Adsorption of MO on TSGO (a) and MB on TAH60 (b) (Reproduced from Ref. 20).

*Fig. 5* Production of molecular responsive photocatalytic NTO surface (a) and the mechanism of molecular responsive photocatalytic degradation (b). (Fig. 5A Adapted with permission from Ref. [32]. Copyright (2001) American Chemical Society)

*Fig. 4* UV-Vis absorption spectra showing selective degradation of MO by TSGO (a) and MB by TAH60 (b) (Reproduced from Ref 20).

*Fig. 6* Formation and action of molecular imprinted NTO photocatalyst. 26

‘TiO₂ microdomain’ and is preferentially destroyed.32 A combination of hydrophilic/hydrophobic effects and chemical interactions (between appropriate functional groups on the TiO₂ catalyst and target molecules) can cause the attraction of specific compounds to the NTO catalyst. This is achieved during catalyst synthesis by creating ‘footprint’. A combination of target molecules on NTO surfaces with or without organic inorganic matrices. P25 catalyst separately imprinted with 2-nitrophenol (2NP) or 4NP targets, in a poly(orthophenylenediamine) matrix exhibited preferential degradation of the targets in aqueous solutions that also contained bisphenol A as a co-pollutant.4 When 2NP and 4NP were degraded in the presence of other co-pollutants such as 2,4-nitrophenol, naphthol, PL or toluene, the selectivity in degrading 2NP and 4NP increased in the following order 2,4-nitrophenol < naphthol < PL < toluene.44 The highest selectivity achieved in the case of toluene as the co-pollutant was because of the hydrophobicity of the photocatalysts.45 However the stability of the organic polymer matrix is questionable in the absence of co-pollutants. This limitation can be overcome by using inorganic silicon dioxide (SiO₂) as a matrix. Imprinting of a SiO₂ matrix containing Al³⁺ ions and P25 TiO₂ with diethylphthalate (DEP) has been reported.46 The resultant catalyst preferentially degrades DEP in the presence of PL in aqueous solution (Fig. 6). Other similar examples include: sol-gel derived TiO₂ film on glass having footprints of either diisopropyl methylphosphonate (DIMP) or diethyl (hydroxymethyl) phosphonate (DEMP) targets, which exhibited selective removal of gaseous DIMP or DEMP in the
Fig. 7 SEM image of titania film (a) and protein permeation results through the film (b). (Adapted with permission from Ref 46. Copyright [2010] American Chemical Society)

Fig. 8 Size of ZnP, 2NPP and ANNP (a) and size exclusion of molecules in EIS-10 (b). (Fig. 8b reproduced from Ref 40)

Scheme 2 Mechanism of photocatalytic selective formation of cyclohexanone from cyclohexane.39

- presence of benzene or heptane,7 ii) P25 film on borosilicate glass imprinted with a salicylic acid target (followed by its removal using three different routes: calcinations, extraction with Na2CO3, or UV illumination, to form the “footprint”) which selectively degraded the target in the presence of PL co-pollutants in aqueous solution39 and iii) 4-(tributylammonium-methyl) benzyltributylammonium chloride and sodium allyl sulphonate imprinted onto P25 using an ‘interval immobilization technique’ for the selective removal of decarboxyl saxitoxin37

Adsorption on the catalyst

- Adsorption of reactants on catalyst surface is one of the prerequisites in any heterogeneous catalytic chemical reaction. Compared to non-porous NTO (nTiO2) catalysts, mesoporous (pore size between 2-50 nm) NTO (mTiO2) shows a peculiar relationship between activity and adsorption.31 A combination of anatase and mesopores in mTiO2 showed a linear relationship between the degree of adsorption of fifteen phenolic compounds and their percentage of conversion.41 Selectivity in the adsorption stage is determined by the amount of NTO catalyst used44 and the type44 or size1, 22, 24, 30, 43, 44 of the target compounds. Positively surface charged TiO2 catalyst exhibited a remarkable enhancement in the aqueous degradation of HBA over BAM, when the catalyst amount was increased from 0.2 to 2 gL-1. Here,
a greater catalyst concentration caused increased HBA adsorption, and thus prevented BAM coming into contact with the catalyst surface. Exploiting the synergic effect of biosorption and photocatalysis of chitosan-TiO₂ composites, Zhao et al. have reported the degradation of MO in the presence of nickel (Ni²⁺) and silver (Ag⁺) ions. Chitosan-TiO₂ composite adsorbed both the metal ions and MO from the aqueous mixture but selectively degraded only the MO, since metal ions are not susceptible to photocatalytic degradation.

Screening molecules based on their size can be a useful tool to achieve selectivity in NTO photocatalysis. A simple and beautiful example of size-selective screening is the separation of the protein β-galactosidase (Stokes radius = 6.86 nm) from a mixture containing bovine serum albumin (Stokes radius = 3.62 nm) and cytochrome C (Stokes radius = 1.63 nm) by a size-nanochannelled TiO₂ membrane (10 µm thick). The TiO₂ membrane became clogged by the bigger β-galactosidase protein whereas smaller cytochrome C molecules easily passed through the channels (Fig. 7). The clogged protein degraded upon UV illumination of the TiO₂ membrane, thus making the membrane a self-cleaning surface. NTO composites with zeolite or mesoporous silica have been reported for size selective adsorption and photocatalysis. FAU-P25 exhibited preferential degradation of the cationic TMA over other cationic species, ANI, and RHB.

Amongst the three cationic compounds in the study, TMA is the smallest ion; it easily passes through the catalyst pores and gets degraded. CMS-P25 (pore diameter 2.7 nm) showed selective degradation of the small molecule 2NP from an aqueous mixture of 2NP, 2-nitro-4-phenylphenol (2NPP) and 4-nitro-2,6- diphenylphenol (4DPP). As the size of the molecule increases it is difficult for it to enter the pores and become adsorbed on the catalyst surface (Fig. 8a). Titanium oxides other than TiO₂ (such as ETS-10 (Engelhardt titanosilicate structure 10) and layered titanates) are capable of selective photocatalysis based on the size exclusion of the target molecules (Fig. 8b). ETS-10, with outer catalytic centres, caused the degradation of the larger molecule, 2,3-dihydroxy naphthalene (3HPP) in preference to 1,3,5-trihydroxy benzene (3HP) and PL. Here the smallest molecule, PL, enters the pores of ETS-10 and remains in the protective environment where there are no catalytic sites. Similarly, when an aqueous mixture of benzene, PL, and 4-butyolphol was treated with lithium and sodium titanates (interlayer distance of 0.7 nm) only benzene (0.60±0.06±0.3 mm) was degraded. No larger molecules PL and 4-butyolphol could not enter the pores of the titanates, and hence remained intact.

## Desorption from the catalyst surface

Desorption of the desired product from the NTO photocatalyst is one of the key processes in selective formation (Scheme 2). Hydrophilic/hydrophobic (polar/nonpolar) interactions play a crucial role in desorption of the desired product from the NTO catalyst surface. NTO incorporated into clays can form hydrophobic surfaces, which have been used for selective formation of different organic compounds. TiO₂ pillared on three different clays (mica, montmorillonite and saponite) produced only 2.2% CO₂ from an aqueous solution of benzene; the remainder of the products were oxygenated organic compounds: maleic acid (45.6%), hydroquinone (2.7%), resorcinol (15.7%), catechol (16%) and PL (16.6%). When acetonitrile (90%)-water (10%) or acetonitrile (100%) solvents were used instead of water in the above reaction, CO₂ formation increased to 35.5% and 73.6%, respectively. This is in contrast to the commonly accepted thinking that photocatalytic total mineralization is more pronounced in aqueous media. The explanation given for the above observation is the existence of three different layers in the reaction mixture: (a) aqueous layer (b) organic layer (of starting compound) and (c) catalyst layer. The oxygenated products (polar) after being desorbed from the hydrophobic surface of the catalyst, remain in the organic layer where there is no catalyst. Selection of the corresponding aldehydes (in high
The aldehydes are desorbed from the hydrophobic catalyst surface before being totally mineralized. Surface silylated NTO\textsuperscript{31} or TiO\textsubscript{2}-mesoporous silica composites\textsuperscript{31} can also form hydrophobic surfaces, from which polar oxygenated products can desorb, resulting in photocatalytic selective formation. Selective formation of PL from benzene\textsuperscript{31} on TiO\textsubscript{2}-mesoporous silica and cyclohexanone from cyclohexane on silylated TiO\textsubscript{2}\textsuperscript{25} has been achieved in this manner.

Hydrophilic NTO surfaces can also achieve selective formation, as in the oxidation of benzylalcohol (aqueous mixture) to benzaldehyde by using non-commercial anatase and rutile TiO\textsubscript{2} photocatalysts.\textsuperscript{25} Here the benzaldehyde formed has to compete with water molecules for adsorption sites on the hydrophilic catalyst surface.\textsuperscript{25} This makes the benzaldehyde desorb into the solution, and leads to its selective formation.

The crystal size of the NTO can influence desorption of oxygenated products. For example, cyclohexanone formed from cyclohexane easily desorbs from larger anatase crystals (10-25 nm) in comparison to their smaller counterparts – this means that larger crystals are more effective for selective formation of cyclohexanone.\textsuperscript{24}

### Doping effect

TiO\textsubscript{2} (containing 2 wt% sulphate) that had been doped with molybdenum oxide (MoO\textsubscript{3}) could convert cyclohexane selectively into benzene, whereas the undoped catalyst caused the total mineralization of cyclohexane.\textsuperscript{55, 56} The reaction was carried out in a continuous flow gas-solid reactor containing MoO\textsubscript{3} doped TiO\textsubscript{2} catalyst coated onto quartz flakes. The reactant feed was a nitrogen stream containing 1000 parts per million (ppm) cyclohexane, 1500 ppm oxygen and 1600 ppm water vapour.\textsuperscript{55, 56} Polymolybdate species present in the doped catalyst poisoned the non-selective sites in TiO\textsubscript{2} thus yielding benzene as the major product.\textsuperscript{55, 56} A similar principle has been exploited for the selective photocatalytic oxidation of alcohols to aldehydes using tungsten oxide (WO\textsubscript{3}) coated TiO\textsubscript{2} (Scheme 3).\textsuperscript{57}

Elimination or alteration of total oxidation centres has been reported in a hydrothermally derived TiO\textsubscript{2} co-doped with tungsten (W) and nitrogen (N) (TiO\textsubscript{2-x}W\textsubscript{x}N\textsubscript{x}).\textsuperscript{32} Co-doping with N in TiO\textsubscript{2-Nx} caused local changes around the W surface entities which limited the "surface stability" and "residence time" of the partial oxidation intermediates (i.e. the desired products).\textsuperscript{14} These local changes led to the selective formation of benzaldehyde from toluene and styrene oxide from styrene when a gas feed of toluene or styrene and 20% (v/v) oxygen/N\textsubscript{2} (75% relative humidity) was fed through a TiO\textsubscript{2-Nx} coated pyrex tube in the presence of simulated sunlight.\textsuperscript{14} Under the same experimental conditions, none of the catalysts P25, undoped TiO\textsubscript{2}, TiO\textsubscript{2-Nx} or TiO\textsubscript{2-Nx} exhibited selective formation, instead yielding the total mineralization of toluene or styrene.\textsuperscript{14}

Plasmonic photocatalysts\textsuperscript{65, 66, 70} or superior oxygen activation\textsuperscript{65} or longer e\textsuperscript{-}\h\textsuperscript{+} pair lifetime\textsuperscript{65} advantages associated with the metal doped and composite NTO photocatalysts have been reported for the selective formation of organic compounds. Gold nanoparticles of size < 5 nm deposited at anatase – rutile interfaces (in Degussa P25), through a deposition – precipitation technique, could render plasmonic photocatalysis to achieve the selective formation of different aromatic aldehydes from their corresponding alcohols.\textsuperscript{65} This aerobic oxidation (under 1 atm of oxygen) of alcohols to aldehydes has been experimented with visible-light (λ = 450 nm) and solar irradiations in toluene (solvent). The plasmonic mechanism involved electron transfer from Au \textrightarrow CB of rutile \textrightarrow CB of anatase, upon light irradiation.\textsuperscript{65} Reduction of oxygen happens on anatase to form O\textsubscript{2} which then oxidizes the alcohol to aldehyde. Superior oxygen activation which led to the selective formation of benzaldehyde from benzyl alcohol was observed in the iridium doped and iridium – palladium co-doped P25 catalysts in a solvent free photocatalysis.\textsuperscript{65} Photodeposited iridium metal cluster on P25 acted as oxygen activation centres for the selective formation of benzaldehyde. Hydrothermally derived titania nanotubes doped with different metal ions (Co\textsuperscript{2+}, Co\textsuperscript{3+}, Ni\textsuperscript{2+}, Fe\textsuperscript{3+} and Mn\textsuperscript{2+}) has been reported for the selective oxidation of benzyl and allylic alcohols in to their corresponding aldehydes in benzonitril fluoride (solvent) under both UV and visible (λ > 420 nm) light irradiation.\textsuperscript{65} The longer life time of e\textsuperscript{-}\h\textsuperscript{+} pairs in metals doped titane nanotubes was responsible for their superior activity compared to the pristine titane.

Sometimes doping can have a negative effect on selective formation. For example, gold (Au) deposition onto Hombikat UV100 TiO\textsubscript{2} decreased the selective formation of cyclohexanone.
Table 1 Experimental conditions and outcomes in some selected examples of photocatalytic organic transformations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant (mol)</th>
<th>Solvent</th>
<th>Product</th>
<th>Conv. (%)</th>
<th>Select. (%)</th>
<th>Irrad. (time)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-TiO$_2$</td>
<td>Benzene (0.5x10$^{-3}$)</td>
<td>Water</td>
<td>Phenol</td>
<td>42</td>
<td>81</td>
<td>UV (6h)</td>
<td>41</td>
</tr>
<tr>
<td>Gr-TiO$_2$</td>
<td>Benzyl alcohol (0.1x10$^{-3}$)</td>
<td>BTF$^a$</td>
<td>Benzaldehyde</td>
<td>62</td>
<td>100</td>
<td>Vis. (20h)</td>
<td>15</td>
</tr>
<tr>
<td>Ir-TiO$_2$</td>
<td>Benzyl alcohol (0.3)</td>
<td>Solvent free</td>
<td>Benzaldehyde</td>
<td>11.5</td>
<td>90</td>
<td>UV (6h)</td>
<td>65</td>
</tr>
<tr>
<td>Comm.TiO$_2$</td>
<td>Benzylamines (0.1x10$^{-3}$)</td>
<td>Acetonitrile</td>
<td>Imines</td>
<td>44-95</td>
<td>49-94</td>
<td>Vis. (5-14h)</td>
<td>80</td>
</tr>
</tbody>
</table>

$^a$mesoporous TiO$_2$, $^b$graphene oxide-TiO$_2$, $^c$benzotriazole, $^d$iridium-TiO$_2$ and $^e$commercial TiO$_2$.

from cyclohexane, when compared to the bare catalyst. This is explained by the electron trapping ability of Au, which leads to the creation of more O$_2^-$ ions and consequently to a loss of selectivity. Also, Au selects another pathway for the decomposition of cyclohexyl hydroperoxide, which is considered to be the intermediate for cyclohexanone formation. Another example of a negative doping effect on selective formation is the doping of TiO$_2$ with zinc oxide (Ti$_x$Zr$_{1-x}$O$_2$), where doping increased the Brønsted acidity and the hydrophilicity of the catalyst. The Brønsted acidity in Ti$_x$Zr$_{1-x}$O$_2$ increased the formation of OH$^-$ whilst the hydrophilicity led to the slow desorption of cyclohexanone (the desired product) from the catalyst. Both of these were detrimental to the selective formation of cyclohexanone from cyclohexane, so that the main product was CO$_2$ (Fig. 9).

