8-2009

SYNTHESIS AND POLYMORPHIC CONTROL FOR VISIBLE LIGHT ACTIVE TITANIA NANO PARTICLES

Sujaree Kaewgun
Clemson University, skaewgu@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_dissertations
Part of the Materials Science and Engineering Commons

Recommended Citation
https://tigerprints.clemson.edu/all_dissertations/389

This Dissertation is brought to you for free and open access by the Dissertations at TigerPrints. It has been accepted for inclusion in All Dissertations by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.
SYNTHESIS AND POLYMORPHIC CONTROL FOR VISIBLE LIGHT ACTIVE TITANIA NANOPARTICLES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Sujaree Kaewgun
August 2009

Accepted by:
Dr. James G. Goodwin, Jr., Committee Chair
Dr. Jian Luo
Dr. Igor Luzinov
Dr. Kathleen Richardson
Dr. Tzuen-Rong J. Tzeng
REMARKS

This dissertation entitled “Synthesis and Polymorphic Control for Visible Light Active Titania Nanoparticles” was written by Sujaree Kaewgun under the guidance and supervision of Burtrand I. Lee who was the candidate’s Committee Chair, advisor, research director, and mentor until December 31, 2008.

Sujaree Kaewgun
June 2, 2009

Dr. Burtrand I. Lee
Professor Emeritus
June 2, 2009
ABSTRACT

Titania (TiO$_2$) is useful for many applications in photocatalysis, antimicrobials, pigment, deodorization, and decomposition of harmful organics and undesirable compounds in the air and waste water under UV irradiation. Among the three phases of TiO$_2$, Rutile, Anatase, and Brookite, studies have been more focused on the anatase and rutile phases.

Pure brookite is the most difficult phase to prepare, even under hydrothermal conditions. Predominantly brookite phase TiO$_2$ nanoparticles were prepared by the Water-based Ambient Condition Sol (WACS) process in our laboratory. The objectives of this research were to enhance visible light active (VLA) photocatalytic properties of polymorphic brookite TiO$_2$ by minimizing the lattice defects and narrowing band gap of titania by nitrogen and/or carbon chromophore, and to investigate the deactivation, reusability, and regeneration of the VLA titania in order to design better titania catalysts for organic compound degradation applications.

In order to study the influence of hydroxyl content on photocatalytic activities (PCAs) of polymorphic titania nanoparticles, the WACS samples were post-treated by a Solvent-based Ambient Condition Sol (SACS) process in sec-butanol (sec-BuOH). All samples were characterized for phase composition, surface area, hydroxyl contamination, and particle morphology by x-ray diffraction, N$_2$ physisorption, FT-IR, solid state $^1$H NMR and scanning electron microscopy, and then compared to a commercial titania, Degussa P25. Evaluation of methyl orange (MO) degradation under UV irradiation results showed that the lower lattice hydroxyl content in SACS titania enhanced the PCA. As-prepared titania and SACS samples, which have similar surface areas and
crystallinity, were compared in order to prove that the superior PCA came from the reduction in the lattice hydroxyl content.

To enhance PCA and VLA properties of WACS, an alternative high boiling point polar solvent, N-methylpyrrolidone (NMP), was utilized in the SACS process at a higher treatment temperature to modify polymorphic titania nanoparticles. This SACS sample was called “SACS-NMP”. SACS, using NMP as the solvent, could also extract lattice hydroxyls, and decorate nitrogen on the titania surface. The PCA of SACS-NMP was superior to that of SACS-sec-BuOH. Nitrogen incorporation of SACS-NMP titania was investigated by CHN analysis and x-ray photoelectron spectroscopy (XPS). VL absorbance for all samples was characterized by UV-Vis absorption spectrophotometry. PCA of MO degradation under UV and VL showed that SACS-NMP is a powerful treatment to enhance PCA by minimizing lattice hydroxyls and doping the titania surface with nitrogen. The effect of calcination conditions on SACS-NMP samples was also studied. The calcination conditions, especially the temperature and calcination atmosphere, have an influence on the BET surface area, crystallite size, titania phase content, and PCA under VL irradiation. SACS-NMP samples calcined in air at 200°C for 2 hours showed the best VL activated photocatalytic performance in this research. Additionally, the SACS-NMP sample exhibited superior VL properties to several available reference anatase titania samples. This could be explained as the effective charge separation by the intercrystalline electron transport from brookite to anatase grains complemented by strong VL absorption by the nitrogen species in NMP.

The deactivation and regeneration of the VLA titania were investigated and compared to a commercial titania, Kronos VLP7000. PCA of the titania under VL for
MO decolorization gradually decreased with increasing testing time and the number of runs. The cause of the deactivation was identified as the deposition of the decomposed MO or the carbonaceous deposit. Among the possible regeneration procedures for used SACS-NMP samples, methanol washing was shown to be the most effective up to ~80% of the PCA recovery. Accordingly, the SACS-NMP samples could not be completely recovered since a regeneration process would possibly remove some of nitrogen species responsible for the VL properties.
DEDICATION

I would like to dedicate my dissertation to my beloved parents, Tanasorn and Jarunee Kaewgun, who made all of this possible through the endless words of encouragement and undoubted confidence in me.
ACKNOWLEDGMENTS

First, I would like to thank Dr. Burtrand I. Lee, my advisor and mentor, who gave me this opportunity to work on this project and also the research assistance position in Materials Science and Engineering. He also guided me through hurdles, and provided constant support to achieve my goal. He would always give very good comments and discuss with me on every obstacles during 3 years of this research. I will be forever grateful to him for his incredible support, encouragement and guidance in conducting my research. He spent a lot of time to review and revise research papers. Without his expert guidance, this project could not have been completed.

Special thanks extended to Dr. James G. Goodwin, my another advisor, who always supported me and helped me a lot. Although his schedule was very busy, he could find the time to help me reviewing the dissertation and giving me very useful comments. I wouldn’t be able to achieve the degree without his support.

I would also like to acknowledge my committee members: Dr. Jian Luo, Dr. Igor Luzinov, Dr. Kathleen Richardson, and Dr. Tzuen-Rong J. Tzeng for their assistance and recommendations and for reviewing my dissertation. Moreover, I would like to thank Dr. David Bruce for his permission for the use of his laboratory facilities. My thanks also go to the numerous individuals in MS&E Department and Clemson Thai Association, for making Clemson to be the place in my memory forever. I gratefully acknowledge Kimberly A. Ivey, Greg, and David White, MS&E for all technical supports, Don, chemistry department, for all recommendations on XRD. I’d like to thank EM lab for helping on SEM, TEM, and XPS.
I appreciate Dr. Lee’s research group members Chris, Hiroki, and Radhika for their friendship and suggestions. Especially Chris, who spent a lot of time on reviewing my papers and my thesis. I also thank Donna, Rupal, and Dr. Tzeng for their collaboration on antibacterial property tests. I extend my thanks to my friends in USA and my beloved friends and family in Thailand for their love and support. I would also like to extend my special thanks to my boyfriend, Pongnarin, for his support, suggestions, comments, time, and inspiration, which have enlightened and entertained me throughout this journey.

Additionally, I’d like to thank my Master’s advisor, Dr. Joongjai Panpranot, at Chulalongkorn university for her time, support, kindness, comments, and she also gave me very good opportunity to come to Clemson.

Finally, I gratefully acknowledge financial supports from the Petroleum Research Fund of American Chemical Society.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>REMARKS</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Crystal formation of titanium dioxide (TiO₂)</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Applications of TiO₂</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Photocatalysis</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Photocatalysts</td>
<td>8</td>
</tr>
<tr>
<td>1.5 Catalyst deactivation and regeneration</td>
<td>9</td>
</tr>
<tr>
<td>1.6 Research objectives</td>
<td>12</td>
</tr>
<tr>
<td>1.7 References</td>
<td>13</td>
</tr>
<tr>
<td>2. LITERATURE REVIEW</td>
<td>17</td>
</tr>
<tr>
<td>2.1 Minimizing the lattice defects on TiO₂ by solvothermal treatment</td>
<td>17</td>
</tr>
<tr>
<td>2.2 Producing visible light active TiO₂ by Doping</td>
<td>18</td>
</tr>
<tr>
<td>2.3 Deactivation and regeneration of TiO₂</td>
<td>21</td>
</tr>
<tr>
<td>2.4 Related work done in our research group</td>
<td>22</td>
</tr>
<tr>
<td>2.5 References</td>
<td>24</td>
</tr>
</tbody>
</table>
## Table of Contents (Continued)