Crystallinity of NTO

Selective formation of organic compounds has been found to be more feasible with moderate crystalline NTO catalysts than with highly crystalline samples. Palmisano et al. have reported photocatalytic conversion of benzyl alcohol (BA) and paramethoxybenzyl alcohol (PMB) into their corresponding aldehydes using various commercially available and housepreared anatase/rutile TiO$_2$ photocatalysts. House prepared samples at room temperature (HPRT), 333 K (HP333), 673 K (HP673) and at 973 K (HP973) showed the following order of selectivity and photocatalytic activity for the conversion of BA and PMBA: HPRT < HP973 < HP333 < HP673 for activity and HPRT < HP973 < HP673 < HP333 for selectivity. HPRT, which has the poorest crystallinity (essentially amorphous) showed the lowest activity and selectivity, whereas HP333 with moderate crystallinity exhibited the highest selectivity for aldehyde formation. High temperature treatment of HP at 673 and 973K imparted high crystallinity to HP673 and HP973 catalysts. This enhanced the photocatalytic activity of HP673, but for HP973, the thermal treatment removed the surface hydroxyl groups, which in turn reduced its photocatalytic activity. The well ordered crystal lattices in HP673 and in HP973 enhanced their total mineralization power, thus making them non-selective photocatalysts. All the commercially available samples tested in the above reaction (which were highly crystalline) caused the total mineralization of BA and PMBA.

Mineralization

Molecules (both the starting compound and intermediates) which remain on the NTO surface are mineralized completely into CO$_2$, water and other inorganic ions. The total mineralization power of NTO mainly depends on two factors: phase and crystallinity. Amongst the different phases of TiO$_2$, anatase is catalytically the most active. However, a combination of anatase and rutile phases has been found to reduce the electron-hole pair recombination, thus giving greater photocatalytic activity. Higher crystallinity of TiO$_2$ on the other hand, enhances the photocatalytic activity of the catalyst. Commercially available Degussa P25 (80% anatase and 20% rutile) is a highly crystalline and photocatalytically active NTO catalyst. It carries a positive surface charge and preferentially adsorbs MO over MB from an aqueous mixture. Despite this, P25 does not give selective degradation of MO over MB (Fig. 10). Under the same experimental conditions, TSC60 (synthesized at 333K) which also carries a positive surface charge, not only preferentially
Conclusions and future prospects

The conventional thinking that NTO is a non-selective photocatalyst has changed dramatically in recent years, and several techniques have been reported to achieve selective NTO photocatalysts. Selective photocatalysis using NTO has a promising future in selective organic transformations as well as in selective degradation. Selective formation and selective degradation can be considered as two sides of a coin, since both involve the same basic principle of photocatalysis. Description of the oxygenated product, moderate crystallinity of NTO and alteration of the surface chemistry of the NTO via doping can be used to tip the balance of the reaction from total mineralization to selective formation. Attraction between the targets and the catalyst, and adsorption of the targets (based on their size and crystallinity) onto the catalyst are responsible for selective degradation reactions. Each of the techniques employed to create selective NTO photocatalysts has been tailored for the particular experimental system studied - selection of a particular technique depends on the experimental need.

Even though there are several successful demonstrations of selective degradation by NTO, their practical application in real systems has to overcome a number of challenges. In real systems, large volume of waste water has to be treated. Surface modified NTO systems by organic grafting, arginine, molecular recognition sites or foot print formation may not be an appropriate option for those systems. Most of these techniques involve complicated catalyst synthesis routes and might not be cost effective in real water treatment applications. Recyclability of these catalysts is also an issue since the surface treating species are prone to photocatalytic degradation.

Selective degradation can be a useful tool in the recovery of metal ions from waste water by using surface charged NTO or NTO composite catalyst systems such as chitosan - TiO_2 or zeolite - TiO_2, which are easy to synthesize and are recyclable. Selective degradation may be constructive in conjunction with other treatment technologies, such as biological oxidation or wetland technology, where the working load of photocatalysis is shared. Here large volumes of waste water can be exposed to sunlight for long time to achieve selective photocatalytic degradation (of toxic substance in less concentration) with the limited UV supply of solar irradiation. Visible spectrum of sunlight can also render selective photocatalytic degradation, through the CT mechanism, if there are compounds which can form charge transfer complexes with the NTO catalyst.

An ideal photocatalytic TiO_2 system for commercial organic transformation applications expects to facilitate complete conversion of fairly large reactant volume with 100% selectivity towards the desired product, under visible light irradiation, in a solvent free or aqueous experimental condition. Conversion (except in solvent free experiments) and selectivity achieved in some of the reported photocatalytic organic transformations are promising (Table 1). However, most of the organic transformations have dealt with low concentrations (< 1 mol) of reactants and some of them were conducted in organic solvents. Use of organic solvents in photocatalytic organic transformations is questionable with regard to its green value aspect. Solvent free organic transformation is best in this regard but with the lowest conversion rate (Table 1). Use of UV radiation is also a hurdle in terms of commercialization of this technology since it is not energy efficient. Modifications of TiO_2 can solve this problem to an extent by reducing the band gap of TiO_2. However, most of these modifications, in this regard, are achieved by doping or by making composite catalysts. Recyclability of these systems has to be confirmed since there is a possibility of leaching of doped species. Considering all these aspects, the authors believe that more investigations are needed toward sunlight irradiated photocatalytic organic transformations by neat TiO_2 in aqueous solvent, based on the CT mechanism.

Acknowledgements

This work is financially supported by the Monash Research Graduate School (MRGS) and Monash Gippsland Campus.

Manoj A. Lazar is grateful to Prof. Douglas R. Macfarlane for his valuable inputs.

Notes and references

Monash University

Declaration for Thesis Publication 2.1.

Declaration by candidate

In the case of Publication 2.1., the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development and execution of the idea, interpretation of the results, and the manuscript preparation</td>
<td>80</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walid A. Daoud</td>
<td>Development of the idea, experimental guidance, interpretation of the results, and manuscript correction</td>
<td></td>
</tr>
</tbody>
</table>

Candidate's Signature

05/12/12

Declaration by co-authors

The undersigned hereby certify that:

(13) the above declaration correctly reflects the nature and extent of the candidate’s contribution to this work, and the nature of the contribution of each of the co-authors.
(14) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
(15) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
(16) there are no other authors of the publication according to these criteria;
(17) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or
publisher of journals or other publications, and (c) the head of the responsible academic unit;
and
(18) the original data are stored at the following location(s) and will be held for at least five
years from the date indicated below:

**Location(s)**

| SASE, Gippsland Campus, Monash, Churchill, VIC-3842, Australia |

[Please note that the location(s) must be institutional in nature, and should be indicated here as a
department, centre or institute, with specific campus identification where relevant.]

**Signature 1**

| 07/12/12 |
Selective adsorption and photocatalysis of low-temperature base-modified anatase nanocrystals†

Manoj A. Lazar* and Walid A. Daoud*

Received 31st July 2011, Accepted 7th September 2011
DOI: 10.1039/c1ra05839a

Anatase titania photocatalysts with positive (TSC60) and negative (TAH60) surface charge were synthesized by extraction with Na2CO3 and NH4OH, respectively, from an acid stabilized sol at low temperature. XRD, TEM, N2 adsorption and ζ-potential were conducted and revealed that the low-temperature synthesized catalysts differ mainly in their surface charge. These catalysts exhibited opposing preferential adsorption and fully selective photocatalysis of methylene blue (MB) and methyl orange (MO) dyes from their aqueous mixture. The preferential adsorption behaviour towards MB and MO was attributed to the catalyst's surface charge whereas the selective photocatalysis was explained by a combined effect of surface charge and crystallinity. On the other hand, the calcined catalysts showed considerable reduction in their dye adsorption capacity and loss of their selective dye degradation. The reduction in surface charge and increase in crystallinity after calcination were found to be responsible for these observations. Degussa P25 was also tested and compared with synthesized catalysts with regard to dye adsorption and photocatalysis. A mechanism for the selective dye positioning on TSC60 and TAH60 coated FTO/ITO plate is also proposed.

Introduction

Nanocrystalline TiO2 is unique in its ability toward photocatalytic mineralization of a wide range of pollutants.1 On one hand, its high activity leads to complete degradation of organic contaminants irrespective of their nature, but on the other hand this limits its use in selective catalysis. By changing the physico-chemical properties of TiO2/titantate, researchers have recently shown that it can be used as a selective photocatalyst in the degradation of contaminants.2-6 organic transformations,7-9 separation of molecules,10 destruction of cancer cells and in drug delivery.11 Selectivity of TiO2 can be achieved through several ways such as controlling the pH of the reaction mixture,2-4 using larger anatase particles (10-25 nm),6 creating molecular recognition sites on TiO2,7 using the less reactive rutile phase,21 or mesoporous anatase,22 and forming nano-channelled TiO2 film with desired pore diameter.23 Molecular imprinting with polymers/inorganic oxides on TiO2 surface, along with the formation of footage of the target molecule, is another established method to achieve selective photocatalysts.7-9 Surface treatments on TiO2 such as organo-grafting with octyl triethoxysilane,15 chelation using arginine16 or silylation,17 could also confer selective photocatalysis in degradations and organic transformation reactions. Exploiting the properties of TiO2-mesoporous silica composites, such as diffusion of the adsorbed substrates,8 hydrophilicity,16 and pore diameter,10 researchers have used them for their selective catalytic applications.

Li-titantate8 and ETS-1026-27 have also showed selective photocatalysis because of their unique interlayer distance properties and pore structures. TiO2 nanotubes engulfed with ferron and produced by a simple synthetic route have successfully been tested for their magnetically guided cancer cell destruction on selected areas and for their cytotoxic photocatalyzed drug release.28

Organic dyes have wide application in our daily life and are integral part of industrial effluent. In reality, out of 450 000 tons of annually produced organic dyes more than 11% is lost in industrial wastes during their manufacture and application processes.29 Since many of these dyes are toxic and most of them are potential carcinogens, their presence in effluents is a major environmental concern. As a consequence, selective adsorption and photocatalytic decomposition of dyes is of great importance. Different adsorbents has been reported for the selective adsorption of cationic and anionic dyes based on the surface charge of the adsorbents and their electrostatic interactions with the dye molecules.30-33 However, selective adsorption of dyes by nanocrystalline titanium dioxide has potential advantage in the simultaneous selective destruction by means of photocatalysis.31 This phenomenon could be further extended to the tailored selection of dyes based on their affinity toward nanocrystalline TiO2 in order to increase the dye adsorption and hence maximize the photon-to-electricity conversion performance of dye sensitized
solar cells (DSSCs). Furthermore, selective positioning of different dyes on TiO₂ could also be possible, which in turn could increase the efficiency of DSSCs.

Our present paper reports the development of two nanocrystalline TiO₂ photocatalysts which show preferential adsorption and fully selective photocatalytic degradation of one dye over the other from an aqueous mixture of methyl orange (MO) and methylene blue (MB). A mechanism for the selective positioning of cationic (MB) and anionic (MO) dyes on the low-temperature synthesized TiO₂ photocatalysts is also proposed.

Experimental methods

Synthesis of the photocatalysts

The synthesis of TiO₂ photocatalysts was carried out through an acid-stabilized sol-gel method, developed by our group, followed by base extraction. TSC60 and TAH60 photocatalysts were synthesized by hydrolysis and condensation reaction of 5% titanium tetraisopropoxide (Sigma Aldrich), to form an acidic aqueous sol containing 5% acetic acid (Rowe Scientific, Australia) and 1.4% hydrochloric acid (Merck). The mixture was heated at 60 °C under vigorous stirring for 2 h. The extraction of TSC60 and TAH60 anatase powder from the sol was achieved by adding sufficient amount of Na₂CO₃ and NH₄OH solutions, respectively. The resulting solids were collected by centrifugation and washed with distilled water, until the pH of the washing became 7, and then dried at 60 °C for 12 h. A portion of the products was then calcined at 500 °C for 2 h to obtain TSC300 and TAH300.

Characterizations

Powder X-ray diffraction was performed with Cu Kα radiation on a Bruker D8 Advance X-ray diffractometer. Transmission electron microscopy was performed on JEOL JEM 2100F FEG TEM, operated at 200 kV. Nitrogen adsorption measurements at 77.4 K were carried out in a static volumetric system (Micromeritics Instrument Corporation, USA, model ASAP 2010) up to 1.12 bar pressure. Zeta-potential analysis was conducted on catalyst samples dispersed in distilled water using a Zeta-Potential/Sizer Instrument (Malvern).

Adsorption studies

Adsorption studies were conducted under dark by stirring 50 mL of 10 mg L⁻¹ MO (λ_max = 466 nm) & MB (λ_max = 662 nm) dye mixture solution with 1 g L⁻¹ P25, TSC60 and TAH60 catalysts separately in a 100 mL beaker for 30 min. Amount of adsorption of each dye was then determined from the decrease in the UV-Vis absorption of each dye which was analyzed by a UV-Vis Spectrophotometer (Varian Carry 3E). The catalyst powder was separated from the mixture by centrifugation, before performing the UV-Vis absorption analysis. The adsorption study of TSC500 and TAH500 was also performed using 50 mL of 10 mg L⁻¹ of individual dye solutions.

Photocatalytic experiments

All photocatalytic reactions were carried out in a 100 mL beaker, placed in an ice bath in order to minimize evaporation, with 50 mL of 5 mg L⁻¹ MO & MB dye mixture solution and a catalyst concentration of 1 g L⁻¹. The reaction mixture was stirred for 30 min under dark, for the adsorption equilibrium to be established, before exposure to UV light and stirring was continued throughout the reaction. Dye degradation was monitored by the decrease in the absorption at λ_max of each collected sample (±4 mL) withdrawn at predetermined time intervals. The catalyst powder was separated from the mixture by centrifugation, before performing the UV-Vis absorption analysis.