### 3. INFLUENCE OF HYDROXYL CONTENTS ON PHOTOCATALYTIC ACTIVITIES OF POLYMORPHIC BROOKITE TITANIA NANOPARTICLES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Introduction</td>
<td>29</td>
</tr>
<tr>
<td>3.2 Experimental</td>
<td>31</td>
</tr>
<tr>
<td>3.3 Results and discussion</td>
<td>37</td>
</tr>
<tr>
<td>3.4 Conclusions</td>
<td>49</td>
</tr>
<tr>
<td>3.5 References</td>
<td>49</td>
</tr>
</tbody>
</table>

### 4. ENHANCING PHOTOCATALYTIC ACTIVITY OF POLYMORPHIC BROOKITE TITANIA NANOPARTICLES BY NMP SOLVENT-BASED AMBIENT CONDITION PROCESS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>53</td>
</tr>
<tr>
<td>4.2 Experimental</td>
<td>55</td>
</tr>
<tr>
<td>4.3 Results and discussion</td>
<td>59</td>
</tr>
<tr>
<td>4.4 Conclusions</td>
<td>70</td>
</tr>
<tr>
<td>4.5 References</td>
<td>74</td>
</tr>
</tbody>
</table>

### 5. STUDY OF VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY ACHIEVED BY NMP SOLVENT TREATMENT OF POLYMORPHIC BROOKITE TITANIA

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>78</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>80</td>
</tr>
<tr>
<td>5.3 Results and discussion</td>
<td>83</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>91</td>
</tr>
<tr>
<td>5.5 References</td>
<td>94</td>
</tr>
</tbody>
</table>
6. VISIBLE LIGHT PHOTOCATALYTIC ACTIVITIES OF POLYMORPHIC BROOKITE TITANIA .......................................................... 96
   6.1 Introduction ............................................................................ 97
   6.2 Experimental .......................................................................... 97
   6.3 Results and discussion .......................................................... 100
   6.4 Conclusions ........................................................................... 106
   6.5 References ............................................................................. 107

7. DEACTIVATION AND REGENERATION OF VISIBLE LIGHT ACTIVE PREDOMINANTLY BROOKITE TITANIA NANOPARTICLES IN THE PHOTOCATALYTIC DEGRADATION OF ORGANIC DYE .......................... 109
   7.1 Introduction ............................................................................ 110
   7.2 Experimental .......................................................................... 111
   7.3 Results and discussion .......................................................... 113
   7.4 Conclusions ........................................................................... 128
   7.5 References ............................................................................. 129

8. SUMMARY AND RECOMMENDATIONS ........................................... 132
   8.1 Summary ................................................................................ 132
   8.2 Recommendations ................................................................... 136

APPENDICES ..................................................................................... 138
   A: EXPERIMENTAL VARIABLES EFFECT ON PHOTOCATALYTIC ACTIVITY .......................................................... 139
   B: TEM IMAGES OF TITANIA SAMPLES ........................................... 141
   C: VISIBLE LIGHT SPETRUM ......................................................... 143
      C.1 Light spectrum ..................................................................... 143
      C.2 Reference ........................................................................... 143
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>9</td>
</tr>
<tr>
<td>3.1</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>59</td>
</tr>
<tr>
<td>4.2</td>
<td>61</td>
</tr>
<tr>
<td>5.1</td>
<td>82</td>
</tr>
<tr>
<td>5.2</td>
<td>85</td>
</tr>
<tr>
<td>6.1</td>
<td>99</td>
</tr>
<tr>
<td>6.2</td>
<td>101</td>
</tr>
<tr>
<td>7.1</td>
<td>115</td>
</tr>
<tr>
<td>8.1</td>
<td>135</td>
</tr>
</tbody>
</table>

1.1 Band gap energies and corresponding radiation wavelengths required for the excitation of various semiconductors
3.1 Experimental conditions utilized to produce mixed phase titania and % titania phase content
3.2 The physical properties of prepared titania samples and the reference P25
4.1 Experimental conditions utilized to produce polymorphic titania and % titania phase content
4.2 The physical properties of prepared titania and the reference P25
5.1 Experimental conditions used to produce polymorphic titania and % content of titania phase
5.2 The physical properties of as-prepared titania and the reference P25
6.1 Experimental conditions utilized to produce all titania samples and % titania phase content
6.2 The physical properties of all titania samples
7.1 The physical properties of fresh and used TiO₂ samples and the reference VLP7000
8.1 The summary of physical and photocatalytic properties of the polymorphic titania samples compared to the available reference titania samples
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>4</td>
</tr>
<tr>
<td>1.4</td>
<td>5</td>
</tr>
<tr>
<td>1.5</td>
<td>7</td>
</tr>
<tr>
<td>1.6</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>23</td>
</tr>
<tr>
<td>3.1</td>
<td>36</td>
</tr>
<tr>
<td>3.2</td>
<td>38</td>
</tr>
<tr>
<td>3.3</td>
<td>43</td>
</tr>
<tr>
<td>3.4</td>
<td>45</td>
</tr>
<tr>
<td>3.5</td>
<td>47</td>
</tr>
<tr>
<td>3.6</td>
<td>48</td>
</tr>
</tbody>
</table>

1.1 The fundamental structure units of anatase (a) two edges are shared per octahedron forming a right-angled configuration, and (b) the 3\(^{rd}\) and 4\(^{th}\) edges are shared into and out of adjacent layers.

1.2 The fundamental structural units of rutile.

1.3 The fundamental structural units of brookite.

1.4 A possible condensation pathway for the titania nuclei rutile, anatase or brookite type nuclei starting from octahedral cations \([\text{TiO(OH)}_2]^2^+\) and \([\text{Ti(OH)}_2(\text{OH})_2]^{2^+}\).

1.5 Schematics of the electron-hole generation in a photocatalyst particle.

1.6 Solar radiation.

2.1 Experimental setup for the synthesis of predominantly brookite phase TiO\(_2\).

3.1 Synthesis diagram for (a) WACS polymorphic TiO\(_2\), and (b) Commercial TiO\(_2\).

3.2 The XRD patterns of the polymorphic titania samples calcined at 200\(^{\circ}\)C, uncalcined, and P25 in different treatments.

3.3 SEM micrographs of (a) WACS-200, (b) SACS1-200, (c) P25, and (d) P25-SACS-200.

3.4 (a) FT-IR spectra of WACS-200, SACS1-200, and SACS2-200; (b) deconvolution of the given FT-IR spectra; (c) ratio \((A_S/A_T)\) of absorbance by FT-IR spectra of surface hydroxyls \((A_S)\) or lattice hydroxyls \((A_L)\) to the reference peak \((A_T)\) at wavenumber 900 cm\(^{-1}\); and inset of Figure 4(c) showing FT-IR peak fitting for WACS-200.