Results

Material properties

Powder XRD analysis showed that both TSC60 and TAH60 comprise of anatase crystals (Fig. 1a) with the characteristic 2θ peak at 25.3°. All other peaks are indexed to the different planes of anatase TiO₂. TSC60 and TAH60 have an average anatase crystallite size of 6 and 5.5 nm, respectively, as calculated using the Scherrer equation (Table 1). Calcination of TSC60 and TAH60 samples at 500 °C increased the crystallinity of the corresponding TSC500 and TAH500 samples as evidenced from their intense diffraction patterns (Fig. 1b). TSC500 and TAH500
Table 1 Crystallite size and surface properties of the catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size/nm</th>
<th>$\zeta$-Potential/mV</th>
<th>Surface area/m$^2$g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC60</td>
<td>6</td>
<td>+40</td>
<td>280</td>
</tr>
<tr>
<td>TAH60</td>
<td>5.5</td>
<td>-35</td>
<td>360</td>
</tr>
<tr>
<td>P25</td>
<td>30</td>
<td>+30</td>
<td>55</td>
</tr>
<tr>
<td>TSC500</td>
<td>15</td>
<td>+17</td>
<td>80</td>
</tr>
<tr>
<td>TAH500</td>
<td>12</td>
<td>-9</td>
<td>90</td>
</tr>
</tbody>
</table>

comprise mainly of anatase phase along with small amount of rutile phase (29 = 27.5) as a result of the high temperature treatment. Calculation also caused enlargement of average anatase crystallite size of TSC60 and TAH500 to 15 and 12 nm, respectively, as calculated using the Scherrer equation (Table 1). Nitrogen adsorption analysis of TSC60 and TAH60 recorded the reported$^{15}$ adsorption isotherm (Fig. S1)$^\dagger$ for mesoporous materials (type II in the initial P/P$^\circ$ region followed by type IV) with H2 type hysteresis loop, one that is usually associated with mesopores having narrow necks and wide bodies ('link bottle' pores)$^{20,21}$ TSC60 and TAH60 showed similar pore size distribution with a maximum average pore diameter of 4 nm (Fig. S2)$^\dagger$. We believe the porous nature of TSC60 and TAH60 originated from the unique dispersion stability of the acid-stabilized sol, where extraction with base resulted in highly porous products. The calculated surface areas of TSC60 and TAH60 were 280 and 360 m$^2$g$^{-1}$, respectively (Table 1). The surface area of calcined samples, TSC500 and TAH500, dropped to 80 and 90 m$^2$g$^{-1}$, respectively, due to crystal growth during the high temperature treatment, which is in agreement with the XRD analysis. TEM analysis revealed that the as-prepared TSC60 and TAH60 catalysts were equi-axed (Fig. S3)$^\dagger$ crystals and has size of 5-8 nm. This is in agreement with the average anatase crystallite size calculated using the Scherrer equation. $\zeta$-potential analysis was conducted on all synthesized and Degussa P25 catalysts in order to study their surface charge, which is shown in Table 1. When dispersions of the catalysts in distilled water were analyzed for $\zeta$-potential, P25 (+30 mV), TSC60 (+40 mV) and TSC500 (+17 mV) showed positive surface charge whereas TAH60 (~35 mV) and TAH500 (~9 mV) showed negative surface charge. Degussa P25 is produced by flame hydrolysis of TiCl$\text{4}$ at >1200 °C with HCl as by-product.$^1$ Although TSC60 and TAH60 powders were extracted from the same acid stabilized sol by the addition of Na$_2$CO$_3$ and NH$_2$OH solutions, respectively, they showed opposite surface charge. Due to calcination, there was a considerable decrease in the surface charge of TSC500 (from +40 to +17) and of TAH500 (from ~35 to ~9).

**Adsorption of dyes**

All the synthesized catalysts and P25 were tested for their dye adsorption behaviour towards cationic (MB) and anionic (MO) dyes. The results of the adsorption studies performed on 50 mL of MO and MB aqueous mixture (±10 mg L$^{-1}$) with a catalyst concentration of 1 gL$^{-1}$ are shown in Fig. 2. P25 and TSC60 exhibited preferential adsorption of MO over MB where TSC60 showed slightly higher adsorption than P25. P25 adsorbed 16% of MO and 3% of MB whereas TSC60 adsorbed 23% of MO and 4% of MB from the solution. Conversely, under the same experimental conditions TAH60 showed almost completely selective adsorption of MB (96%) over MO (3%). It was found that the adsorption capacity of TSC60 and TAH60 decreased substantially after heat treatment. The adsorption of TSC60 decreased from 23% to 1% for MO but for MB it increased from 4% to 8%, while the adsorption of TAH500 for MB decreased from 96% to 18%.

**Selective photocatalysis**

Photocatalytic degradation studies were conducted on 50 mL of ±5 mg L$^{-1}$ aqueous mixture of MO and MB under UV light irradiation. TSC60 and TAH60 catalysts selectively degraded MO and MB dyes, respectively, from their 5 mg L$^{-1}$ aqueous mixture under UV light exposure. Fig. 3 shows the decrease in concentration of each dye from the reaction mixture after contact with TSC60 (Fig. 3a & c) and TAH60 (Fig. 3b & d), for 480 min under UV light irradiance. TSC60 degraded MO in the first 120 min, during which time MB remained intact. Afterwards

---

This journal is © The Royal Society of Chemistry 2012

RSC Adv., 2012, 2, 447-452 | 449

---
the degradation of MB commenced. The degradation rate of MB was three times slower than MO. Interestingly, these observations were exactly the opposite with TA\(\text{H}60\) where it completely degraded MB in the first 60 min and then started to degrade MO, where MB degradation was eight times faster than MO. Under the same experimental conditions neither P25 nor calcined samples, TSC500 and TA\(\text{H}500\), showed any significant selectivity for the degradation of MO and MB dyes. With P25 the photocatalytic oxidation reaction of both dyes commenced simultaneously with almost complete degradation achieved within 90 min (Fig. 4a & d). TSC500 (Fig. 4b & e) and TA\(\text{H}500\) (Fig. 4c & f) also did not show any significant selectivity toward MO and MB degradation. However, a complete degradation of both dyes was achieved in 270 min compared with 480 min for TSC60 and TA\(\text{H}60\).

Discussion

Origin of surface charge and preferential adsorption of dyes

Incompletely saturated co-ordinations on the outermost atoms cause metal oxides to adsorb ions from the surroundings which contribute to their surface charge.\(^{37,38}\) This depends on the pH and ionic composition of the medium.\(^{37,38}\) In the synthesis of TSC60, extraction of the solid product from the acid stabilized sol with Na\(_2\)CO\(_3\) solution caused the adsorption of H\(^+\) ions on the TiO\(_2\) surface and hence the resulting catalyst has a positive surface charge. While in the case of TA\(\text{H}60\), isolation with NH\(_2\)OH caused the adsorption of OH\(^-\) on the catalyst surface resulting in a catalyst with a negative surface charge (Fig. 5). Calcination of TSC60 and TA\(\text{H}60\) at 500 °C caused the removal of some of the adsorbed species which in turn reduced the surface charge of the calcined catalysts (Table 1). Refluxing the positively surface charged anatase TiO\(_2\) particles with 10 M sodium or potassium hydroxides has resulted in the formation of titanate nanotubes with negative surface charge.\(^{39}\) Calcination of these titanate nanotubes in air at 400 °C caused the loss of -OH groups which in turn resulted in reduced surface charge.

Organic dyes are one of the major components in industrial effluent. Selective adsorption of dyes is therefore of prime importance with regard to their recovery or degradation. Recently, researchers have shown\(^{37}\) that exfoliated graphene oxide (EGO) with negative surface charge acts as good adsorbent for cationic dyes including MB. However, reduced graphene oxide (rGO) which does not possess high negative charge has
proven as good adsorbent for anionic dyes. Herein, MO, being an anionic dye, gets preferentially adsorbed by TSC60 which has a high positive surface charge leaving MB intact in solution. On the other hand the negative surface charge of TAH60 causes preferential adsorption of the cationic MB from the dye mixture (Fig. S5).1

Our findings indicate promise in the use of these catalysts in the recovery of dyes from industrial effluent since the attached dye molecules were easily desorbed from TSC60 and TAH60 by extraction with acetone. This also confirms that the nature of adsorption of MO and MB on TSC60 and TAH60 is through electrostatic force of attraction and not by strong chemical bonding, which is in agreement with the findings of Budykin et al.24 P25 with a positive surface charge also showed preferential adsorption of the anionic MO over the cationic MB dye. Budykin et al.24 have reported similar type of preferential adsorption of an anionic dye, Eriochrome Black T, over MB with P25. When negatively surface charged titanate nanotubes, derived by NaOH and KOH treatment of P25, were used the preferential adsorption was reversed toward MB. Calculation of these nanotubes caused the loss of –OH groups which resulted in 30% reduction in the MB adsorption capacity. In our study, calcination of the catalyst samples caused the removal of H+ and OH− groups in TSC500 and TAH500, respectively, which resulted in the reduction of their surface charge (Table 1). The decreased surface charge of TSC500 and TAH500 was reflected in their dye adsorption ability (Fig. 2).

Selective adsorption studies of dyes have further implication in improving the efficiency of dye sensitized solar cells (DSSCs). Higher amount of dye adsorbed on TiO2 without dye aggregation, could lead to better performance of the DSSCs. Tailored selection of dyes with higher affinity toward TiO2 could be achieved by understanding their adsorption behaviour.24,25

Selective positioning of dyes, with different absorption wavelengths, on TiO2 surface has been found to increase the efficiency of DSSC. Lee et al.24,25 have demonstrated the selective positioning of three organic dyes N719, N749 and P5 on TiO2 surface by mimicking the stationary-mobile phase concept of column chromatography.

Herein, we propose a simple method (Fig. 6) for the selective positioning of anionic dye (MO) and cationic dye (MB) using TSC60 and TAH60 for use in DSSCs. By coating TSC60 and TAH60, one after the other, on FTO/ITO glass substrate as shown in Fig. 6b and dipping the coated substrates in dye solutions, selective positioning of MO and MB will result. High temperature treatment of TiO2 is a common practice in the fabrication of DSSCs. But this could cause the loss of surface charge and significant drop in surface area thus decreasing the dye adsorption on TiO2. In our approach, however, this can be avoided since our low-temperature derived TiO2 has comparable crystallinity so that they can act as good electron transport medium. It has also been proven as good candidate in photocatalytic degradation reactions.31

Selective photocatalysis of dyes

The most exciting observation in our study is the complete and totally opposite selectivity exhibited by TSC60 and TAH60 (Fig. 3) toward the photocatalytic degradation of MO and MB dyes. Researchers have reported on preferential degradation of MO and MB by nanocrystalline TiO2.31 However, to the best of our knowledge this is the first report of complete selectivity achieved by nanocrystalline TiO2 in the degradation of MO and MB from their aqueous mixture. The selectivity shown by TSC60 and TAH60 toward the degradation of MO and MB, respectively, was quite interesting especially because both TSC60 and TAH60 showed identical properties, such as crystalline phase, size, morphology, pore diameter, and pore size distribution except that TAH60 has slightly higher surface area than TSC60. ζ-potential analysis revealed that TSC60 has a positive surface charge while TAH60 has a negative surface charge (Table 1) which led to the preferential adsorption of MO on TSC60 and MB on TAH60 (Fig. 2). Thus, the adsorbed MO gets selectively degraded by TSC60 (Fig. 3a & c) and MB by TAH60 (Fig. 3b & d) from the dye mixture solution. It has been reported that the replacement of surface-bonded fluorides in TiO2 micropores by hydroxyl groups through washing with NaOH, accelerated the rate of degradation of MB over MO. The observed selectivity was explained by preferential adsorption of MB on the hydroxyl surface-modified catalyst.31

We believe that the preferential adsorption of MO and MB by TSC60 and TAH60 is not the only reason for their selective degradation. If that was the case, P25 would have also shown selectivity towards MO over MB in their photocatalytic oxidation reaction since ζ–potential analysis showed that P25 has a positive surface charge (Table 1) and the adsorption study confirmed preferential adsorption of MO over MB by P25 (Fig. 2). However, it is clear from Fig. 4a & d, that the rate of degradation of MO and MB over P25 was almost identical where the reaction was completed in 90 min. Liu et al.31 have reported favored decomposition of MO over MB by P25 as attributed to the less abundance of {001} facets in P25. However we could not observe any significant selectivity by P25 in the degradation of MO and MB, Degussa P25 is the bench mark TiO2 photocatalyst due to its unique ability to destroy wide range of pollutants with great pace.3 Its high reactivity arises from its unique material properties, particularly its high crystallinity, which might be the reason why it did not show any selectivity in the degradation of MO and MB. This is further confirmed by the total time (90 min) taken by P25 to complete the degradation of MO and MB compared to 480 min for TSC60 and TAH60. This demonstrates that not only the surface charge of TSC60 and TAH60 but also their controlled reactivity that makes them selective photocatalysts.
When the calcined samples TSC500 and TAH500 were tested for their photocatalytic dye degradation, they did not show any significant selectivity either as shown in Fig. 4 b & c. Calculation of TSC60 and TAH60 caused the loss of H+ and OH- ions, respectively, thereby decreasing the surface charge of TSC500 and TAH500 as revealed by the \( \zeta \) potential analysis (Table 1). This in turn decreased their preferential adsorption capacity (Fig. 2). In addition, calculation caused an increase in crystallinity which is evident from the high intense diffraction patterns of TSC500 and TAH500 in comparison with TSC60 and TAH60 (Fig. 1). It has been reported that highly crystalline TiO2 is superior for photocatalytic applications than the less crystalline or amorphous samples. The combined effect of decreased surface charge and increased crystallinity of TSC500 and TAH500 could be responsible for the loss of selectivity.

Conclusions

To summarize, we demonstrated a relatively simple way to synthesize TiO2 photocatalysts with desired surface charge and controlled reactivity. These catalysts showed preferential adsorption and fully selective degradation of cationic (MB) and anionic (MO) dyes. The observed selectivity for the dye adsorption by TSC60 and TAH60 could have wide implications in 1) the recovery or destruction of precious dyes or harmful pollutants, respectively, from a mixture of their counterparts and 2) the tailored adsorption and selective positioning of sensitizers on TiO2 for the fabrication of more efficient DSSCs.

Acknowledgements

This work was financially supported by MRGS and School of Applied Sciences and Engineering, Monash University. The authors are grateful to Dr W. S. Tang, J. K. Tadvan, Dr M. Dauquah, C. Ongkudon, Dr V. Verheyen and A. Cruiskshank for their experimental assistance and Monash Electron Microscopy Centre, for providing their technical support.

References

Supplementary Information

Selective adsorption and photocatalysis of low-temperature base-modified anatase nanocrystals

Manoj A. Lazar and Walid A. Daoud*

School of Applied Sciences and Engineering, Monash University, Churchill, VIC 3842, Australia. Fax: Fax: (+61) 3 990 26738; Tel: (+61) 3 990 26411

Fig. S1 N$_2$ adsorption isotherms of TSC60 and TAH60.
**Fig. S2** Pore size distribution of TSC60 and TAH60.

**Fig. S3** TEM images of (a) TSC60 and (b) TAH60.
**Fig. S4** Structure of (a) Methyl orange (MO) and (b) Methylene blue (MB).

**Fig. S5** Schematic representation of adsorption of (a) MO on TSC60 and (b) MB on TAH60.
**Fig. S6** UV-Vis absorption spectra (left) of \( \approx 10 \text{ mgL}^{-1} \) aqueous mixture of MO & MB before (OS) and after contact with (a) TSC60, (b) TAH60 and (c) P25 for 30 minutes under dark.
Fig. S7 UV-Vis absorption results of adsorption studies of $\approx 10 \text{ mgL}^{-1}$ aqueous solution of MO and MB separately (OS) with TSC60 & TSC500 (a & b) and with TAH60 & TAH500 (c & d) for 30 minutes under dark.
Monash University

Declaration for Thesis Publication 2.2.