3.5 Solid state \(^1\text{H}\) MAS NMR spectra of (a) WACS and (b) SACS1.

3.6 Methyl orange degradation under UV light irradiation of (a) uncalcined WACS and SACS samples compared to commercial P25 and treated P25 and (b) calcined WACS and SACS samples.
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>The XRD patterns of the prepared titania samples and P25. A=anatase, B=brookite, and R=rutile. ..........................................................60</td>
</tr>
<tr>
<td>4.2</td>
<td>The effect of calcination temperature for SACS samples on BET surface area and nitrogen content. .................................................................63</td>
</tr>
<tr>
<td>4.3</td>
<td>TEM micrographs of (a) WACS-200, (b) SACS, (c) SACS-200, (d) SACS-300, (e) SACS-400, and (f) SACS-500.........................................................64</td>
</tr>
<tr>
<td>4.4</td>
<td>UV/Vis spectra of as-prepared SACS samples; Inset shows UV/Vis spectra of WACS-200 and P25..............................................................67</td>
</tr>
<tr>
<td>4.5</td>
<td>(a) FT-IR spectra using ATR of the prepared titania samples; (b) deconvolution of the FT-IR spectra; (c) ratio ($A_S/A_T$) of absorbance by FI-IR spectra of surface hydroxyls ($A_S$) or lattice hydroxyls ($A_L$) to the reference peak ($A_T$) at wavenumber 900 cm$^{-1}$; and inset of Figure 5(c) shows FT-IR fitting result of WACS-200.................................71</td>
</tr>
<tr>
<td>4.6</td>
<td>Methyl orange degradation under UV light of (a) uncalcined and calcined WACS and SACS samples compared to commercial P25 and (b) SACS samples calcined at vary temperature........................................73</td>
</tr>
<tr>
<td>4.7</td>
<td>Methyl orange degradation under VL irradiation of SACS-200, WACS-200 and P25..............................................................................74</td>
</tr>
<tr>
<td>5.1</td>
<td>The XRD patterns of the prepared titania samples and P25 (A=anatase, B=brookite, and R=rutile).................................................................84</td>
</tr>
<tr>
<td>5.2</td>
<td>The effect of calcination temperature and time for SACS samples on BET surface area...........................................................................86</td>
</tr>
<tr>
<td>5.3</td>
<td>The effect of calcination temperature for SACS samples on (a) nitrogen content, and (b) carbon and hydrogen content. .......................88</td>
</tr>
<tr>
<td>5.4</td>
<td>UV/Vis spectra of as-prepared SACS samples.................................................................89</td>
</tr>
<tr>
<td>5.5</td>
<td>N 1s XPS spectra of (a) SACS-200/2/A, and (b) SACS-200/2/N. ...................................................................................................................92</td>
</tr>
<tr>
<td>5.6</td>
<td>MO degradation under VL irradiation of (a) SACS samples calcined in air compared to WACS-200 and commercial P25, and (b) uncalcined SACS and SACS samples calcined in nitrogen. ........93</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>High resolution TEM of polymorphic brookite titania (PBT) particles showing well crystallized grains.</td>
<td>100</td>
</tr>
<tr>
<td>6.2</td>
<td>UV/Vis spectra of all titania samples compared.</td>
<td>102</td>
</tr>
<tr>
<td>6.3</td>
<td>Methyl orange degradation under VL irradiation of all titania samples compared.</td>
<td>103</td>
</tr>
<tr>
<td>6.4</td>
<td>Proposed electron transport mechanism of the enhanced VLA in PTB-SACS crystals.</td>
<td>104</td>
</tr>
<tr>
<td>6.5</td>
<td>Hydrogen evolution from water by titania samples tested under VL.</td>
<td>107</td>
</tr>
<tr>
<td>7.1</td>
<td>The XRD patterns of the prepared titania samples and VLP7000 (A=anatase, B=brookite, and R=rutile).</td>
<td>114</td>
</tr>
<tr>
<td>7.2</td>
<td>UV/Vis spectra of (a) fresh titania samples, and (b) fresh and used WACS samples.</td>
<td>116</td>
</tr>
<tr>
<td>7.3</td>
<td>The stabilities, determined by the MO degradation, of (a) WACS-200 under UV irradiation, (b) NMP-200 under UV irradiation, (c) NMP-200 under VL irradiation, (d) VLP7000 under VL irradiation, and inset of (d) showing the first reaction cycle of MO degradation under VL exposure of NMP-200 and VLP7000.</td>
<td>120</td>
</tr>
<tr>
<td>7.4</td>
<td>FT-IR spectra of (a) fresh and used WACS-200 samples, inset of (a) showing that of MO, and (b) fresh and used NMP-200 samples.</td>
<td>123</td>
</tr>
<tr>
<td>7.5</td>
<td>Percent of weight loss, calculated from TGA at temperatures between 425°C and 800°C.</td>
<td>124</td>
</tr>
<tr>
<td>7.6</td>
<td>C 1s XPS spectrum of (a) NMP-200, and (b) NMP-200-VL#1.</td>
<td>124</td>
</tr>
<tr>
<td>7.7</td>
<td>The regeneration of NMP-200-VL#1, evaluated by the MO degradation under VL irradiation, by (a) washing, and (b) recalcination.</td>
<td>127</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>Effect of VL intensity on the photocatalytic activity of SACS-NMP sample calcined at 200°C for 2 hours in air (NMP-200).</td>
<td>139</td>
</tr>
<tr>
<td>A.2</td>
<td>Effect of WACS-200 sample loading on the photocatalytic activity under UV exposure.</td>
<td>139</td>
</tr>
<tr>
<td>A.3</td>
<td>Effect of NMP-200 sample loading on the photocatalytic activity under UV exposure.</td>
<td>140</td>
</tr>
<tr>
<td>A.4</td>
<td>Effect of NMP-200 sample loading on the photocatalytic activity under VL (14Watts) exposure.</td>
<td>140</td>
</tr>
<tr>
<td>B.1</td>
<td>TEM images of (a) fresh NMP-200, (b) NMP-200-UV#1, (c) NMP-200-VL#1, and (d) WACS-200-UV#1.</td>
<td>141</td>
</tr>
<tr>
<td>C.1</td>
<td>Light spectrum of a fluorescent lamp and a halogen lamp.</td>
<td>143</td>
</tr>
</tbody>
</table>
CHAPTER ONE
INTRODUCTION

1.1 Crystal formation of titanium dioxide (TiO$_2$)

Titanium (IV) dioxide (TiO$_2$) or titania, which can exist in both crystalline and amorphous forms, is a white powder. The amorphous TiO$_2$ is not photocatalytically active [1, 2]. There are three crystalline TiO$_2$ polymorphs: anatase, rutile, and brookite. They all have similar chemical properties and similar band gap energies (≈3.1 ± 0.1 eV), but different crystalline structures. Anatase and rutile are tetragonal while brookite is orthorhombic [2-10]. All of the three polymorphs consist of (TiO$_6^{2-}$) octahedra, but each of them shares edges and corners in different manners. The fundamental structural units of anatase, rutile, and brookite are shown in Figures 1.1 [2, 4, 10], 1.2 [2, 4, 10], and 1.3 [11, 12], respectively. Anatase has four edges shared per octahedron, without shared corner oxygen atoms. The anatase structure looks like zigzag chains of octahedra, linked to each other through shared edges. Rutile has two opposite edges of each octahedron shared, which forms a linear chain along the (001) direction. The linear chains are then joined to each other by sharing corner oxygen atoms. Even though, anatase has more edge sharing, the interstitial spaces between octahedra are larger than rutile. Therefore, anatase is less dense than rutile (the densities of anatase and rutile are 3.84 and 4.26 g cm$^{-3}$, respectively) [4]. Brookite TiO$_2$ structure has octahedral linkages with three edges shared per octahedron [11, 12].

Various methods have been developed to synthesize TiO$_2$. These include flame synthesis [13], oxidation of titanium trichloride (TiCl$_3$) [14], thermolysis of titanium...
tetrachloride (TiCl₄) [8], hydrolysis of TiCl₄ [15, 16], hydrothermal synthesis of TiCl₄ [10], sol-gel with titanium isopropoxide [4, 17], and solvothermal synthesis [18]. In aqueous TiCl₄ solution, a possible titania formation pathway is given in Figure 1.4 [10]:

(a) At room temperature, TiCl₄ solution contains a number of [Ti(OH)₂(OH₂)₄]²⁺ monomers. As the TiCl₄ concentration increases, the Ti(IV) species exist in the form of [TiO(OH)₅]²⁺. (b) As the temperature increases to the reaction temperature, the solution is saturated. The species in the solution are unstable and combine together througholation or oxolation to form nuclei. Later, these nuclei grow to reach the critical nuclei size and become stable. The [Ti(OH)₂(OH₂)₄]²⁺ monomers can form different structures of polymers by sharing equatorial or apical edges during the formation of original nuclei, while the [TiO(OH)₅]²⁺ monomers can only form linear chain polymers by sharing equatorial edges. Anatase nuclei can be created from skewed chains, whereas rutile nuclei can be formed from linear chains. Essentially, nuclei grow to anatase first and then to rutile crystallites. Anatase crystallites are able to continuously grow and become unstable compared to the rutile phase. Thus, rutile TiO₂ is more thermodynamically stable than the anatase phase [10, 19]. There are few studies on brookite TiO₂ due to the difficulty to prepare pure brookite. Mixtures of anatase and brookite titania with predominantly more anatase were synthesized by a low temperature sol-gel technique [20] or precipitation [12]. The publications from our group [21-27] reported that by utilizing a process called water-based ambient condition sol (WACS), mixed phase but predominantly brookite nanoparticles are produced. The WACS process will be explained in the literature review section.
Figure 1.1 The fundamental structure units of anatase (a) two edges are shared per octahedron forming a right-angled configuration, and (b) the 3\textsuperscript{rd} and 4\textsuperscript{th} edges are shared into and out of adjacent layers.
Figure 1.2 The fundamental structural units of rutile.

Figure 1.3 The fundamental structural units of brookite.
**Figure 1.4** A possible condensation pathway for the titania nuclei rutile, anatase or brookite type nuclei starting from octahedral cations $[\text{TiO(OH}_2)_3]^{2+}$ and $[\text{Ti(OH}_2($OH$_2$)$_4$]^{2+}$ [10].
1.2 Applications of TiO₂

TiO₂ is the best known photocatalyst and is widely-used for commercial applications such as an antimicrobial agent, water/air purification, deodorizing, pigment, and decomposition of most organic compounds under ultraviolet (UV) irradiation [6, 28-41]. One widely referenced example is Degussa Aeroxide TiO₂ P25 [42] which consists of 79% anatase and 21% rutile. Many studies of titania have been conducted, especially for the anatase and rutile phases of TiO₂. Anatase TiO₂ has been reported as more photocatalytically active than rutile under UV [6, 28, 29, 31, 32, 35, 38-41, 43-45]. Nevertheless, rutile phase is most widely used as a white pigment in paint, paper, rubber, plastics and cosmetics because of its high refractive index, tinting strength, and inert chemical properties [10]. Brookite phase is currently not commercially available and its photocatalytic properties have not been widely studied.