Declaration by candidate

In the case of Publication 2.2., the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development and execution of the idea, interpretation of the results, and the manuscript preparation</td>
<td>80</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Usman A. Rana</td>
<td>Assistance in one experimental part and its result interpretation.</td>
<td></td>
</tr>
<tr>
<td>Walid A. Daoud</td>
<td>Development of the idea, experimental guidance, interpretation of the results, and manuscript correction</td>
<td></td>
</tr>
<tr>
<td>Douglas R. Macfarlane</td>
<td>Development of the idea, experimental guidance, interpretation of the results, and manuscript correction</td>
<td></td>
</tr>
</tbody>
</table>

| Candidate's Signature | 05/12/12 |

Declaration by co-authors

The undersigned hereby certify that:

(1) the above declaration correctly reflects the nature and extent of the candidate’s contribution to this work, and the nature of the contribution of each of the co-authors.
(2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
(3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
(4) there are no other authors of the publication according to these criteria;
(5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
(6) the original data are stored at the following location(s) and will be held for at least five years from the date indicated below:

<table>
<thead>
<tr>
<th>Location(s)</th>
<th>SASE, Gippsland Campus, Monash, Churchill, VIC-3842, Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>School of Chemistry, Monash, Clayton, VIC-3168, Australia</td>
</tr>
</tbody>
</table>

[Please note that the location(s) must be institutional in nature, and should be indicated here as a department, centre or institute, with specific campus identification where relevant.]

<table>
<thead>
<tr>
<th>Signature 1</th>
<th>05/12/12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signature 2</td>
<td>07/12/12</td>
</tr>
<tr>
<td>Signature 3</td>
<td>05/12/12</td>
</tr>
</tbody>
</table>
2.2. Understanding the Chemistry of TiO\textsubscript{2} Colloidal Systems: Preferential Adsorption and Selective Photocatalytic Degradation

Manoj A. Lazar\textsuperscript{*1,2}, Usman Ali Rana\textsuperscript{3}, Walid A. Daoud\textsuperscript{*4} and Douglas R. MacFarlane\textsuperscript{*2}

\textsuperscript{1}School of Applied Sciences and Engineering, Gippsland, Monash University, Churchill VIC, 3842, Australia. \textsuperscript{2}School of Chemistry, Clayton, Monash University, VIC, 3168, Australia, \textsuperscript{3}Sustainable Energy Technologies (SET) center, College of Engineering, King Saud University, PO Box: 800, Riyadh – 11421, Saudi Arabia, \textsuperscript{4}School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong.

Abstract

Nanocrystalline TiO\textsubscript{2} photocatalysts were synthesized through a low – temperature sol – gel method, by precipitating the powder catalysts at different pHs. These TiO\textsubscript{2} catalysts were characterized by different techniques such as powder X-ray diffraction, nitrogen sorption and transmission electron microscopy. Synthesized TiO\textsubscript{2} samples were moderately crystalline and have almost similar BET surface area, pore size distribution and crystallite size. These catalysts were found to differ mainly in their surface charge as revealed from the $\zeta$-potential and impedance measurements. The synergic effect of surface charge and moderate crystallinity of these TiO\textsubscript{2} catalysts were demonstrated successfully for the preferential adsorption and selective degradation of methyl orange and methylene blue dyes. The origin of permanent surface charge, on the sol – gel derived TiO\textsubscript{2} samples, is explained based on the fundamental principles of colloidal chemistry.
**Introduction**

Among the various available water decontamination technologies, photocatalysis using nanocrystalline titanium dioxide catalyst is unique in terms of activity, catalyst stability (reusability) and simplicity. The non-selective catalytic behavior of titanium dioxide has been exploited for the destruction of a huge spectrum of water contaminants. However, attempts to explore the feasibility of selective photocatalysis by titanium dioxide are also receiving more attention, in recent times. Consequently, selective formation of organic compounds or selective/preferential degradation of pollutants has been achieved. In general, crystalline anatase TiO$_2$ has been found to be non-selective in photocatalytic applications. How to produce a TiO$_2$ selective photocatalyst for degradation reactions very much depends on the nature of pollutants. Hydrophilic/hydrophobic, electrostatic or chemical interactions between TiO$_2$ photocatalysts and target compounds can determine the extent of attraction of the latter towards the photocatalyst. This difference in attraction results in selective adsorption of particular compound/s on the TiO$_2$ surface which are then degraded selectively. Adsorption of the pollutants on TiO$_2$ is another stage where screening of compounds could be possible. Amount of the TiO$_2$ catalyst used or size of the target compounds has been reported to achieve selectivity in the adsorption process which then contributes to the selective degradation catalysis. However, high crystallinity of the TiO$_2$ photocatalyst has found to be detrimental in some selective photocatalysis studies, even after the selective adsorption of compounds. This is because the superior activity of TiO$_2$ catalyst arises from its highly crystalline lattice arrangement. Preferential degradation of charged pollutants has been achieved based on the electrostatic interactions between photocatalyst and pollutants. Incorporation of TiO$_2$ into zeolites is one of the techniques to achieve this. The negative charge density on zeolite selectively attracts the positively charged pollutants. These are then preferentially degraded by the incorporated TiO$_2$ in the zeolite. It is known that the ‘point of zero charge’ (pHpzc) of TiO$_2$ is between pH = 6.1-6.3. TiO$_2$ surfaces with positive or negative charge can be produced below and above pHpzc, respectively. The conventional way of doing this is by changing the pH of the reaction mixture by adding acid/base. However, the extent of surface charging depends on the surface area and size of agglomeration of the TiO$_2$ nano-particles in solution. Smaller surface area and bigger particle size generally results in weakly surface charged surfaces. This could happen especially in high temperature treated TiO$_2$ samples. Recently we have
reported the low-temperature synthesis of anatase nano-crystals with positive and negative surface charges.\textsuperscript{16} These catalysts acquired their surface charge in their sol-gel synthesis route and neither washing several times with distilled water nor drying at 80 °C could remove their surface charge. Since we adopted a low-temperature synthesis method the resulting TiO\textsubscript{2} catalysts are produced with moderate crystallinity. The synergic effect of surface charge and moderate crystallinity of our synthesized catalysts produced complete selective degradation of cationic and anionic dyes.

The present paper describes the pH dependant precipitation of anatase nano-crystals with varying surface charges. The surface charge of TiO\textsubscript{2} is explained based on the fundamentals of colloidal chemistry. Their photocatalytic behavior is tested for the degradation of an aqueous mixture of anionic (methyl orange) and cationic (methylene blue) dyes.

**Experimental**

**Synthesis of TiO\textsubscript{2} photocatalysts**

In a typical synthesis, an acid stabilized 5\% titanium tetra isopropoxide (Sigma Aldrich) sol was achieved in 5\% acetic acid (Rowe Scientific, Australia), 1.4\% hydrochloric acid (Merck) and water. This acid stabilized sol was kept under vigorous stirring at 60 °C (2 h) for the hydrolysis and condensation reactions to occur to form nanocrystalline TiO\textsubscript{2} sol. Precipitation of the photocatalysts from the acid stabilized sol was carried out at seven different final pHs, ranging from 4 to 10, by adding the required amount of 10\% sodium carbonate solution. The pH of the TiO\textsubscript{2} precipitation was monitored by using a calibrated (with acidic and basic buffers) pH meter (lab CHEM-pH). The precipitated powder photocatalysts were separated by centrifugation, washed several times with distilled water and then dried at 80 °C over night. The samples were ground well using a motor and pestle and thus obtained catalysts were named as TSC4, TSC5, TSC6, TSC7, TSC8, TSC9 and TSC10, according to their final pH of precipitation.

**Characterizations**

**Powder X-ray diffraction**
powder X-ray diffraction was performed with Cu Kα radiation on a Bruker D8 – Focus PXRD. Samples were scanned between 20 = 5 - 70° at a scanning speed of 3° min⁻¹.

**Transmission electron microscopy (TEM)**

TEM was performed by JEOL JEM 2100F FEG TEM, operated at 200 kV. Small amount of powder samples were dispersed in ethanol by ultra-sonication for 15 minutes. One drop from the ultra-sonicated sample was then spread over carbon coated copper grid for TEM analyses.

**Nitrogen sorption analysis**

Nitrogen sorption measurements were carried out at 77.4 K in a static volumetric system (Micromeritics Instrument Corporation, USA, model ASAP 2010) up to 1.12 bar pressure. Degassing of the samples was done prior to nitrogen adsorption. During degassing, samples were heated initially up to 60 °C with a temperature ramp rate of 5 °C min⁻¹ and at an evacuation rate of 5 mm Hg sec⁻¹ to a final vacuum set point of 50 µm Hg. Samples were held at 60 °C for 2 h before reaching the final degassing temperature of 80 °C, at the same temperature ramp rate, for 6 h.

**ζ-potential analysis**

ζ-potential analyses were conducted by using a Zeta-Potential/Sizer Instrument (Malvern). A pinch of each samples were dispersed in distilled water, by ultra-sonication for 2 minutes, before performing the ζ-potential analysis.

**Impedance measurements**

The impedance analysis was performed on all synthesized catalysts dispersed in water (2 mg/ml) using Solartron A.C DI 1296 Impedance Spectrometer. A dip type cell was used to carry out these impedance measurements having platinum electrodes and Nyquist plots were made from the impedance data obtained from these experiments.

**Adsorption studies**
For adsorption studies, separate experiments were conducted under dark by stirring 50 mL of \( \approx 5 \text{ mg L}^{-1} \) MO (\( \lambda_{\text{max}} = 466 \text{ nm} \)) & MB (\( \lambda_{\text{max}} = 662 \text{ nm} \)) dye mixture solution with 2 g L\(^{-1} \) of TSC4 \( \rightarrow \) TSC10 catalysts in a 100 mL beaker at room temperature. Amount of dye adsorbed was determined from the decrease in the UV-Vis absorption of each dye in samples stirred for 5 and 30 minutes, by using a UV-Vis Spectrophotometer (Varian Carry 3E). The catalyst powder was separated from the mixture by centrifugation, prior to the UV-Vis absorption analysis.

**Photocatalytic experiments**

50 mL of \( \approx 5 \text{ mg L}^{-1} \) MO & MB dye mixture solution and 2 g L\(^{-1} \) of each catalyst was used in all photocatalytic reactions which were carried out in a 100 mL beaker, placed in an ice bath in order to minimize evaporation. Adsorption equilibrium between the catalyst and the dye molecules was established by stirring the reaction mixture for 30 min in the dark before exposure to UV light and stirring was continued throughout the reaction. Dye degradation was calculated from the decrease in the absorption at \( \lambda_{\text{max}} \) of both dyes in the withdrawn reaction mixtures (\( \approx 4 \text{ mL} \)) at required time intervals. The catalyst powder was separated from the mixture by centrifugation, before performing the UV-Vis absorption analysis. Recyclability of the catalyst was tested by performing the photocatalytic experiments under similar conditions with once used catalysts separated by centrifugation and washing.

![Figure 1 Powder X-ray diffraction patterns of TSC4 \( \rightarrow \) TSC10 photocatalysts.](image-url)
Results and discussion

Characterization

Powder X-ray diffraction analysis was performed on all the low-temperature synthesized TiO$_2$ samples. Figure 1 represents the diffraction patterns obtained for TSC4 → TSC10 samples. All TiO$_2$ samples generated similar powder X-ray diffraction patterns. The characteristic peak observed at $2\theta = 25.3^\circ$, in all samples, corresponds to the (101) plane of the catalytically most active anatase phase of TiO$_2$. All other peaks in the diffraction patterns are attributed to the other various planes of the anatase phase of TiO$_2$. Absence of peaks at $2\theta = 27.4^\circ$ and $30.8^\circ$ eliminate the formation of other main phases of TiO$_2$ such as rutile and brookite in any of the synthesized samples. The X-ray diffraction patterns of all TiO$_2$ samples are less intense (moderate crystallinity) when compared to that of reported calcined samples. This is as expected since the maximum temperature of our catalysts syntheses was only 80 °C. High crystallinity of nano TiO$_2$ is favourable for its superior photocatalytic activity. However, the moderate crystallinity of our catalyst systems was one of the key factors for their selective photocatalytic properties.

Nitrogen adsorption - desorption properties of all synthesized samples (TSC4 → TSC10) were analysed at constant temperature, 77 K (liquid nitrogen temperature), by varying the nitrogen pressure between 10^{-5} to 1 bar. Isotherms generated by all synthesized samples are shown in Figure 2a. Type II adsorption isotherm was observed at initial P/P$_0$ region (up to around 0.5) followed by type IV. This observation is well reported for meso-porous titanium dioxide materials. On desorption of the adsorbed nitrogen, from the meso-pores, a hysteresis loop was produced in all TiO$_2$ samples, as obvious from the Figure 2a. This happens when the materials have narrow necked - wide bodied meso-pores, also known as ‘ink bottle’ pores. Slow desorption of the condensed nitrogen from the ‘bottle neck’ pores, compared to desorption from the bottle body’ pores, produces the hysteresis loop. Pore size distribution curves of TSC4 → TSC10 are shown in Figure 2b. As seen from the figure, the synthesized TiO$_2$ samples have a uniform pore size distribution. The average pore diameter of all TiO$_2$ samples is between 3.5 and 4.5 nm. BET specific surface area of the synthesized TiO$_2$ samples were determined from the volume of nitrogen gas adsorbed and is given in Table 1. Higher BET specific surface (> 250 m$^2$g$^{-1}$) areas were achieved for the synthesized TiO$_2$ catalysts compared to that of the reported high temperature treated TiO$_2$ samples. The higher surface area observed is the advantage of the low-temperature (80 °C)
TiO$_2$ synthesis. High surface area can give superior adsorption properties to the TiO$_2$ catalysts.

![Nitrogen sorption isotherms (a) and pore size distributions (b) of TSC4 → TSC10, at liquid nitrogen temperature.](image)

**Figure 2** Nitrogen sorption isotherms (a) and pore size distributions (b) of TSC4 → TSC10, at liquid nitrogen temperature.

![TEM images of representative TiO$_2$ samples.](image)

**Figure 3** TEM images of representative TiO$_2$ samples.

TEM analysis was performed on three synthesized TiO$_2$ samples ie. TSC4, TSC7 and TSC10. All the analysed TiO$_2$ samples were equi-axed crystals of size ranging between 5 – 10 nm. X-ray diffraction, nitrogen sorption and TEM characterizations revealed that TSC4 → TSC10 comprised of anatase phase and their attributes such as crystallinity, surface area, pore size distribution, morphology and size are almost identical. This is as expected since all these TiO$_2$ catalysts were derived from a parent acid stabilized nanocrystalline TiO$_2$ sol. Addition of Na$_2$CO$_3$ is just to precipitate the formed TiO$_2$ nanocrystals from sol state to powder form.
Table 1 BET Surface area, pore size distribution and ζ- potential of TSC4 → TSC10 photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²g⁻¹)</th>
<th>Average pore diameter (nm)</th>
<th>ζ – potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC4</td>
<td>258</td>
<td>3.5</td>
<td>+32</td>
</tr>
<tr>
<td>TSC5</td>
<td>283</td>
<td>3.5</td>
<td>+41</td>
</tr>
<tr>
<td>TSC6</td>
<td>273</td>
<td>4.3</td>
<td>+07</td>
</tr>
<tr>
<td>TSC7</td>
<td>256</td>
<td>3.6</td>
<td>-44</td>
</tr>
<tr>
<td>TSC8</td>
<td>279</td>
<td>4.0</td>
<td>-46</td>
</tr>
<tr>
<td>TSC9</td>
<td>262</td>
<td>3.9</td>
<td>-47</td>
</tr>
<tr>
<td>TSC10</td>
<td>267</td>
<td>3.9</td>
<td>-46</td>
</tr>
</tbody>
</table>

ζ- potential values obtained for TSC4 → TSC10 powder catalysts dispersed in distilled water are given in Table 1. Remember that all these catalysts, after being precipitated from the TiO₂ sol at different pHs, have undergone 4 – 5 times of washing using distilled water and drying at 80 °C overnight before reaching the well ground powder form. TiO₂ catalysts precipitated at a final pH = 4 and pH = 5, < pHpzc of TiO₂, acquired positive surface charge (by protonation through a charging mechanism as shown in equation 1) as is obvious from their positive ζ- potential values (Table 1). TSC7 → TSC10, which were precipitated at a final pH > pHpzc of TiO₂, acquired negative surface charge (by the de-protonation through equation 1) as demonstrated from their negative ζ- potential values (Table 1). As expected TSC6 catalyst which was precipitated at pH = 6 (≈ pHpzc of TiO₂) showed almost neutral value of ζ- potential.