1.3 Photocatalysis

The photocatalytic reaction is initiated when TiO₂ semiconductors are exposed to UV light and absorb energy equal to or more than their band gap. Electrons (e⁻) are promoted from the valence band to the conduction band. When this happens, the absence of an electron in the valence band creates a positively charged hole (h⁺) as shown in equation (1.1) and the reaction diagram shown in Figure 1.5.

$$TiO₂ \xrightarrow{hv} e^- + h^+$$ (1.1)

Super oxide anions (O₂⁻) and hydroxyl free radicals (•OH) are then produced in contact with from oxygen and water, respectively via a redox reaction on the TiO₂ surface. •OH reacts with volatile organic compounds (VOCs), and the organic matter
eventually decomposes and ultimately becomes carbon dioxide and water. Meanwhile, \( \text{O}_2^- \) attaches to the intermediate product in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water \([3]\). The reduction of \( \text{H}^+ \) can lead to hydrogen generation. On the other hand, there is a competing electron and hole recombination step which reverts back to the initial state and results in process inefficiencies and energy waste supplied by the photon \([46, 47]\).

**Figure 1.5** Schematics of the electron-hole generation in a photocatalyst particle \([21]\)

Titania is activated by UV in the sun light for photocatalytic reaction; nonetheless, UV is only 6% of sunlight. Visible light, defined as wavelengths \(~400-700\) nm, is the major fraction (about 50%) of solar radiation (Figure 1.6), and the remaining is infrared radiation. The band gap of titania is approximately \(3.1 \pm 0.1\) eV which can absorb wavelengths shorter than 388 nm, obviously out of the visible light region. For efficient utilization of solar energy or visible light (VL) by titania photocatalysts, narrowing its band gap is required. Many researchers have studied visible light active
(VLA) anatase and rutile titania doped with transition metals such as Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Os$^{3+}$, Re$^{5+}$, V$^{4+}$, and Rh$^{3+}$ or non-metals such as N, C, F, P, or S to narrow its band gap. Few studies of visible light active polymorphic doped titania with predominantly the brookite phase have been carried out [45, 48].

![Figure 1.6 Solar radiation (http://www.greenmillennium.com/)](image)

**Figure 1.6** Solar radiation (http://www.greenmillennium.com/)

### 1.4 Photocatalysts

A photocatalyst is defined as a substance that is activated by the absorption of energy from light equal to or more than its band gap energy, without being consumed [46]. Many factors that influence the photocatalytic properties are morphology and crystal structure, surface area, particle size, surface charge, light absorption properties, and resistance to mechanical stresses [32]. Metal oxide semiconductors are the most suitable photocatalysts because they are photostable in water [49]. The band gap energies
and corresponding radiation wavelengths required for the excitation of various semiconductors are given in Table 1.1.

**Table 1.1** Band gap energies and corresponding radiation wavelengths required for the excitation of various semiconductors [46]

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band gap energy (eV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (rutile)</td>
<td>3.0</td>
<td>413</td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
<td>335</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
<td>516</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.3</td>
<td>539</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>2.8</td>
<td>443</td>
</tr>
</tbody>
</table>

TiO$_2$ is the most UV active photocatalyst, followed by ZnO, since TiO$_2$ is highly stable chemically, and highly oxidizing. Other metal oxides, such as ZrO$_2$, SnO$_2$, WO$_2$, and MoO$_3$ are much less active and do not have the same application prospects as TiO$_2$ [46]. In addition, TiO$_2$ is relatively inexpensive compared to others.

### 1.5 Catalyst deactivation and regeneration

A catalyst is a substance which accelerates the chemical reaction rate and is regenerated in the reaction. It means that the catalyst should not be changed in the
reaction process; however, almost all catalysts deactivate or lose activity in any catalytic processes [50].

1.5.1 Causes and mechanisms of deactivation

The catalyst degradation can be caused by many reasons. These can be basically grouped into five mechanisms: (1) poisoning, (2) fouling or coking, (3) thermal degradation, (4) loss of catalytic phases by vapor compound formation and transport, and (5) attrition. Moreover, all mechanisms can be categorized for three main types: chemical [(1) and (4)], mechanical {(2) and (5)}, and thermal (3). In this research, a photocatalytic reaction was operated at room temperature in liquid phase. Therefore, only poisoning and/or fouling/coking are possible causes of deactivation.

Poisoning is the strong chemisorption of reactants, products, or impurities on catalytic sites. Species which act as poisoning species depend upon their adsorption strength relative to other species competing for catalytic sites. The mechanism of poisoning can be illustrated in the following steps. First, the strongly adsorbed poison physically blocks adsorption or reaction sites on the catalyst surface. Second, it modifies the abilities to adsorb and/or dissociate reactant molecules of nearest and next nearest neighbor sites. Third, the strongly adsorbed poison restructures the surface which possibly causes changes in catalytic properties. Fourth, the adsorbed poison blocks of adsorbed reactants to each other. Finally, it prevents the surface diffusion of adsorbed reactants.

Fouling, coking, and carbon deposition are the physical deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores. Possible effects of carbon deposition are being: (1)
strongly chemisorbing as a monolayer or physically adsorbing in multilayers and blocking access of reactants to catalyst surface sites, (2) totally encapsulating an active site and completely deactivating that site, (3) blocking micro and mesopores so that reactants cannot get into these pores, and (4) in extreme cases, building up in pores, and then stressing and fracturing the support material, causing disintegration of the catalyst.

Carbon is a product of CO disproportionation while coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces. Moreover, coke forms may vary from primarily carbon to high molecular weight hydrocarbons, depending upon the forming conditions.

1.5.2 Regeneration of deactivated catalysts

The catalyst regeneration ability relies on the reversibility of the deactivation process. Some poisons can be removed by chemical washing, heat treatments, or oxidation. Carbon, coke formation, and carbonaceous deposition are relatively easily removed by gasification with hydrogen, water, or oxygen. The temperature required for the gasification at a reasonable rate varies with the type of gas, the catalyst activity, and the structure of the carbon or coke. Since carbon removal with oxygen is very rapid at moderate temperatures (e.g. 400-600°C), industrial processes typically regenerate in air catalysts with carbon or coke deposited. Nevertheless, the generation in air can result in further catalyst deactivation by hot spots or over-temperatures.
1.6 Research objectives

Every photocatalytic application desires enhancements of photocatalytic activity. One avenue to accomplish this is by the generation of visible light active titania. The objectives of this research were as follows:

1) To minimize the lattice defects of titania, specifically caused by entrapped OH, by extracting OH from the titania lattice via solvothermal treatment or the SACS process. This process was proposed instead of calcination to expel the entrapped OH because of the desired high surface area. High temperature calcination would reduce the surface area, which results in reducing the catalytic activity. The negative effect of the lattice hydroxyls may be caused by the formation of Ti-OH as defects in the titania structure [51] or as sites for the recombination of e⁻-h⁺ [1, 52-55]. The mechanism will be discussed further in chapters 4, 5, and 6.

2) To narrow the band gap of titania by doping non-metals and co-doping with transition metals into titania. The optimum dopant concentration, reaction and treatment conditions (time and temperature) were investigated.

3) To produce the most VLA photocatalyst by applying both SACS technique and doping. The optimum conditions for synthesizing VLA predominantly brookite titania were investigated.

4) To investigate the photocatalytic deactivation, reusability, and regeneration of VLA titania in order to design better titania catalysts for organic compound degradation applications.
1.7 References


[42] Degussa, AEROXIDE and AEROPEAL Titanium Dioxide as Photocatalyst, degussa technical information, 2005.


In 1985, Ohtani et al. [1] first reported that brookite titania has the potential to be more photocatalytically active than anatase and rutile. However, very few studies on brookite titania have been done. Due to a lack of thorough investigations, the photocatalytic properties of predominantly brookite titania under both UV and Visible Light (VL) irradiation have much room for growth and better understanding.

2.1 Minimizing the lattice defects on TiO$_2$ by solvothermal treatment

Sato et al. [2] reported that solvothermal synthesis is an excellent technique to synthesize highly crystalline fine particles. Yin et al. [3] reported that solvothermal titania samples prepared with ethanol and methanol showed a much higher photocatalytic activity for hydrogen evolution (10:90 volume % methanol/water solution at 60$^\circ$C) than titania samples prepared by hydrothermal reactions followed by calcination. They explained this by a decreasing recombination rate of electrons and holes with an increasing degree of crystallinity or by a decreasing of the density of defects in titania [4, 5]. Another study showed that nitrogen-doped titania samples prepared by a homogenous precipitation-solvothermal process in methanol or ethanol solutions possessed a superior photocatalytic activity for nitrogen monoxide destruction than those prepared in an aqueous solution. Yin et al. [6] explained their results by a greater degree of crystallinity and by a higher specific surface area.
It is known that photocatalytic activity depends on both the specific surface area and lifetime of the photoinduced electron (e−) and hole (h+). Ohtani et al. [7] concluded that the recombination of photoinduced electrons and holes is fast in amorphous titania, since it contains a large number of defects which act as electron-hole recombination centers. There are two types of structural defects of particular interest: surface defects and bulk defects inside titania particles. Surface defects increase the photocatalytic activity because they can act as active sites for adsorption and dissociation of molecules on titania surface [8-11]. It is thought by most researchers [7, 9, 12-14] in the TiO2 photocatalysis field that the OH defects decrease the photocatalytic activity since these defects produce sites for the recombination of e− and h+.