Figure 4 display the Nyquist plots for both positive and negative surface charge containing TiO₂ aqueous solutions respectively. The impedance data for TSC6 aqueous solution (having near neutral surface charge) was used in both figures for reference or as a control sample. The resistivity of these catalysts aqueous solutions was estimated from the touchdown values on
Figure 4 Impedance analysis results of TSC4 → TSC6 (a) and TSC6 → TSC10 (b), in distilled water.

The real axis (Z' axis) in these Nyquist plots. It can be clearly seen that the TSC6 aqueous solution showed the highest resistivity, which can be related to the near neutral surface charge on the TiO₂ particles for this catalyst containing aqueous solution. In the case of positive surface charge containing systems (Figure 4a), a continuous decrease in the real axis intercept (touchdown) can be seen in going from sample TSC6 → TSC4. This shows that the sample which was synthesized at pH = 4 and 5 (TSC4 and TSC5) has higher positive surface charge (and accompanying counterion) compared to the sample synthesized at pH = 6 (TSC6).

In the case of negative surface charge containing systems, a sudden decrease in the value of real axis intercept (touchdown) can be observed in going from TSC6 to the catalyst sample TSC7. The negative surface charge on the TiO₂ contributes to the observation of lower resistance value for TSC7 in this case. All TiO₂ samples synthesized at pH 7 and onwards, exhibited this similar decrease in the resistivity (lower touchdown values) compared to the TSC6 sample. However, no particular order of resistivity change can be seen for the samples onward from TSC7 to TSC10.

Origin of surface charge

Preferential adsorption of ions is one of the ways of gaining charges on a surface in a liquid and this is a common charging mechanism at an interface. The pH of the solution has a great influence in determining the surface charge and potential of insoluble inorganic oxides; here the inorganic oxide is TiO₂. Then the potential-determining ions which get adsorbed on TiO₂ surface, are H⁺ and OH⁻, most likely through a reaction mechanism as shown in equation...
The system thus forms a system of reversible reactions. The selection between protonation and deprotonation depends on the pH of the solution and the electro-kinetic measurements have proven that pHpzc of TiO_2 is in between pH = 6.1 - 6.3. Below pHpzc TiO_2 surface gets protonated and above pHpzc it gets deprotonated through the charging mechanism (equation 1).

Availability of large surface for protonation/deprotonation is the key factor to acquire maximum surface charge on TiO_2. The best result can be achieved in the case of finely subdivided particles. Hence the advantage of our catalyst synthesis method where the TiO_2 particles are well dispersed in the acid stabilized sol form. Also, our synthesized catalysts (TSC4 → TSC10) possess higher surface areas (Table 1) as realized from the N_2 sorption studies. Most of the reported works in photocatalysis, in terms of making surface charge on TiO_2, dealt with the high temperature treated powder samples and by adding acid or base to the reaction mixture. In these cases the catalyst powders may not be finely subdivided (agglomerated) and also high temperature treatment always results in reduced surface areas. Furthermore, removal of most of the surface bound hydroxyl groups on TiO_2 could happen in high temperature treatments. Our low-temperature TiO_2 sol

Figure 5 Schematic showing the interface in positively (a), negatively (b) surface charged TiO_2 samples in aqueous solution (brown ring – active surface, light green – stern layer and yellow – surface of shear) and (c) energy levels at different regions in colloidal dispersions.
synthesis and followed base precipitation eliminates all of these possibilities, thus creating higher surface charges on TSC4, TSC5 and TSC7 → TSC10 powder catalysts.

Figure 5 depicts a schematic of a plausible interface in our charged TiO$_2$ surfaces in solution. In TSC4 and TSC5, positively charged TiO$_2$ surface (active surface-brown ring in Figure 5a) is immediately surrounded mainly by Cl$^-$ counter ions (from the HCl contained parent TiO$_2$ sol), at a distance ‘δ’ from the active surface is the ‘Stern layer’ (light green in Figure 5a).$^{43,44}$ The ‘surface of shear’ (yellow) which moves along with the TiO$_2$ particle in an external electric field (e.g. ζ- potential measurements) is situated just close to the Stern layer and the potential at the surface of shear is the ζ- potential (Figure 5c). It is important to note that the actual potential at the surface of TiO$_2$ samples (active surface) will be higher than the obtained ζ- potential values shown in Table 1. In the case of TSC7 → TSC10, the situation is the same, except that the active surface contains negative surface charges immediately surrounded by Na$^+$ counter ions (from the added Na$_2$CO$_3$ during the precipitation of TiO$_2$ powder), as shown in Figure 5b. Beyond the surface of shear will be the diffuse layer which extends into the bulk of the solution.

**Selective degradation**

All the synthesized TiO$_2$ photocatalysts (TSC4 → TSC10) were tested for their selective degradation properties against methyl orange (MO) and methylene blue (MB) aqueous dye mixture, under UV light irradiation. Figure 6 summarizes the results obtained for the selective dye degradation experiments with TSC5 → TSC7 photocatalysts. TSC4 (Figure S4 a and b) and TSC5 (Figure 6 a and b) catalysts, with positive surface charge, selectively degraded the anionic MO dye first, followed by the degradation of the cationic dye MB. TiO$_2$ samples with negative surface charge, TSC7 → TSC10 (Figure 6e and f & Figure S4 c→h), exhibited selective degradation of the cationic MB dye, before commencing the degradation of the anionic MO dye. The positive surface charge on TSC4 and TSC5 and the negative surface charge on TSC7 → TSC10 catalysts resulted in the selective adsorption of MO and MB dyes (Figure 7 and Figure S3), respectively, contributing to their selective degradation ability. A second contributing factor towards their selective degradation capability is their moderate crystallinity. We have reported that despite of the selective adsorption of MO on Degussa P25 (it has a positive surface charge) photocatalyst it could not exhibit selective degradation of MO in an aqueous mixture of MO and MB.$^{16}$ The reason was the superior catalytic activity.
Figure 6 UV-Vis spectra and corresponding concentration vs time plot of selective photocatalysis by TSC5 (a and b), TSC6 (c and d) and TSC7 (e and f).
arising from its high crystallinity. Here the low-temperature synthesis imparted moderate crystallinity to TSC4 → TSC10 TiO₂ catalysts.

A very interesting observation was arose in the selective degradation experiment with TSC6 (Figure 6c and d). TSC6 has near neutral surface charge and did not exhibit selective degradation of MO or MB. Instead TSC6 degraded both MO and MB dyes at the same time and almost with same rate. This also confirms the synergism of crystallinity and surface charge in our selective degradation studies.

In the selective degradation experiments with TSC7 → TSC10, a slight blue shift in the λ_{max} of MO along with the increase in absorbance was observed in samples irradiated with UV light for one hour, as revealed by UV-Vis analysis (Figure 6e and f & Figure S4 c → h). However, the absorbance started to decrease in samples after one hour of UV irradiation. We believe that this is because of the interference of MB degradation intermediate/s which slowly get degraded under long UV exposure. More analyses are needed to clarify this observation which is not in the aims of present study.

Recyclability of our surface charged TiO₂ samples was tested by conducting a second run of the selective degradation of a MO and MB aqueous dye mixture. The catalyst used in the first run was separated by centrifugation, washed with distilled water and dried prior to use in second run of similar experimental conditions. Results of recyclability experiments of representative TiO₂ samples, TSC5 and TSC7, (results of other TiO₂ samples can be found in
Figure 8 UV-Vis absorbance spectra showing the reusability of TSC5 (a) and TSC7 (b) catalysts for their selective degradation reaction.

supporting information) are shown in Figure 8. Very interestingly, TSC4, TSC5 and TSC7 → TSC10 samples retained their almost complete selective degradation ability in the second run. This shows the strength of H\(^+\) and OH\(^-\) ions adsorption on to TiO\(_2\) samples to impart stable surface charges.

Conclusions

We have demonstrated a simple way of synthesizing TiO\(_2\) photocatalysts with neutral or permanent positive/negative surface charges through a low – temperature sol – gel route. The origin of surface charge on the TiO\(_2\) samples can be understood on the basis of the principles of colloidal chemistry. The synergistic effect of moderate crystallinity and the surface charge of the samples impart a selective photocatalytic degradation of methyl orange and methylene blue dyes. The catalysts almost completely retain their selective degradation ability in a second run. These findings are promising for the selective adsorption and selective degradation of other charged compounds.
Acknowledgements

This work was financially supported by Monash Graduate School and Gippsland Campus scholarships. Manoj A. Lazar is grateful to Kamran Khajehpour, Mega Kar and Vanessa Armel for their experimental assistance and Monash Electron Microscopy Centre, for providing their technical support.

References

Supplementary Information

Catalysts Synthesis

*pH of precipitation*

Precipitation of TSC catalysts was carried out by adding \( \approx 10 \% \) Na\(_2\)CO\(_3\) solution into the acid stabilized TiO\(_2\) sol. Fig. S1 represents the pH titration curve of catalyst precipitation. Initial pH of the TiO\(_2\) sol was \( \approx 1.1 \). Final pH of the catalyst precipitations were 4, 5, 6, 7, 8, 9 and 10, accordingly the precipitated TiO\(_2\) catalysts were named TSC4, TSC5, TSC6, TSC7, TSC8, TSC9 and TSC10. The obvious plateau in Fig S1 (in the pH range 3.3 – 5) is the buffering region of acetic acid, a constituent in the TiO\(_2\) sol. The plateau observed above the pH = 9, in TSC10, is the saturation pH of 10% Na\(_2\)CO\(_3\) solution.

![Figure S1 pH titration curves of the precipitation of TSC4 – TSC10 catalysts from an acid stabilized sol by using 10% Na\(_2\)CO\(_3\) solution.](image)

*Figure S1 pH titration curves of the precipitation of TSC4 – TSC10 catalysts from an acid stabilized sol by using 10% Na\(_2\)CO\(_3\) solution.*
Thermo Gravimetric Analysis (TGA)

Figure S2 shows the TGA curves obtained for the TSC4 – TSC10 TiO₂ catalysts. Approximately 6 – 12 % weight loss was observed when the catalysts were heated to 500 °C. Weight loss displayed in the temperature range 70 - 150 °C, in all samples, was attributed to the removal of adsorbed water molecules, H⁺ and OH⁻ ions from the catalyst surface. TSC4 and TSC5 catalysts showed a second stage of weight loss of ≈ 3 %, at 350 °C, by the decomposition of acetic acid presented on them. Since their precipitation was stopped in acidic medium some of the acetic acid might have contaminated these samples. The second stage of weight loss was not observed for catalyst samples TSC6 – TSC10.

Figure S2 TGA curves obtained for TSC4 → TSC10 catalysts.
Adsorption properties

Adsorption ability of TSC4 → TSC10 TiO₂ photocatalysts was analysed by conducting the adsorption studies at room temperature, in the dark. Approximately 100 mg of catalyst sample was dispersed, by stirring, in 50 mL of 5 mgL⁻¹ MO and MB dye mixture aqueous solution. Samples were removed from the reaction mixture after 5 and 30 minutes of stirring in the dark. The amount of dye adsorbed was determined from the UV – Vis absorbance (Figure S3 a → d) of the solution after separating the catalyst by centrifugation. TSC4 and TSC5 catalysts exhibited preferential adsorption of MO (13 – 22 %) over MB whilst TSC7 → TSC10 catalysts showed almost complete selective adsorption (87 – 94 %) of MB over MO. The maximum adsorption of dyes was achieved in the first 5 minutes of contact with the catalysts. TSC6 did not exhibit any significant adsorption of either MO or MB.
Figure S3 UV-Vis. absorbance spectra of dye adsorption by TSC4 → 6 (a and b) and TSC7 → 10 (c and d).

Figure S4 UV-Vis. absorbance spectra and corresponding concentration vs time plot of selective dye degradation by TSC4 (a & b), TSC8 (c & d), TSC9 (e & f) and TSC10 (g & h).
Figure S5 UV-Vis. absorbance spectra showing the results of selective dye degradation by TSC4 (a), TSC6 (b), TSC8 (c), TSC9 (d), and TSC10 (e) catalysts, in the second run.
Figure S6 UV-Vis absorbance spectra showing the reusability of TSC4 (a), TSC8 (b), TSC9 (c), and TSC10 (e) catalysts for their selective degradation reaction.
3. Near-ambient synthesis, characterization and formation mechanism of potassium titanate nanorods from anatase TiO$_2$

3.1. Introduction

Nanocrystalline Ti-O compounds are unequivocally regarded as potential candidates in the energy and environmental sectors.$^{1,2}$ Among these compounds alkali titanates with the general structure $A_2Ti_6O_{2n+1}$ ($A=$Na, K and Li), where $n$ varies from 1 to 9, have promising applications especially in Li-ion batteries$^3$ and as fuel cell electrolytes.$^4$ The disadvantages associated with the conventional alkali titanate syntheses such as high processing temperatures and micro-meter scale formation have been addressed by adopting a comparatively low temperature hydrothermal alkali treatment of nanocrystalline TiO$_2$, pioneered by Kasuga et al.$^5$ Inspired by this work, researchers could successfully achieve the formation of fibrous 1D titanate nano structures.$^6-8$ However large scale production of the alkali titanates by this hydrothermal treatment is limited due to the high pressures required. Moreover, most of the reported moderate temperature syntheses of alkali titanates use high temperature treated TiO$_2$ as the precursor; otherwise the resulting titanates have poor crystallinity.$^9$ There are few reports that discuss the synthesis of alkali titanates at atmospheric pressure; reports indicate that complete conversion of the precursor to titanate$^{10}$ could not be achieved even after 12 days of synthesis, or that the formed titanates were in micrometer scale. $^{11}$ Daoud et al. have developed a low temperature (40-60 °C) process for the synthesis of nanocrystalline anatase TiO$_2$ by adopting a modified sol-gel method,$^{12}$ without compromising the crystallinity. This method was successfully applied to self cleaning cotton,$^{13}$ keratins$^{14}$ and also in the near-ambient formation of TiO$_2$-B.$^{15}$

This chapter describes the near-ambient synthesis of high surface area crystalline potassium titanate nanostructures, and their formation mechanism. The maximum temperature employed in the process was 110 °C without any autoclaving.
Figure 3.6 Schematic of hydrothermal (a) and (b) near-ambient syntheses methods.

3.2. Experimental

3.2.1. Low-temperature sol-gel synthesis of anatase TiO$_2$ precursor

In a typical synthesis, an acid stabilized 5% titanium tetra isopropoxide (Sigma Aldrich) sol was achieved in 5% acetic acid (Rowe Scientific, Australia), 1.4% hydrochloric acid (Merck) and water. This acid stabilized sol was kept under vigorous stirring at 60 °C (2 h) for the hydrolysis and condensation reactions to occur to form a nanocrystalline TiO$_2$ sol. Precipitation of the anatase precursor from the acid stabilized sol was carried out by adding the required amount of 10% sodium carbonate solution. The precipitated anatase TiO$_2$ powder was separated by centrifugation, washed several times with distilled water and then dried at 80 °C overnight. The samples were ground well using a mortar and pestle.

3.2.2. Near-ambient synthesis of potassium titanate nanostructures

Conversion of anatase TiO$_2$ into potassium titanate nanostructures was carried out by refluxing ≈ 3 g of low-temperature derived anatase nanoparticles with ≈ 120 mL of 8 M potassium hydroxide solution. The reflux was done at 110 °C for 72 h. The reaction mixture
was always under uniform stirring by using a teflon coated magnetic bar. Aliquots were withdrawn from the reaction mixture at different time intervals of 6, 12, 24, 36, 48, 60 and 72 h. The powder samples, after separation by centrifugation and several times of washing with distilled water, were dried over night at 110 °C. The well ground titanate samples were named as KTTN6, KTTN12, KTTN24, KTTN36, KTTN48, KTTN60 and KTTN72 where the number represents the time of KOH treatment.

The influence of KOH concentration on the potassium titanate formation was studied. Potassium titanate samples were synthesized from the anatase precursor by refluxing ≈ 1 g of TiO$_2$ precursor with 40 mL of 8, 20 and 30 M KOH solutions in three separate experiments. The reflux temperature was 110 °C and the reaction continued for 6 days (144 h). Two samples were obtained, from each set of experiments, at 72 h and 144 h. The samples were separated by centrifugation and washed thoroughly with distilled water and dried over night at 110 °C. The samples thus obtained were named as KTTN-8-72, KTTN-8-144, KTTN-20-72, KTTN-20-144, KTTN-30-72 and KTTN-30-144 where the first number in each sample code represents the concentration of KOH and the last one represents the time of reflux.

3.2.3. Characterization

3.2.3.1. Powder X-ray diffraction

Powder X-ray diffraction was performed with Cu Kα radiation using a PHILIPS XPert MPD X-ray diffractometer. A small amount of powder material was spread over the sample stage and was scanned in the 2θ range of 5 – 70° with a scanning rate: 0.5° sec$^{-1}$.

3.2.3.2. Nitrogen sorption analysis

Nitrogen sorption measurements were carried out at 77.4 K in a static volumetric system (Micromeritics Instrument Corporation, USA, model ASAP 2010) up to 1.12 bar pressure. Degassing of the samples was done prior to nitrogen adsorption. During degassing, samples were heated initially to 80 °C with a temperature ramp rate of 5 °C min$^{-1}$ and at an evacuation rate of 5 mm Hg sec$^{-1}$ to a final vacuum set point of 50 µm Hg. Samples were held at 80 °C
for 2 h before reaching the final degassing temperature of 110 °C, at the same temperature ramp rate, for 6 h.

3.2.3.3. ζ–potential analysis

ζ–potential measurements were conducted by using a Zeta-Potential/Sizer Instrument (Malvern). A pinch of each sample was dispersed in distilled water, by ultra-sonication for 2 minutes, before performing the ζ–potential analysis.

3.2.3.4. Scanning electron microscopy (SEM)

SEM was performed on a JEOL JEM 2100F FEG SEM, operated at 15 kV. Small amounts of powder samples were dispersed in ethanol by ultra-sonication for 30 minutes. One drop from the ultra-sonicated sample was then spread over copper film mounted on an aluminium stub and allowed the alcohol to evaporate. The samples were then sputter coated with platinum before performing the SEM analysis.
3.3. Results and discussion

3.3.1. Powder X-ray diffraction

Figure 3.2 X-ray diffraction patterns of anatase precursor and potassium titanate samples.

Powder X-ray diffraction of the anatase precursor and potassium titanates are shown in Figure 3.2. The intensity and the sharpness of the diffraction peaks were not as high as high temperature treated titanium-oxide samples, which is as expected. The nature of the diffraction patterns indicates that the low-temperature derived titanium-oxide samples are moderately crystalline. All diffraction patterns observed for the TiO$_2$ precursor were attributed to different planes of the anatase phase. The characteristic anatase peak appeared at $2\theta = 25.3^\circ$ which corresponds to the (101) plane of anatase and the diffraction peaks obtained at $2\theta = 38.1^\circ$, $48^\circ$, $54.2^\circ$ and $62.7^\circ$ correspond to the (004), (200), (211) and (204) planes of the anatase, respectively. Other common phases of TiO$_2$ such as rutile or brookite were found to be absent in the precursor since their characteristic $2\theta$ reflections ($27.4^\circ$ for rutile and $30.8^\circ$
for brookite) were not observed. These findings confirm that the low-temperature sol-gel synthesis of TiO$_2$ resulted in the formation of moderately crystalline anatase titania.

Potassium titanate synthesis was carried out by the KOH (8 M) refluxing, at 110 °C, of low-temperature derived anatase TiO$_2$. Aliquots were withdrawn from the reaction mixture at different time intervals and were characterized by powder X-ray diffraction. It is obvious from the Figure 3.2 that the diffraction patterns obtained for the potassium titanate aliquots were different from the anatase precursor. The characteristic anatase peak presented in the diffraction pattern of anatase, at $2\theta = 25.3^\circ$, started to diminish from the very first potassium titanate sample (KTTN6) withdrawn, after 6 h of KOH reflux at 110 °C. This peak then completely disappeared in the KTTN36 sample (36 h of KOH reflux) and in potassium titanate samples thereafter (KTTN48, KTTN60 and KTTN72). All other anatase indexed diffraction peaks which were present in the diffraction pattern of the precursor exhibited the same trend and disappeared completely after 36 h of reaction. Instead, well defined peaks which are indexed to crystalline titanate$^7$ were recorded. The reflection at $2\theta = 10.2^\circ$ in the diffraction patterns of the potassium titanate samples is a distinctive alkali titanate peak from its (200) plane. The intensity and sharpness of this characteristic peak improved from KTTN6 → KTTN72 indicating that the crystallinity of the formed potassium titanate is increasing with reaction time. Other titanate peaks were recorded at different $2\theta$ values such as $2\theta = 24.3^\circ$, $29.2^\circ$, $42.6^\circ$, $48^\circ$ and $59.4^\circ$. These were the reflections from (110), (310), (603), (020) and (423) planes of titanate, respectively. The quality of these titanate peaks was also improved with reaction time. These results confirm the successful conversion of anatase TiO$_2$ into potassium titanate under ambient reaction conditions. The complete conversion of TiO$_2$ into potassium titanate has occurred after 36 h of the KOH (8 M) reflux. Contrary to the reported ambient synthesis of potassium titanate,$^{10}$ here we could achieve a complete conversion of the anatase to titanate.
3.3.2. Nitrogen sorption

Nitrogen sorption properties of the anatase precursor and potassium titanate aliquots were collected at liquid nitrogen temperature, 77.4 K. The curves in Figure 3.3 represent the nitrogen adsorption and desorption isotherms obtained for the low-temperature synthesized anatase TiO$_2$ and potassium titanate samples derived from it. Nitrogen sorption of all samples at 77.4 K generated type II adsorption isotherms in the initial $P/P_0$ region, up to around 0.5, followed by a type IV isotherm. This behaviour is usually associated with mesoporous materials whose pore size is between 2 – 100 nm.$^{16,17}$ On reducing the nitrogen pressure (in the $P/P_0$ range: 1 – 0.45), the amount of nitrogen desorbed from the pores was less than the amount that adsorbed at the same pressure. This delayed desorption of nitrogen from the pores produces hysteresis loops in the curves of all samples. The presence of hysteresis in the adsorption – desorption isotherm is an indication of the shape of the mesopores. Pores with narrow necks and wider

![Figure 3.3 Nitrogen sorption isotherms of anatase TiO$_2$ precursor and potassium titanate samples.](image-url)
bodies or “ink bottle” shaped mesopores usually exhibit this phenomenon.\(^\text{16, 17}\) Here, capillary condensed nitrogen desorbs slowly from the “bottle neck” pores at liquid nitrogen temperature. As seen in the Figure 3.2, the nature of the hysteresis loop obtained for the anatase precursor was a stepped loop and there was a transition from stepped loop to a smooth one in the potassium titanate samples, as indicated in a red circle for KTTN6, KTTN12 and KTTN24. The change in the shape of hysteresis loops could be due to the destruction and reconstruction of pores in TiO\(_2\) precursor towards titanate formation. This was further confirmed from the pore size distributions of the TiO\(_2\) precursor and potassium titanate samples.

Figure 3.4 Pore size distribution curves of anatase TiO\(_2\) precursor and potassium titanate samples.

Figure 3.4 summarizes the pore size distribution results of the TiO\(_2\) precursor and potassium titanate aliquots. Anatase TiO\(_2\) precursor showed a narrow and uniform distribution of pores and its average pore diameter was \(\approx 3.5\) nm. It is obvious from the Figure 3.3 that all pores in TiO\(_2\) were less than 8 nm in size, since the distribution curve touched the pore diameter axis (‘X’ axis) at 8 nm. Contrary to the results obtained for TiO\(_2\), potassium titanate samples
showed a broader pore size distribution which extends even above 10 nm, in the pore diameter axis. There was a clear shift in the average pore diameter values of titanate samples towards higher pore diameters. Very interestingly, titanate samples after 36 h of KOH treatment exhibited a bimodal pore distribution. The first peak was at ≈ 4 nm, which was present in all titanate samples, and a second peak which increased from 5.9 nm in KTTN36 to 6.9 nm in KTTN72. The shift in the average pore diameter from 3.5 nm (in TiO$_2$ precursor) to 3.9 nm in KTTN6, KTTN12 and KTTN36 could be due to the grain boundary increase and joining of adjacent pores as a result of the refluxing at 110 °C. The bimodal pore distribution observed in KTTN36 → KTTN72 titanate samples may be because of complete structural collapse and reconstruction of the precursor. This argument is supported by the SEM analysis results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>ζ - potential (mV)$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KTTN6</td>
<td>252</td>
<td>-35.5</td>
</tr>
<tr>
<td>KTTN12</td>
<td>225</td>
<td>-38.3</td>
</tr>
<tr>
<td>KTTN24</td>
<td>177</td>
<td>-38.6</td>
</tr>
<tr>
<td>KTTN36</td>
<td>255</td>
<td>-36.4</td>
</tr>
<tr>
<td>KTTN48</td>
<td>219</td>
<td>-37.1</td>
</tr>
<tr>
<td>KTTN60</td>
<td>262</td>
<td>-35.9</td>
</tr>
<tr>
<td>KTTN72</td>
<td>232</td>
<td>-36.5</td>
</tr>
</tbody>
</table>

$^{a}$ measured in distilled water

Table 3.1 Surface area, and ζ - potential of potassium titanate samples.
BET surface area determined for the potassium titanate samples from the nitrogen sorption results are shown in Table 3.1. The specific surface areas calculated for the titanate samples were between 219 – 262 m$^2$g$^{-1}$ except for KTTN24. The specific surface area obtained for KTTN24 was 177 m$^2$g$^{-1}$. The reduction in the surface area of KTTN24 may be due to the structural collapse of the material during titanate formation. This has been further confirmed from the SEM images of the KTTN24 sample.

3.3.3. ζ – potential

Surface charge on the synthesized potassium titanate powder samples was determined by measuring their ζ – potential values in distilled water; Table 1. KOH treatment imparted negative surface charge onto all titanate samples, as is obvious from their negative ζ – potential values. Titanates have been reported to gain negative surface charge in aqueous medium by the dissociation of surface acidic groups.18

3.3.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analysis was performed on anatase precursor and titanate aliquots. SEM images of KTTN6 → KTTN72, at different magnifications, and of TiO$_2$ precursor are shown in Figure 3.5 → 3.8. An interesting finding revealed from the SEM analysis is that the final morphology of titanate nanorods results from a two stage structural transformation of the anatase precursor (Figure 3.8d). The first transformation was from the equi-axed morphology of anatase precursor19 to the long nanoweb morphology observed in the 6 h treated aliquot (KTTN6) which was retained in the 12 h aliquot as well (KTTN12). Very surprisingly, a total structural collapse occurred in the KTTN24 SEM images (Figure 3.6a → c). This might have started sometime after 12 h of KOH reflux. The second transformation was from this collapsed structure to nanorods, as evidenced in the SEM images of KTTN36 → KTTN72 aliquots.
Figure 3.5 SEM images of KTTN6 (a,b and c) and KTTN12 (d, e and f) at different magnifications.
Figure 3.6 SEM images of KTTN24 (a, b and c) and KTTN36 (d, e and f) at different magnifications.
Figure 3.7 SEM images of KTTN48 (a, b and c) and KTTN60 (d, e and f) at different magnifications.
It is worth noting that powder XRD patterns, nitrogen adsorption – desorption isotherms and pore size distribution curves obtained for titanate samples together confirm that complete conversion to potassium titanate was achieved in samples withdrawn after 36 h onwards of KOH reflux. Also, the reduction in BET surface area obtained for KTTN24 could be because of the structural collapse, as confirmed from the SEM analysis. These results suggest that the titanate nanorod formation passes through two stages, separated by a total structural collapse, where the first stage comprises TiO$_2$ – titanate mixture and the second stage involves complete converted titanate structures.
Figure 3.9 SEM images of KTTN6 showing intermediate structures (a, b and c) and well defined nanoweb (d, e and f).
Figure 3.10 SEM images of KTTN24 showing the structural collapse.
Scheme 3.1 Mechanism of potassium titanate nanostructures formation in near-ambient synthesis conditions.

3.3.4.1. Mechanism of nanorod formation

The complete picture of the base mediated formation of elongated titanate structures from TiO$_2$ nanoparticles is still a matter of debate.$^{20}$ However, the mechanism does seem to involve the dissolution of the TiO$_2$ precursor followed by the formation of lamellae shaped sheets. These sheets can then scroll into nanotubes or can shape into nanofibres/rods/ribbons. The former case is usually achieved in NaOH treatment whereas the latter takes place with KOH treatment.$^{20}$ The near-ambient synthesis of potassium titanate developed here has also passed through the sheet like structures before converting to the nanoweb in KTTN6. Figure 3.9a and b represent such isolated lamellae structures observed in KTTN6. These sheets then join together and wrinkle to form nanoweb. The wrinkling stage of these sheets can be as shown in
Figure 3.9c. During the titanate synthesis, total collapse of these nanoweb to different morphologies takes place, as evidenced from the SEM images of KTTN24 (Figure 3.10). Reformation of nanorods starts again but this time the material completely coverts to potassium titanate. Based on the SEM analysis results a two stage wrinkling mechanism of potassium titanate nanorod formation is proposed, as shown in Scheme 3.1.