2.2 Producing visible light active TiO2 by Doping

Several journal articles addressing doped titania have been published for visible light active photocatalytic applications; however only a few authors [2, 6] have studied doped brookite phase titania. In order to more efficiently utilize solar energy or visible light, narrowing the titania band gap is necessary. Doped titania has been reported to be an efficient way to extend the light adsorption from UV light to the visible light region since the substitution of the lattice oxygen with dopants such as N [15-25], C [26-29], F [30-33], or S [34] narrows the titania band gap. There are two approaches for modifying TiO2 by doping. The first approach is to substitute with metallic ions such as Cr, Fe, or Ni into Ti sites [35, 36]. The second approach is substitutional anionic species, N, C, S, F, or P doping. Asahi et al. [16] claimed that anionic doping is superior to cation metal doping since cation metals often give localized d states deep in the band gap of titania.
and produce recombination centers of $e^-$ and $h^+$. Therefore, non-metal doping was focused for the predominantly brookite titania.

Asahi et al. [16] reported that N-doped anatase titania showed higher photodegradation activities of methylene blue and gaseous acetaldehyde than undoped titania under visible light (wavelength < 500 nm). They accounted for the improvement by N-substitution into oxygen sites of titania. The substitutional N doping was the most effective among other non-metals doping since its $p$ states contribute to the band-gap narrowing by mixing with O 2$p$ states. Sulfur doping showed similar band gap narrowing; however, its large ionic radius creates difficulty in incorporating it into TiO$_2$ crystals. The substitution with S requires a much higher formation energy than the substitution with N. N-doped TiO$_2$ responds to visible light because of an N-induced midgap level introduced slightly above the (O-2$p$) valence band edge as determined by Nakamura et al. [21]. The authors concluded that N ions were substituted at oxygen sites in TiO$_2$ to narrow the titania band gap.

Recently, many studies have been reported on the preparation of nitrogen doped titania by using various techniques such as annealing under gaseous NH$_3$ flow [18, 19, 21, 37], sputtering TiO$_2$ with N$_2$ gas [16], using aqueous ammonia solution [22, 38], urea [17, 25], amine precursor solution [15, 24], or solvothermal treatment in an N-organic solvent [2, 6]. Irie et al. [18] studied the effect of nitrogen concentration on photocatalytic decomposition of 2-propanol (IPA) to CO$_2$ by N-doped TiO$_2$. TiO$_2$ alone under visible light did not generate CO$_2$ since undoped-TiO$_2$ is not visible light sensitive. As the nitrogen concentration was increased, a longer exposure to visible light was required to decompose IPA. It was explained that the oxygen sites are partially replaced
with nitrogen atoms while TiO$_2$ is simultaneously reduced, which causes an increase in oxygen vacancies. The oxygen vacancies promote the recombination of e$^-$ and h$^+$. Sakatani et al. [39] studied TiO$_2$ co-doped with a metal and N species which exhibited higher photocatalytic activity for acetaldehyde decomposition under visible light irradiation than N doped TiO$_2$. Another publication from this group [40] showed that La$^{3+}$ and N co-doped TiO$_2$ obtained by calcining the La$^{3+}$ doped precursor oxide under NH$_3$ rich atmosphere decomposed acetaldehyde under visible light. La$^{3+}$ doping improved the photocatalytic activity since it hindered the formation of Ti$^{3+}$, lattice defects and crystal growth. The number of the N species seemed to control the absorption of visible light and the activity under visible light irradiation.

Doped TiO$_2$ with other non-metals such as S, F, or C have been reported and have also shown improvement in photocatalytic activity. Ohno et al. [41] reported that S doped titania showed strong absorption for visible light and high activity for the degradation of methylene blue. The chemical states of S atoms incorporated into TiO$_2$, obtained from XPS, are S$^{6+}$ species which are probably responsible for the absorption in the visible light region. Umebayashi et al. [34] improved visible light activated degradation of methylene blue of anatase titania by sulfur doping. Carbon-doped anatase titania exhibited photocatalytic activity for trichloroacetic acid degradation under visible light irradiation compared with undoped titania [28]. Wang and Lewis [29] concluded that the substitutional carbon dopants incorporated into titania drastically affect its electronic structure, thus improving its photocatalytic activity. Ho et al. [30] reported that porous F-doped TiO$_2$ exhibited high visible light photocatalytic activity for the degradation of 4-chlorophenol. They demonstrated that the visible light active property
of the F-doping was probably due to the excitation of the extrinsic absorption bands by
oxygen vacancies rather than the excitation of the intrinsic absorption band of bulk TiO₂.

2.3 Deactivation and regeneration of TiO₂

Deactivation of TiO₂ is a serious problem in photocatalytic reactions, especially
liquid phase reactions, since it is able to severely reduce photocatalytic activity. It is
generally known that the presence of water in the photocatalytic reaction increases the
recombination of electrons-holes [42-44]. Phillips and Raupp [45] reported that water
and organic species adsorbed on TiO₂ surfaces possibly cause the reduction of
photocatalytic activity, i.e., the deactivation of photocatalysis. A study of deactivation
and regeneration for photocatalytic oxidation of toluene by mixed anatase and rutile TiO₂
was reported by Cao et al. [43]. They concluded that severe deactivation of TiO₂ is due
to the accumulation of partially oxidized intermediates, such as benzaldehyde and
benzoic acid, on active sites. For complete recovery of deactivated catalysts, the
regeneration requires a calcination temperature above 420°C in air, which may cause the
phase transformation of anatase to rutile and sintering of the TiO₂ nanoparticles.

TiO₂ deactivation during gas phase reaction has been widely studied [46-50].
Nonetheless, those studies were evaluated for only anatase and/or rutile phases.
Vorontsov et al. [50] reported that the drop in photocatalytic activity during gaseous
acetone oxidation at a temperature of approximately 100°C is due to an accumulation of
acetone partial oxidation products. For the photocatalytic oxidation of gas-phase toluene,
the accumulation of benzoic acid on the TiO₂ surface appears to be responsible for the
catalyst deactivation [49]. The gas-phase photocatalytic oxidation of dimethyl sulfide
was showed to cause the sulfur deposits on TiO$_2$ surface, along with a decrease in activity [47]. The deactivated catalyst could not recover with gas-phase treatments, indicating the irreversible nature of the deactivation.

The deactivation and regeneration of the visible light active polymorphic brookite titania, which was significantly more photocatalytically active than commercial anatase titania samples [51-53], have never been reported.

2.4 Related work done in our research group

In 2006, our group at Clemson University [54] first reported the synthesis of mixed phase with predominantly brookite titania nanoparticles by the ambient condition WACS. They controlled the anatase and rutile phases “impurities” in the brookite titania phase by using different acid concentrations, water to isopropanol ratio, temperature, and time. Bhave et al. [55] studied the experimental variables in the predominantly brookite titania synthesis. The WACS process diagram is given in chapter 3 (Figure 3.1(a)) using titanium tetrachloride (TiCl$_4$) in a 1:2 ratio of water-isopropanol system with hydrochloric acid under a refluxing condition at 83°C for 15 hours as described in our previous papers [54-56]. The experimental setup for the titania synthesis is shown in Figure 2.1. All TiO$_2$ powders were calcined in air at 200°C for 2 hours to drive off residual impurities while minimizing phase transformation. Nolph et al. [56] investigated the photocatalytic activity of the predominantly brookite titania under UV exposure compared to other titania phases. We have found superior photocatalytic properties of brookite relative to anatase and rutile phases. However, the photocatalytic activity of
predominantly brookite titania, even under visible light, has the potential to be improved by applying other treatment techniques.

Since our WACS process was carried out in a water system, undesired entrapped protons or lattice hydroxyls were in titania structure. The lattice hydroxyls could act as bulk defects which generated sites for the recombination of e⁻ and h⁺ [7, 9, 12-14]. A few studies done in our lab on BaTiO₃ applied a solvothermal treatment or SACS process to extract entrapped protons in the barium titanate lattice affecting the preferred tetragonal crystalline phase [57, 58]. Thus, SACS technique was introduced to the WACS process as post-treatment to minimize OH defects in TiO₂ at temperatures below 200°C.