3.3.5. Effect of KOH concentration

3.3.5.1. Powder X-ray diffraction

The effect of the concentration of KOH on potassium titanate formation was probed by refluxing the anatase TiO$_2$ precursor using 8, 20 and 30 M KOH solutions for 72 h and 144 h. Figure 3.11a shows the XRD patterns obtained for the samples removed after 72 h of KOH reflux. It is evident from the figure that the intensity of the peaks increases with increase in KOH concentration. This is an indication that the potassium titanate formed at higher KOH concentration has superior crystallinity. A shift in the characteristic titanate peak towards higher 2$\theta$ values was observed from 10° → 10.7° → 11° in KTTN-8-72, KTTN-20-72 and KTTN-30-72, respectively. Longer reaction time of 144 h resulted in additional peaks in the potassium titante samples (Figure 3.11b) along with an increase in the intensity of the existing peaks. Only in KTTN-8-144 a new peak was formed at 2$\theta$ = 12.8°. All these observations are attributed to the changes happening in the structure of potassium titante resulting from the different reaction conditions.$^7,8$
Figure 3.11 XRD patterns of potassium titanate samples synthesised using different KOH concentrations after (a) 72 h and 144 h.
3.4. Conclusions

Near-ambient formation of potassium titanate nanostructures was successfully achieved by the KOH treatment of anatase TiO$_2$ at 110 °C. XRD patterns of potassium titanate aliquots revealed that the complete formation of potassium titante was achieved after 36 h of KOH reflux. SEM images of the titanate samples recorded a structural collapse of once formed nanoweb structures and their reformation again into nanorod morphology. Based on the SEM analysis results a two stage wrinkling mechanism of potassium titanate nanorod formation is proposed. Higher concentrations of KOH were found to increase the crystallinity of the potassium titanate and also caused a shift in the characteristic XRD peak towards higher 2θ values. Formation of new peaks was observed in potassium titanate samples on longer reaction times of KOH reflux.
3.5. References

4. Selective Adsorption of Cationic Methylene Blue Dye by Negatively Surface Charged Potassium Titanate

4.1. Introduction

Organic dyes are an integral part of modern human life and are widely applied in textile, paper, cotton, wool and cosmetic industries. Around 75 tonnes of dyestuffs are produced annually and ~11% is discharged in industrial effluents during their manufacturing and application stages.\(^1\) This is a significant amount and presence of these dyestuffs in water bodies is a serious threat to the environment. Some of these dyestuffs and their precursors are suspected carcinogens.\(^2\) Removal of dyes from effluents is therefore an essential step in the dye industry and adsorption of dyes on solid adsorbents is a simple way to achieve this. Cationic and anionic dyes can be easily adsorbed on oppositely charged adsorbents because of the electrostatic force of attraction between the adsorbent and the dye.\(^3\) Different adsorbents have been reported for the adsorption of charged dyes from their aqueous solution.\(^4-7\) Titanium oxides with positive or negative surface charge have been successfully demonstrated for the selective adsorption of methyl orange (anionic) and methylene blue (cationic) dyes.\(^3, 8\)

Methylene blue (MB) is a cationic dye commonly used for dying cotton, wool and silk.\(^5\) MB is an eye irritant, can cause eye burns or even permanent damage to eyes.\(^5\) Oral ingestion of MB can cause nausea, vomiting, mental confusion and methemoglobinemia.\(^5, 9, 10\) Therefore, the removal of MB from industrial effluent, before discharging to the environment, is essential. This chapter describes preliminary studies about the selective adsorption of the cationic methylene blue (MB) dye on potassium titanate samples derived by the KOH reflux of anatase TiO\(_2\) (synthesis of these titanate samples is described in chapter 3). Intermediate samples before the complete conversion into potassium titanate (KTTN6, 12 and 24) and KTTN72 as a representative sample of completely converted potassium titanate were chosen for the selective adsorption experiments. The selective photocatalytic degradation efficiency of these potassium titanate samples is also described.
4.2. Experimental

4.2.1. Adsorption studies

For adsorption studies, separate experiments were conducted in the dark by stirring 50 mL of \(\approx 5 \text{ mg L}^{-1}\) MO (\(\lambda_{\text{max}} = 466 \text{ nm}\)) & MB (\(\lambda_{\text{max}} = 662 \text{ nm}\)) dye mixture solution with 2 g L\(^{-1}\) of KTTN6, KTTN12, KTTN24 and KTTN72 samples in a 100 mL beaker at room temperature. Amount of dye adsorbed was determined from the decrease in the UV-Vis absorption of each dye, in samples stirred for 30 minutes, by using a UV-Vis Spectrophotometer (Varian Carry 3E). The catalyst powder was separated from the mixture by centrifugation, prior to the UV-Vis absorption analysis.

4.2.2. Photocatalytic experiments

50 mL of \(\approx 5 \text{ mg L}^{-1}\) MO & MB dye mixture solution and 2 g L\(^{-1}\) of each catalyst was used in all photocatalytic reactions which were carried out in a 100 mL beaker, placed in an ice bath in order to minimize evaporation. Adsorption equilibrium between the catalyst and the dye molecules were established by stirring the reaction mixture for 30 min in the dark before exposure to UV light; stirring was continued throughout the reaction. Dye degradation was calculated from the decrease in the absorption at \(\lambda_{\text{max}}\) of both dyes in the withdrawn reaction mixtures \(\approx 4 \text{ mL}\) at required time intervals. The catalyst powder was separated from the mixture by centrifugation, before performing the UV-Vis absorption analysis.

4.3. Results and discussion

4.3.1. Selective adsorption

Figure 4.1 represents the adsorption results of potassium titanate samples with 5 mgL\(^{-1}\) MO and MB aqueous dye mixture solution. All samples selectively adsorbed the cationic dye MB from the aqueous mixture as is obvious from the decrease in the UV-Vis absorbance at \(\lambda_{\text{max}} = 662 \text{ nm}\) (Figure 4. 1a). The adsorption of the anionic dye MO by the potassium titanate samples was marginal as is clear from the insignificant decrease in the UV-Vis absorbance at \(\lambda_{\text{max}} = 466 \text{ nm}\). The amount of dye adsorbed was calculated and is shown in Figure 4.1b. The MB adsorption capacity of all samples was above 90%, whereas that for MO adsorption was 6-13%. 
Figure 4.1 UV-Vis spectra showing the selective adsorption of MB over MO (a) and the percentage of adsorption (b) (Initial concentration of each dye is 5 mgL$^{-1}$).
The selective adsorption of the cationic dye MB by potassium titanate samples occurs due to the negative surface charge (Table 3.1) acquired during their formation from TiO$_2$ through KOH reflux. The electrostatic force of attraction between the cationic MB dye and the negative charge density on titanate samples caused the selective absorption of MB. The superior amount of MB adsorption exhibited by the potassium titanate is also attributed to its higher surface area, as revealed from the nitrogen sorption analysis (Table 3.1). These findings are promising for the removal or recovery of dyestuffs from industrial effluents.

4.3.2. Selective photocatalysis

Potassium titanate samples were tested for their selective photocatalytic ability towards MO and MB dye mixture in aqueous solution (5 mgL$^{-1}$). Despite of the superior selective adsorption of MB dye by the titanate, their photocatalytic degradation ability was poor. Figures 4.2 and 4.3 show the UV-Vis absorption spectra of the reaction mixture containing MO and MB dye mixture and titanate samples, after UV light exposure. It is obvious from the figure that even after 240 minutes of UV light irradiance the MO degradation was not initiated. The sudden decrease observed in the UV-Vis absorbance of MB ($\lambda_{\text{max}} = 662$ nm) was due to its selective adsorption on the titante surface. The presence of MB was further confirmed by the persistence of the blue colour on the titante samples even after 240 minutes of UV exposure.

This poor photocatalytic performance of the titanate samples further evidences the conversion of the anatase precursor by KOH reflux as discussed in chapter 3, the original anatase showing strong photocatalytic efficiency as illustrated in chapters 2.1 and 2.2.
Figure 4.2 UV-Vis absorption spectra showing the results of selective degradation experiment of MO & MB dye mixture solution by (a) KTTN6 and (b) KTTN12.
Figure 4.3 UV-Vis absorption spectra showing the results of selective degradation experiment of MO & MB dye mixture solution by (a) KTTN24 and (b) KTTN72.
4.4. Conclusion

Near-ambient derived potassium titanate samples were demonstrated as promising adsorbents for the cationic dye methylene blue. This can be further applied to a wide spectrum of cationic dyes and other positively charged specie for their selective recovery or removal from industrial effluents. However, these titante samples were found to act as poor photocatalysts and would therefore not be suitable for an application requiring degradation.
4.5. References


5. Conclusions and Future Works

This thesis illustrates the advantage of low-temperature sol-gel synthesis in achieving titanium dioxide nanomaterials with tailored surface charge and moderate crystallinity. The surface charge and crystallinity of these TiO$_2$ samples are demonstrated in accomplishing selective degradation of charged dyes. The thesis also describes the near-ambient formation of potassium titanate nanostructures from TiO$_2$ precursor. The key findings of this doctoral project can be summarized as follows:

- Anatase TiO$_2$ samples have been synthesized through a low-temperature sol-gel route.

- Nitrogen sorption and X-ray diffraction analyses reveal that the low-temperature synthesized TiO$_2$ samples have higher surface area ($< 250$ $\text{m}^2\text{g}^{-1}$) and moderate crystallinity. TEM images confirm they are equi-axed nanoparticles of size ranging between 5-8 nm.

- The surface charge of the low-temperature synthesized TiO$_2$ samples is tailored by precipitating the powder samples at different final pHs. $\zeta$-potential and impedance analyses showed that TiO$_2$ samples precipitated at a final pH value which is below (pH = 4 and 5) or above (pH = 7→10) the pH$_{pzc}$ of the material, possessed positive and negative surface charges respectively. Precipitation at pH$_{pzc}$ (pH = 6) rendered near neutral surface charge to the TiO$_2$ powder.

- The presence of surface charge on TiO$_2$ is explained based on the fundamentals of colloidal chemistry.

- Calcination of the low-temperature derived TiO$_2$ samples imparted higher crystallinity, but caused the removal of their surface charges.

- TiO$_2$ samples with positive surface charge preferentially adsorbed the anionic dye, methyl orange, over the cationic dye, methylene blue, from their aqueous solution. A reference TiO$_2$ sample, Degussa P25, with a positive surface charge also preferentially adsorbed the anionic methyl orange dye over methylene blue. Negatively surface charged TiO$_2$ samples selectively adsorbed methylene blue over methyl orange.
samples precipitated at pH$_{pzc}$ and the calcined TiO$_2$ samples showed insignificant adsorption of both dyes.

- Low-temperature synthesized TiO$_2$ samples with either positive surface charge on negative surface charge selectively degraded methyl orange dye or methylene blue dye, respectively under UV light exposure. The TiO$_2$ precipitated with neutral surface charge, calcined TiO$_2$, and Degussa P25 showed insignificant selectivity in the dye degradation.

- Dye degradation results suggest a synergistic effect of surface charge and moderate crystallinity, achieved through the low-temperature synthesis, in accomplishing selectivity in photocatalysis.

- A mechanism for the selective positioning of dyes on the TiO$_2$-FTO glass electrode is proposed, for use in dye sensitized solar cells.

- Low-temperature sol-gel synthesized anatase TiO$_2$ nanoparticles are completely transformed into potassium titanate nanorods by refluxing with potassium hydroxide under near-ambient experimental conditions.

- X-ray diffraction patterns of potassium titanate aliquots suggested that the complete conversion of the anatase precursor is achieved after 36 h of KOH reflux. $\zeta$-potential analysis confirmed that the titanates are negatively charged.

- SEM analysis of potassium titanate aliquots evidenced that the formation of nanorods is a two stage process where collapsing of the formed nanorods happens before reforming into potassium titanate nanorods. A ‘two stage wrinkling mechanism’ of nanorod formation is proposed, based on the SEM results.

- Potassium titanate samples selectively adsorbed the cationic methylene blue dye over methyl orange from their aqueous mixture. However, near-ambient synthesised potassium titanate nanostructures were found to be unsuitable for the photocatalytic degradation of methylene blue and methyl orange dyes under UV light irradiance.
The findings from this doctoral thesis contribute the following to the scientific community: (1) a simple and near-ambient synthesis route to produce titanium-oxide nanostructures with tailored surface charge, (2) demonstration of synergism of surface charge and crystallinity in achieving the selective photocatalytic degradation of charged pollutants, (3) insights about titanium dioxide colloidal systems and (4) a new ‘two stage wrinkling mechanism’ of potassium titanate nanorod formation.

The findings of this project have a number of follow-up investigations. Selective adsorption and degradation achieved with the surface charged TiO$_2$ are extendable to the wide spectrum of charged compounds. The feasibility of selective dye positioning, using surface charged TiO$_2$, to improve the performance of dye sensitized solar cells should be investigated. Further characterizations of the potassium titanate aliquots should be done to reveal the exact stoichiometry of the potassium titanate nanorods. Titanates may also be good candidates in Li$^+$- ion batteries. Therefore, it is interesting to test the Li$^+$ insertion capacity of the near-ambient synthesized potassium titanate nanorods.
Nanostructured Thin Films as Functional Coatings

Manoj A. Lazar, Jajil K. Tadvani, Wing Sze Tung, Lorena Lopez, Walid A. Daoud
School of Applied Sciences and Engineering, Monash University, Churchill, VIC 3842, Australia

E-mail: Walid.Daoud@sci.monash.edu.au

Abstract. Nanostructured thin films is one of the highly exploiting research areas particularly in applications such as photovoltaics, photocatalysis and sensor technologies. Highly tuned thin films, in terms of thickness, crystallinity, porosity and optical properties, can be fabricated on different substrates using the sol-gel method, chemical solution deposition (CSD), electrochemical etching, along with other conventional methods such as chemical vapour deposition (CVD) and physical vapour deposition (PVD). The above mentioned properties of these films are usually characterised using surface analysis techniques such as XRD, SEM, TEM, AFM, ellipsometry, electrochemistry, SAXS, reflectance spectroscopy, STM, XPS, SIMS, ESCA, X-ray topography and DOSY-NMR. This article presents a short review of the preparation and characterisation of thin films of nanocrystalline titanium dioxide and modified silicon as well as their application in solar cells, water treatment, water splitting, self-cleaning fabrics, sensors, optoelectronic devices and lab on chip systems.

1. Introduction

Thin film technology could be referred to as old wine in a new bottle, since it is one of the newest sciences of one of the oldest arts [1]. Most of the feature activities of thin films, with thickness ranging from monolayer of nanometer level to several micrometres, are represented by a research area called surface engineering [2]. The application of a thin film depends on its features, such as thickness, electron transportation, magnetism, super conductivity and optics. Although the major exploitation of thin film science was in the fields of tribology and microelectronics, today thin film research in the areas of energy generation, catalysis and sensor technology has tremendously been increasing [3]. Consequently, in addition to the conventional thin film processing technologies such as chemical vapour deposition (CVD) and physical vapour deposition (PVD), technologies such as sol-gel process [3] and chemical solution deposition (CSD) [4] were utilized; particularly for the inexpensive production of epitaxial films (films with ordered crystal structure). Nanocrystalline TiO2 thin films are widely used in photocatalysis [5], photovoltaics [6] and self-cleaning surfaces [7]. Likewise porous silicon thin films have versatile applications such as sensors, optoelectronic devices and lab on chip systems [8,9].

2. Photoactive Self-cleaning Fibers

With the increasing demand toward functional and intelligent fibrous materials due to the busy lifestyle and greater desire for convenience, textiles with easy-care functions have become increasingly popular in recent time [10-12]. Great strides are being devoted toward the development of
permanent self-cleaning fibrous materials with environmental friendly functionalities such as antimicrobial and deodorization [13,14].

Inspired by photoelectrolysis of water in 1960s [13-15], there has been an increasing interest in the novel concept of producing photoactive self-cleaning materials. After depositing a photoactive substance such as titanium dioxide on a substrate surface, the substrate can catalytically decompose adsorbed organic contaminants or harmful microorganisms through photochemical reactions, photooxidation and photoreduction, in the presence of ultraviolet light (figure 1).

With the advancement of bottom up nanotechnology approaches, the potential of photo-induced self-cleaning fibrous materials has been explored [12,16,17]. Reminiscence of a 1951 film “The Man in the White Suit”, fabrics that do not need laundering are no longer confined to the realm of science fiction [16,17]. In 2004, Daoud and Xin [16] first introduced self-cleaning cotton using a low temperature sol-gel method. In this approach, nanocrystalline anatase titanium dioxide colloid was synthesized through hydrolysis and condensation of titanium tetraisopropoxide. The cotton fibers were then treated with the colloid where a thin film of anatase titanium dioxide was formed on fibers surface through a conventional coating process [16].

![Concept of Self-Cleaning Fibers](image)

**Figure 1.** Concept of Self-Cleaning Fibers

Although these pioneering self-cleaning fibrous materials have been receiving increasing interest, this research effort has been limited to cellulose fibers such as cotton and hemp due to the low chemical, thermal and photostability of protein fibers such as wool and silk [16-25]. Recently, there has been a breakthrough, when Daoud et al. successfully produced non-antiproliferative and non-cytotoxic self-cleaning keratin fibers (figure 2) using a modified low temperature sol-gel method [26,27]. This process can introduce photocatalytic self-cleaning functions onto a fibrous substrate without affecting the intrinsic properties of the fibrous material through reducing the loading of titanium dioxide nanoparticles and optimizing the application process. Much effort has continuously been dedicated to the development of such innovative self-cleaning fibrous materials [7,26-30].

With the use of self-cleaning clothing, contamination of rivers and streams caused by effluent from the laundry process can be reduced. Depleting natural resources can also be saved through reducing the use of detergents and water. It may take some time for the society to adapt to the idea of self-cleaning clothes, but this invention shows a potential in changing the way we live by rendering conventional laundering routines obsolete.
Figure 2. Stain degradation of concentrated coffee on: (a) pristine white; (b) coated white wool; (c) pristine beige; (d) coated beige wool fabric after solar simulated irradiation.

3. TiO$_2$ thin films for solar cells and water splitting

Due to the depleting and polluting state of fossil fuels, researchers are in search for alternative energy sources that are economic and eco-friendly. It is projected that thin film technology will play an increasingly important role in the near future in the development of alternative energies, particularly photovoltaics, as shown in figure 3.

Figure 3. Projected global shipments of thin films for photovoltaics (P), fuel cells (F), batteries (B), nuclear (N), concentrating solar power (C) and geothermal (G), 2008 and 2013.

Source: BCC Research.
Among the various promising solutions for sustainable energy production, photovoltaics research is a highly fertile land for thin film technology to nourish. Solar technologies based on “excitonic”, electronically excited molecular states, photovoltaic systems such as dye-sensitised heterojunctions, are low cost and use highly processable material components [6,31]. In dye-sensitised solar cells (DSSC), a semiconductor oxide thin film of TiO₂ with its mesoporous solid pore architecture contributes to a greater impregnation of the dye, easy electron transfer from the dye to the collector electrode and increased electron-hole pair density at the hybrid interface [3]. Fabrication of a nanocrystalline TiO₂ thin film can be achieved using several technologies, among which CVD [1], PVD [1], spin coating [32], doctor blading [33], screen printing [34], electrochemical methods [35] and chemical solution deposition (CSD) [4] are commonly used. A combination of sol-gel method, potentiostatic electrochemical growth, and plasma etching has been employed for the fabrication of TiO₂ thin films of one dimensional wires and three dimensional gyroid arrays [31]. Nanocrystalline films of TiO₂ with different morphologies such as nanotubes [35,36], nanorods [37] and nanowires [38] are efficient for use in DSSC because of their ability in forming direct connection of the point of photogenerated with the collecting electrode [37].

The thickness of the TiO₂ film is of great importance in DSSC since it should be within the electron diffusion length for optimal performance of the device [39]. Normally the thickness is in the range of 10-15μm and the size of TiO₂ particles is ~20 nm [40] but it varies in accordance with the dye used. Effect of film thickness on device performance has been well studied by a number of research groups [41-43].

The light harvesting of a DSSC can be improved by mixing large titania particles (200-400 nm) in a 15-30 nm sized TiO₂ film or printing on the top of the film, which in turn scatter the photons by multiple reflections thereby increasing the optical path length beyond the film thickness [44]. Various surface modifications such as deposition of titanium organic sol, [34] treatment with TiCl₄, [45] use of dendrimers [46] and coating with ZnO [47] or ZrO₂ [48] on the TiO₂ film have been carried out for improving the performance of the DSSC. Phase and morphological characterisation of the TiO₂ film involves the use of common techniques such as XRD, SEM, AFM and TEM. In-situ evaluation of hybrid interfaces can be monitored by DOSY-NMR and SAXS [3]. Impedance Spectroscopy for DSSC and other characterisation techniques are well explained by M. D. Archer and A. J. Nozik [49].

Hydrogen generation by water splitting, pioneered by Fujishima and Honda [15], is another promising tool for clean fuel production by using solar energy. Although the mostly exploited form of nanocrystalline TiO₂ mediated photocatalytic water splitting is the suspended form [50], thin film technology is also contributing to this field. Both photocatalytic (oxidation and reduction on a photocatalyst) and photoelectrochemical (oxidation and reduction at spatially separated anode and cathode) hydrogen generation can be achieved using nanocrystalline TiO₂ thin films [51].

Matsuoka et al have reported the fabrication of visible light-responsive TiO₂ thin films, for photocatalytic water splitting, by a magnetron sputtering deposition method [52]. They studied the effect of heat treatment on the absorption properties of the films and clarified their findings using TEM and secondary ion mass spectroscopy (SIMS) characterisation techniques. Recently Frites and Khan have reported the photoelectrochemical splitting of water using hydrogen-modified TiO₂ films fabricated by thermal treatment of Ti metal sheet followed by reduction [53]. Carbon-doped TiO₂/ITO photoanode made by pulsed laser deposition under a partial methane atmosphere is another recent report on photoelectrochemical splitting of water [54].

Vertically oriented Ti-Fe-O nanotube array films for water photoelectrolysis were achieved by G. K. Mor et al using co-sputtering of Ti and Fe foils followed by their anodisation and annealing. They developed films with different thickness and different Ti/Fe composition by varying the power and temperature during the sputtering process. The Ti/Fe composition was investigated using glancing angle XRD (GAXRD) and XPS [55]. A detailed review of TiO₂ thin film mediated solar water splitting has been reported by Varghese, Ranjan and Grimes [56].
4. TiO₂ thin films for water treatment

Today, one of the main environmental concerns in many countries is water pollution and scarcity. Extensive work has been carried out to develop water treatment technologies among which heterogeneous photocatalysis using semiconductors is one of the most promising technologies [5,57]. These methods offer the advantage of mineralizing pollutants into CO₂ and H₂O, in contrast to conventional techniques such as activated carbon or air stripping that only transfer contaminants form one phase to another [5,57,58].

A wide range of nano-sized metal oxides can be used for heterogeneous photocatalysis. Anatase TiO₂ appears to be the most efficient photocatalyst in various environmental applications due to its effectiveness to generate hydroxyl radicals, non-toxicity, non-photoroscorrosivity, chemical inertness, high photo-activity, mechanical stability, relatively low cost, favourable photosensitivity in the ultraviolet region of the solar spectrum, [5,59,60] and the ability to decompose organic pollutants in both the liquid and gaseous phase under UV light illumination. Nanostructured anatase, in the form of powder suspension, has extensively been used in water treatment. It was shown by Neppolian et al [61] that TiO₂ powder in conjunction with solar irradiation is a suitable technique for removal of a common organic blue dye, one of the most popular textile dyes used in jeans. Barakat et al [62] have reported the ability of TiO₂ powder to remove cyanide and Cu (II) ions, one of the heavy metals that can cause water toxicity.

However, many problems have arisen from the use of TiO₂ powder suspensions in water treatment. These include the difficulty in the separation of powder from the suspension, aggregation of suspended particles especially at high concentrations, and the difficulty in applying suspensions in continuous flow systems. As a result, the immobilization of TiO₂ in the form of a thin film on support substrates has emerged as an alternative water treatment method.

The efficiency of TiO₂ thin film versus Degussa P25 TiO₂ powder toward 3,5-dichlorophenol degradation was evaluated by Arabatzis et al [63] who showed that a TiO₂ photocatalytic film can efficiently decompose 3,5-dichlorophenol, although relatively higher decomposition rate was observed with TiO₂ powder. The difference in efficiency can be attributed to the thin film’s surface area being smaller than the powder’s surface area. Therefore, since considerable research has shown that the specific surface area depends on the particle size; many attempts have been undertaken to obtain TiO₂ nanostructured thin films with the smallest crystal size possible. In addition to the crystal size, other films properties have been targeted for improvement, such as adherence to substrate, surface roughness, and porosity.

Many characterisation techniques have been used to determine the properties of TiO₂ nanostructured thin films among which; XRD is used to identify the TiO₂ crystalline phases and the crystal size, XPS is used to determine the homogeneity and stoichiometry of the thin film, SEM is used to observe surface properties and film thickness, and UV-Vis spectrophotometer and TOC are used to determine the photocatalytic activity. Zaleska et al [64] used AFM as a new technique to visualise the photodegradation of lauric acid at a TiO₂ anatase single crystal surface.

Currently, studies are focused on producing TiO₂ nanostructured thin films with high photocatalytic efficiency by producing thin films with small particles size, high homogeneity, and a reduced band-gap to shift the absorption to the visible region [65].

5. Porous silicon

It is anticipated that the silicon’s role in our daily life will become more significant in the future. Silicon-based semiconductors are the main component of many electronics due to the following reasons: controllable conductivity, good integrability with contemporary semiconductor technology, and its low cost. But the use of silicon in microelectronic industries is considerably limited due to its band structure. Low quantum efficiency is the main reason for using molecular semiconductors such as GaAs and InP or organic materials instead of silicon in many optoelectronic devices. In addition, devices based on these materials are very costly and cause environmental concerns due to the lack of recycling of constituting heavy metals [66].
The discovery of visible orange photoluminescence at room temperature from porous silicon by L. Canham in 1990 altered the views and perspectives of the optical properties of silicon [67]. Since the mid 1950s when Uhlir [68] discovered porous silicon by electropolishing, the main usage of porous silicon was limited to silicon on insulator (SOI), silicon on sapphire (SOS) and fully isolation with porous oxidized silicon (FIPOS) systems until 1990s [69,70]. Later on intensive research focused on the luminescent properties of porous silicon to fabricate silicon LEDs which was thought to be impossible to achieve. In 2000, Parkhutik reported a survey on the number of publications and scientific fields where researchers focused more on the means to form porous silicon layers [71].

Today silicon LEDs with about 10% efficiency are in use and researchers are working on fabricating solid state laser based on photonic crystals using porous silicon super lattices [72]. Controlable pore sizes (from micro to macro), extraordinary large surface area (200-1000 m²/cm²) and porosity (up to 98%), convenient surface chemistry, controlable dielectric function, biocompatibility, and integrability with silicon microelectronic systems were the other key factors for researchers to find novel and smart applications for porous silicon thin films [8,9,73-77].

Many applications have been developed owing to the tuneable and unique properties of porous silicon, such as electrical sensing with the aid of sensitivity of resistance and dielectric properties to changes in surface chemistry; optical sensing based on photoluminescence or interferometric properties; micro electro mechanical systems (MEMS) technology based on macroporous silicon fabrication; X-ray filters, photodetectors, waveguides, and Brag reflectors from a combination of dielectric function and photoluminescence properties of meso and macro porous silicon [9,66,78-86].

Due to the importance of porous silicon, numerous fabrication methods such as electrochemical, stain, plasma, hydrothermal, and metal-assisted etching have been proposed. Electrochemical etching had been the most popular method due to its acceptable reproducibility. The ability to tailor porous silicon with precise microstructures such as pore shape and size, porosity and surface area, thickness, and surface functional groups is the main reason for the widely use of this method [77].

Large surface area and chemically tuneable surface have made porous silicon a promising host for various materials that alter the optical and electrical properties toward novel application such as photocatalysis, batteries, and optical devices. Various composite systems based on porous silicon have been successfully proposed [87,88]. Using porous silicon as a carrier for TiO₂ particles is a potential way to improve the photocatalytic properties of TiO₂ due to the large surface area of the porous silicon and also easier way to collect and separate photocatalyst particles after finishing the mission [89].

The sol gel process has been the most commonly adopted method used to prepare TiO₂ thin films and nanoparticles and has also been used as an impregnation method to drive TiO₂ nanoparticles in the into the pores of porous silicon. Simplicity, low costs, tolerance to atmospheric condition, and ability to provide a highly homogenized thin films are some of the reasons for using the sol gel method. Another significance of porous silicon as carrier for photocatalytic purposes is the photo and electromluminescence properties of porous silicon. In this regard, porous silicon provides TiO₂ particles with photons required to conduct the photocatalytic reactions [90]. Gole et al. suggested the introduction of nitrogen doped titania nanostructures into the pores of porous silicon and produce visible light through the electromluminescence of porous silicon thus activating the photocatalyst. This device could then be incorporated in a microreactor. A scheme of this promising photoreactor principle is shown in figure 4. Porous silicon emits visible light, hence the use of nitrogen doped TiO₂ to shift the absorption to the visible region. Stability of this modified titania is, however, an issue to be evaluated more in detail [89,91]. Porous silicon/titania composite could be a promising system for other applications such as gas sensing, solar cells, and photoluminescent devices [92].
6. Conclusion

With the advancement in the processing technologies and characterization techniques, thin film science became one of the highly fruitful research areas. Thin films with desired features could be fabricated by using conventional methods such as CVD and PVD whereas sol-gel and CSD routes were found to be more practical. Thin films of nanocrystalline TiO₂ and porous silicon were proved good candidates for use in alternative energy, catalysis and optoelectronic devices. Due to the mineralising ability toward pollutants, TiO₂-coated fabrics could provide self-cleaning surfaces and TiO₂ thin films are used in wastewater treatment. By enhancing the dye impregnation and assisting in the transport of electrons, TiO₂ thin films could improve the efficiency of DSSC. TiO₂ thin film mediated photocatalytic and photoelectrochemical water splitting is a promising tool for the production of hydrogen as a clean fuel. Porous silicon on the other hand is widely contributing in the fabrication of electroluminescent devices, photonic crystals and gas and molecular biosensors. Nanocrystalline TiO₂-loaded porous silicon films are now emerging as a potential candidate in the field of photocatalysis, solar cells, and gas sensing.

References
[14] Fujishima A and Zhang X 2006 C.R. Chim. 9 750
[29] Tung W S and Daoud W A 2009 Acta Biomater. 5 50
[37] Liu B and Aydil S 2009 J. Am. Chem. Soc. 131 3985
[54] Zhou Bin, Schulz M, Lin H Y, Shah S I, Qu J and Huang C P 2009 Appl. Cat. B. Environ. 92 41
[59] Hyeok C, Elias S, Dionisios D and Dionysiou 2007 Desalination 202 199
[61] Neppolian B, Choi H C, Sakthivel S, Arabindoo B and Murugesan V 2002 *Chemosphere* 46 1173
[68] Uhlin A 1956 *Bell system tech.* 35 333.
[70] Imai K 1981 *Solid-State Electron.* 24 159
[76] Tadvani J and Falamaki C 2008 *Nanotechnology.* 19 295701
[77] Zhang X 2004 *J. Electrochem. Soc.* 151 C69