**Figure 2.1** Experimental setup for the synthesis of predominantly brookite phase TiO₂ [59].


2.5 References


CHAPTER THREE

INFLUENCE OF HYDROXYL CONTENTS ON PHOTOCATALYTIC ACTIVITIES
OF POLYMORPHIC BROOKITE TITANIA NANOPARTICLES


Abstract

Polymorphic titania nanoparticles, prepared by a Water-based Ambient Condition Sol (WACS) process, were post-treated by a Solvent-based Ambient Condition Sol (SACS) process in sec-butanol. All samples were characterized for phase composition, surface area, hydroxyl contamination, and particle morphology by x-ray diffraction, N₂ physisorption, FT-IR, solid state Magic Angle Spinning (MAS) ¹H NMR and scanning electron microscopy. The results were compared to a commercial titania, Degussa P25. Evaluation of methyl orange degradation under UV irradiation results showed that the lower lattice hydroxyl content in SACS titania nanoparticles enhances photocatalytic activity. As-prepared titania and post-treated SACS samples, which have similar surface areas and crystallinity, were compared in order to prove that the superior photocatalytic activity came from a reduction in lattice hydroxyl content.

3.1 Introduction

Titania (TiO₂) is well known for many applications in photocatalysis, antimicrobials, pigment, water/air purification, deodorization, and decomposition of harmful organics and undesirable compounds in the air and in waste water under ultraviolet light (UV) irradiation [1-6]. One well known example is Degussa Aeroxide
TiO\textsubscript{2} P25 (P25) [7] which consists of 79\% anatase 21\% rutile. Three TiO\textsubscript{2} polymorphs which have similar chemical properties, but different crystalline structures are anatase, rutile and brookite. Anatase and rutile have a tetragonal structure [3], whereas brookite is orthorhombic [8]. Anatase TiO\textsubscript{2} is the major product of industrial manufacturing and has been reported as the most photocatalytically active under UV [2, 3, 6]. At ambient conditions, rutile TiO\textsubscript{2} is the most thermodynamically stable phase. Anatase and rutile are more commonly studied than brookite. Pure brookite is the most difficult phase to prepare, even under hydrothermal conditions. Polymorphic TiO\textsubscript{2} nanoparticles were prepared by a Water-based Ambient Condition Sol (WACS) process in our laboratory [8-10]. In WACS process, titanium tetrachloride was used as the precursor in a water-isopropanol solution in the presence of a certain amount of hydrochloric acid under refluxing condition. In photocatalysis, when titania is exposed to UV light and absorbs energy equal to or greater than its band gap of approximately 3.2 eV, electrons (e\textsuperscript{−}) are jumped from the valence band to the conduction band and positive holes (h\textsuperscript{+}) are created in the valence band. Super oxides anions (O\textsubscript{2}\textsuperscript{−}) and hydroxyl free radicals (\textbullet OH) are produced via redox reaction of water on titania surface. These powerful oxidizing and reducing agents will then disintegrate and rearrange the Volatile Organic Compounds (VOCs) structure [2].

Sato et al. [11] reported that solvothermal synthesis is an excellent technique to synthesize high crystalline anatase, rutile, and brookite titania depending on the reaction conditions. Yin et al. [12] studied the photocatalytic activity of anatase titania prepared from protonic layered tetratitanate in supercritical alcohols. They reported that the solvothermal titania samples prepared with ethanol and methanol showed a much higher
photocatalytic activity for hydrogen evolution than titania samples prepared by hydrothermal reactions followed by calcination. They accounted for the results by a decreasing recombination rate of electrons and holes with an increasing degree of crystallinity in titania [13, 14]. Yin et al. [15] showed that nitrogen-doped titania samples prepared by a homogenous precipitation-solvothermal process in methanol or ethanol solutions showed a superior photocatalytic activity under visible light and UV light for nitrogen monoxide destruction than those prepared in an aqueous solution. The results were explained by a greater degree of crystallinity of the structure, and by a higher specific surface area.

A solvothermal treatment developed in our lab [16] was used to study the effect of lattice hydroxyls and entrapped protons on the photocatalytic activities of titania. In this paper, we focused on the degree of hydroxylation rather than the degree of crystallinity for photocatalytic activity. We minimized the hydroxyl contents in WACS sample via a Solvent-based Ambient Condition Sol (SACS) process. The physical characteristics and photocatalytic activities of WACS and SACS were compared with a commercial reference, Degussa P25. The photocatalytic activities were evaluated by the photocatalytic degradation of methyl orange under UV irradiation.

3.2 Experimental

3.2.1 Catalyst synthesis

Polymorphic TiO$_2$ nanoparticles were prepared by WACS process as shown in Figure 3.1(a) using titanium tetrachloride (TiCl$_4$ – Reagent grade obtained from Aldrich Chemical) in a 1:2 ratio of water-isopropanol system with 0.3 M hydrochloric acid under
refluxing condition at 83°C for 15 hours as described in our previous papers [8-10]. The SACS techniques developed by our research group [16] have been used as a post-treatment of particles produced by WACS process. This solvothermal treatment was carried out in sec-butanol at 100 and 165°C for 4 hours in a sealed Teflon container. The nomenclature of titania samples are shown in Table 3.1. The process of preparing the commercial reference Degussa P25 is shown in Figure 3.1(b) for a comparison [7]. All TiO₂ powders were calcined in air at 200°C for 2 hours before further examination.

3.2.2 Catalyst Characterization

The phase composition and crystallite size of the TiO₂ samples were determined by using an X-Ray Diffractometer (XRD), XDS 2000, Scintag PAD V utilizing CuKα radiation at 1.5406 Å, accurately measured with a step size of 0.020° over a range of 20 to 35°, 2θ angular region. The phase composition of titania was calculated from the following equations [17]:

\[ W_A = \frac{k_A A_A}{k_A A_A + A_R + k_B A_B}, \]  
\[ W_B = \frac{k_B A_B}{k_A A_A + A_R + k_B A_B}, \]  
\[ W_R = \frac{A_R}{k_A A_A + A_R + k_B A_B}, \]

where \( W_A, W_B, \) and \( W_R \) represent the weight fractions of the anatase, brookite, and rutile phases, respectively; \( A_A, A_B, \) and \( A_R \) are integrated intensities of the anatase (101) peak, brookite (121) peak, and rutile (110) peak, respectively; \( k_A \) is 0.886 and \( k_B \) is 2.721 [17]. Anatase (101) and brookite (120) overlap peaks were de-convoluted by using 0.9 intensity ratio of \( I^{(121)}_{\text{brookite}}/I^{(120)}_{\text{brookite}} \) [18, 19]. The crystallite size was calculated from
the full-width half-height of the diffraction peaks using the Scherrer equation (Equation 4) where λ is X-ray wavelength, 1.5418 Å for CuKα and β is the full-width half-height of the peak of interest: (121) for brookite, (110) for anatase and (101) for rutile.

\[
t = \frac{0.9 \cdot \lambda}{\beta \cdot \cos(\theta)}
\] (4)

The BET surface area, pore volume, average pore diameter, and pore size distribution of TiO₂ were determined by N₂ physisorption at -196°C using a Micromeritics ASAP 2020 automated system. Each sample was degassed at 200°C for 3 hours prior to N₂ physisorption. TiO₂ particle size was observed using SEM micrographs obtained from a Hitachi’s HD-2000 with an accelerating voltage of 200.0 kV.

The vibrational bands for total water and OH groups were observed by Fourier-Transform Infrared Spectroscopy (FT-IR). IR spectra were recorded by using Thermo-Nicolet Magna model 550 FT-IR spectrometer equipped with a Thermo-Spectra Tech foundation series diamond Attenuated Total Reflection (ATR) accessory using DTGS KBr as detector and Ever-Glo mid IR source. Absorption bands were observed from 4000 cm⁻¹ to 525 cm⁻¹ with 32 sample scans and 4.0 cm⁻¹ resolution. Diamond was used as the background spectrum. ATR spectral results can be affected by several factors, such as the wavelength of infrared radiation, refractive index, and depth of penetration. To confirm that the ATR is valid for the semiquantitative analysis of hydroxyls, the FT-IR spectra were also obtained by using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. In DRIFT, titania powders were ground and mixed with KBr, background reference, (10% by weight) to increase the proportion of the infrared beam that is reflected by titania. Prior to DRIFT operation, the samples were purged in N₂ for 15 minutes. FT-IR spectra were collected from 4000 cm⁻¹ to 525 cm⁻¹ with 256 sample
scans and with 4.0 cm\(^{-1}\) resolution. Semiquantitative analysis of the hydroxyls was carried out by taking the peak ratios of the absorption bands for hydroxyls and that of titania following our previous work for barium titanate [16, 20-22]. The deconvolution of FT-IR spectra as given in Figure 4(b) was achieved by using “fityk 0.7.4” curve fitting program (GNU General Public License, version 2, as published by the free software foundation).

Solid state \(^1\)H MAS NMR measurements, used to distinguish and analyze the amount of surface hydroxyls and lattice hydroxyls, were carried out using a Chemagnetics spectrometer (7.05 T, 300 MHz) equipped with a variable temperature double-resonance probe. Samples were loaded into 5-mm Zirconia PENCIL™ rotors and spun at 6-10 kHz. Single-pulse (SP) Bloch-decay spectra were collected with a 5.0-\(\mu\)s (90°) \(^1\)H pulse, a spectral width of 50 kHz, and a repetition delay of 10 seconds. \(^1\)H NMR chemical shifts were referenced to tetrakis(trimethylsilyl)silane at 0 ppm.

3.2.3 Photocatalytic Activity Test

The photocatalytic activities were evaluated by the photocatalytic degradation of Methyl Orange (MO) under UV irradiation. The reaction was performed using 0.1 g of the titania powder added to 100 ml of 20 \(\mu\)M MO solution. Prior to the reaction, the suspension and solution were stirred for 30 minutes without UV exposure and continuously stirred throughout the reaction. The UV light source used was a Spectroline black light lamp (Model BIB-150B operating at 365 nm and 182 W) which was suspended 36 cm above the MO solution. A constant sample amount was taken at constant time increments, then separated by vacuum filtration (Whatman Anodisc 47 mm discs with 0.02 \(\mu\)m pores) to remove all titania powders from the solution to prevent
scattering. The quantitative spectral results at each time increment of MO were monitored by a UNICAM UV/vis spectrometer (Model: 5625). The MO degradation percent value, D, was calculated by Equation 5 at a chosen constant wavelength of 490 nm where \( A_0 \) is the initial 490 nm absorbance peak intensity, and \( A \) is the instantaneous 490 nm peak intensity.

\[
D = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\%
\]  

(5)

**Table 3.1** Experimental Conditions utilized to produce mixed phase titania and % titania phase content.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% Content of TiO(_2) Phase (wt%)(^a)</th>
<th>Mode of Formation</th>
<th>Preparation or Post-treated Temperature (°C)</th>
<th>Preparation or Post-treated Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WACS</td>
<td>48 An, 50 Br, 2 Ru</td>
<td>WACS</td>
<td>83</td>
<td>15</td>
</tr>
<tr>
<td>WACS-200</td>
<td>45 An, 53 Br, 2 Ru</td>
<td>Calcination of WACS</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS1</td>
<td>46 An, 51 Br, 3 Ru</td>
<td>SACS of WACS</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>SACS1-200</td>
<td>44 An, 54 Br, 2 Ru</td>
<td>Calcination of SACS1</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS2</td>
<td>47 An, 50 Br, 3 Ru</td>
<td>SACS of WACS</td>
<td>165</td>
<td>4</td>
</tr>
<tr>
<td>SACS2-200</td>
<td>41 An, 56 Br, 3 Ru</td>
<td>Calcination of SACS2</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>P25</td>
<td>79 An, - Br, 21 Ru</td>
<td>Obtained from Degussa</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>P25-200</td>
<td>79 An, - Br, 21 Ru</td>
<td>Calcination of P25</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>P25-SACS</td>
<td>79 An, - Br, 21 Ru</td>
<td>SACS of P25</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>P25-SACS-200</td>
<td>79 An, - Br, 21 Ru</td>
<td>Calcination of P25-SACS</td>
<td>200</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\)Obtained from XRD data by calculating from equation 1-3; An=Anatase, Br=Brookite, and Ru=Rutile.
Figure 3.1 Synthesis diagram for (a) WACS polymorphic TiO₂, and (b) Commercial TiO₂
3.3 Results and discussion

3.3.1 X-ray Diffraction

The x-ray diffraction patterns of TiO$_2$ particles for calcined and uncalcined TiO$_2$ powders are shown in Figure 3.2. The phases obtained were confirmed by comparison with the accepted standard peaks from JCPDS [18, 23, 24]. XRD peaks of the prepared titania samples were broadened due to the crystallite sizes that were considerably small (6-8 nm), as shown in Table 3.2 and SEM images [25]. The phase composition of TiO$_2$, calculated from XRD data, is shown in Table 3.1. The phase composition of uncalcined (WACS, SACS1, and SACS2) and calcined titania samples at 200°C for 2 hours (WACS-200, SACS1-200, and SACS2-200) were ~50-56% brookite, ~41-48% anatase, and a small amount of rutile (<3%). Therefore, calcination at 200°C for 2 hours did not introduce a greater portion of rutile in the structure. The crystallite sizes of anatase and brookite phases of as-prepared titania samples, calculated from the XRD data using the Scherrer equation as reported in Table 3.2, are approximately 6-8 nm which is ~ three times smaller than anatase phase crystallite size of P25. The as-prepared WACS and post-treatment SACS samples have similar crystallinity, which was determined by the sharpness or the full-width half-height of XRD peaks.

3.3.2 N$_2$ Physisorption

The results of BET surface area, pore volume, and average pore diameter analysis of titania samples are given in Table 3.2. The BET surface area of polymorphic titania samples was three times larger than that of P25 samples. The BET surface area of calcined titania samples was found to be ~4% less than that of the uncalcined samples for WACS and SACS because the titania nanoparticles were sintered during the heat
treatment. SACS2 and SACS2-200 samples exhibited ~5-10% greater BET surface area, pore volume, and average pore size than the WACS and WACS-200 powders. This is likely due to the extraction of water from WACS TiO$_2$ nanopores. Moreover, the BET surface area of SACS1 and SACS1-200 samples, which were post-treated at 65$^\circ$C less than the reaction temperature of SACS2 and SACS2-200, were ~10-17% greater than the SACS2 and SACS2-200 samples. Previous studies in other groups found that a lower solvothermal treatment temperature tends to result in particles with larger surface areas [26-28], likely due to a particle coarsening effect at elevated treatment temperatures.

![XRD patterns](image)

**Figure 3.2** The XRD patterns of the polymorphic titania samples calcined at 200$^\circ$C, uncalcined, and P25 in different treatments.
Table 3.2 The physical properties of prepared titania samples and the reference P25.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallite size (nm)(^a)</th>
<th>BET surface area (m²/g)(^b)</th>
<th>Pore Volume (cm³/g)(^b)</th>
<th>Pore size average (Å)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
<td>Rutile</td>
<td></td>
</tr>
<tr>
<td>WACS</td>
<td>6</td>
<td>8</td>
<td>19</td>
<td>163</td>
</tr>
<tr>
<td>WACS-200</td>
<td>6</td>
<td>7</td>
<td>18</td>
<td>157</td>
</tr>
<tr>
<td>SACS1</td>
<td>6</td>
<td>6</td>
<td>21</td>
<td>200</td>
</tr>
<tr>
<td>SACS1-200</td>
<td>6</td>
<td>8</td>
<td>18</td>
<td>189</td>
</tr>
<tr>
<td>SACS2</td>
<td>6</td>
<td>8</td>
<td>21</td>
<td>171</td>
</tr>
<tr>
<td>SACS2-200</td>
<td>6</td>
<td>8</td>
<td>16</td>
<td>173</td>
</tr>
<tr>
<td>P25</td>
<td>21</td>
<td>-</td>
<td>40</td>
<td>56</td>
</tr>
<tr>
<td>P25-200</td>
<td>33</td>
<td>-</td>
<td>82</td>
<td>57</td>
</tr>
<tr>
<td>P25-SACS-200</td>
<td>33</td>
<td>-</td>
<td>82</td>
<td>57</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from XRD data using the Scherrer equation (Equation 4). Error of measurement = ±5%.

\(^b\) Using N\(_2\) physisorption at -196°C. Error of measurement = ±10%.

3.3.3 Scanning Electron Microscopy

The average particle size of the as-prepared TiO\(_2\), as shown by SEM micrographs in Figure 3.3 (a-b) was in the range of 10-15 nm which is about 2.5 times smaller than P25 (Figure 3.3 (c)) and SACS-treated P25 samples (40 nm) (Figure 3.3 (d)). The average particle size of calcined titania samples was slightly larger than the uncalcined samples agreeing with the BET surface area data.

3.3.4 FT-IR spectra

The surface hydroxyls and lattice hydroxyls absorbance bands of WACS-200, SACS1-200, and SACS2-200, observed in FT-IR spectra, are shown in Figure 3.4(a). The deconvolution procedure resulted in 4 peaks, fitting results of the obtained spectra in
Figure 3.4(b), at 1625 cm\(^{-1}\), 2730 cm\(^{-1}\), 3130 cm\(^{-1}\), and 3400 cm\(^{-1}\). Distinct absorption bands can be found at wavenumbers of 3400-3500, and at 1625 cm\(^{-1}\), which can be attributed to \(\text{OH}\) stretching vibrations of hydrogen-bonded \(\text{OH}\) groups (lattice hydroxyls), and adsorbed molecular water absorption bands (surface hydroxyls), respectively [29-36]. The semiquantitative comparison of deconvoluted band intensities, as given in Figure 3.4(b), shows that WACS-200, relatively, has a larger lattice hydroxyl peak at 3400 cm\(^{-1}\) than SACS1-200 and SACS2-200. To investigate the amount of hydroxyls, the measured peak intensities of the hydroxyls were normalized with the band intensity of the Ti-O stretching band. Band intensity ratios (\(A_S/A_T\) and \(A_L/A_T\)) of the surface hydroxyl absorbance peak (\(A_S\)) at wavenumber 1625 cm\(^{-1}\) and a deconvoluted peak at 3400 cm\(^{-1}\), the lattice hydroxyl peak (\(A_L\)) to the reference peak for titania (\(A_T\)), at 900 cm\(^{-1}\), were calculated using the baseline method as outlined in the literature [16, 20-22].

FT-IR data analysis, given in Figure 3.4(c), showed that SACS1, SACS1-200 and SACS2-200 have fewer surface hydroxyls and ~40% less lattice hydroxyls than WACS and WACS-200; it follows that the solvothermal treatment (SACS1, SACS1-200 and SACS2-200) extracted the surface and lattice hydroxyls from the titania particles. The FT-IR peak fitting result of WACS-200 is given in the inset of Figure 3.4(c). The spectra obtained from DRIFT (spectra not given in this paper) were near identical to those from the ATR technique. SACS1-200 also showed the same trend, i.e., less lattice and surface hydroxyls than WACS-200.

3.3.5 Solid state \(^1\)H NMR

Solid state \(^1\)H NMR spectra are shown in Figure 3.5(a) and 3.5(b) for uncalcined WACS and SACS samples, respectively. WACS samples exhibited a single broad peak
centered at a chemical shift of $\delta = 7.0$ ppm, which is assigned to bridging OH groups or lattice hydroxyls. SACS1 sample displayed a broad resonance peak centered at 7.6 ppm, which is associated with the lattice hydroxyls, and a sharp peak at $\sim 1.4$ ppm, that is attributed to surface OH groups or water [16, 37, 38]. To determine the relative amount of lattice hydroxyls, the normalized integrated proton signals with respect to their sample weight for the resonance of lattice hydroxyls were calculated. The results showed that the relative lattice hydroxyl content of SACS1, 1.65, is $\sim 40\%$ less than WACS which is 2.82. Therefore, SACS1 has a significantly lower amount of lattice hydroxyls compared to WACS. These qualitative NMR results are supported with the semi-quantitative analysis of FT-IR in Figure 3.4 (C). As seen in Figure 3.1(a), the WACS process is water based and the resulting titania is expected to be contaminated with 'OH entrapped in the titania lattice which will result in cation defects in titania lattice as called “OH defects”. Hayashi and Torii demonstrated from FT-IR spectra that Ti-OH was formed via hydrothermal titania synthesis at low temperatures [39]. Hydrothermal synthesis can easily produce OH defects not only in TiO$_2$ but also in BaTiO$_3$ [40, 41]. The OH defects provide sites for the recombination of photoexcited electrons (e$^-$) and positive holes (h$^+$) [26, 42-45].

3.3.6 Methyl Orange Degradation

The photocatalytic activities of uncalcined and calcined prepared titania samples compared to P25 samples, determined by the MO degradation, are shown in Figure 3.6(a) and 3.6(b). A standard MO degradation percentage for comparison between samples was arbitrarily set at 80%. Degradation by uncalcined samples was significantly slower than those samples calcined at 200°C for 2 hours, due to the removal of surface hydroxyls
and/or organic residues in uncalcined samples. Uncalcined SACS (SACS1) exhibited ~36% superior MO degradation to WACS. The photocatalytic activities of the polymorphic titania samples are all higher than commercial P25 and post-treated P25 samples. The photocatalytic activity of P25-SACS-200 did not yield significant improvement over P25 or P25-200. Post-processing of P25 was expected to have little effect since the high temperature flame hydrolysis process, as shown in Figure 3.1(b), utilized to produce P25 should yield particles with no or little 'OH contamination.

Figure 3.6(b) shows that MO for SACS1-200 and SACS2-200 samples was degraded 15 minutes or 40% faster than that of WACS-200, since SACS1-200 and SACS2-200 have fewer hydroxyls in its lattice than in the WACS-200 sample. This is supported by data obtained from FTIR and $^1$H NMR analysis and the measured pore volume of the samples. It is known that the superior photocatalytic activity can come from greater surface area or higher crystallinity. Therefore, in this study, the samples (WACS-200 and SACS2-200), which do not have a significant difference in surface areas and have similar crystallinity, were compared. It can be concluded that the higher photocatalytic activities of calcined SACS samples are mainly caused by fewer lattice hydroxyls. The negative effect of the lattice hydroxyls may be caused by the formation of Ti-OH as defects in the titania structures [39]. It is believed by most researchers in TiO$_2$ photocatalysis field that OH defects among other bulk defects decrease the photocatalytic activity since these defects produce sites for the recombination of electrons and holes [26, 42-45]. Therefore, extracting 'OH from the titania lattice would be expected to reduce OH defects which increased the photocatalytic activity.
Figure 3.3 SEM micrographs of (a) WACS-200, (b) SACS1-200, (c) P25, and (d) P25-SACS-200.
Figure 3.4 (a) FT-IR spectra of WACS-200, SACS1-200, and SACS2-200; (b) deconvolution of the given FT-IR spectra; (c) ratio ($A_S/A_T$) of absorbance by FT-IR spectra of surface hydroxyls ($A_S$) or lattice hydroxyls ($A_L$) to the reference peak ($A_T$) at wavenumber 900 cm$^{-1}$; and inset of Figure 3.4(c) showing FT-IR peak fitting for WACS-200.
Figure 3.5 Solid state $^1$H MAS NMR spectra of (a) WACS and (b) SACS1.
Figure 3.6 Methyl orange degradation under UV light irradiation of (a) uncalcined WACS and SACS samples compared to commercial P25 and treated P25 and (b) calcined WACS and SACS samples.
3.4 Conclusions

The greater the lattice hydroxyl content in polymorphic titania, the lower the photocatalytic activity. These results have shown that the solvothermal post-treatment is a useful technique to remove the lattice hydroxyls from the titania structure as shown in the comparison between WACS and SACS. By comparison, samples with similar surface area and crystallinity, calcined and solvothermal-treated titania samples, with reduced lattice hydroxyls, are more photocatalytically active than uncalcined or hydroxylated samples. The increase in the surface area of SACS samples is not the main factor for the improvement of photocatalytic activity, but fewer lattice hydroxyls are. Moreover, all prepared polymorphic titania samples showed excellent photocatalytic activity by MO degradation under UV when compared to commercial P25.

3.5 References

[18] JCPDS #29-1276.
[23] JCPDS #29-1272.
[34] M. Primet, P. Pichat, M.V. Mathieu, J Phys Chem-Us 75 (1971) 1221-&.

CHAPTER FOUR

ENHANCING PHOTOCATALYTIC ACTIVITY OF POLYMORPHIC BROOKITE TITANIA NANOPARTICLES BY NMP SOLVENT-BASED AMBIENT CONDITION PROCESS


Abstract

Solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent, is a post-treatment technique utilized to modify polymorphic titania nanoparticles prepared by a water-based ambient condition sol process. All samples were characterized by x-ray diffraction, N$_2$ physisorption, CHNS analysis, UV-Vis absorption spectrophotometry, FT-IR, and TEM and compared to a commercial reference titania product, Degussa P25. Photocatalytic activity, evaluated by the degradation of methyl orange under ultraviolet (UV) and visible light (VL), showed that SACS, with NMP as the solvent, is a powerful treatment to enhance TiO$_2$ photocatalytic activity by minimizing lattice hydroxyls and doping titania samples with nitrogen.

4.1 Introduction

One of the most well-known photocatalysts is titanium dioxide or titania (TiO$_2$), and it is commonly used for industrial applications such as an antibacterial agent, water/air purifier, deodorizer, pigment, semiconductor and, in general, decomposition of organic compounds under UV light irradiation [1-6]. There are three TiO$_2$ polymorphs: anatase, rutile, and brookite, which have similar chemical properties and band gap energies (~3.1 ± 0.1 eV), but different crystalline structures. Anatase and rutile are tetragonal [3], however brookite is orthorhombic [7]. Anatase TiO$_2$ has been reported to
be more photocatalytically active under UV exposure than rutile [2, 3, 6], but rutile TiO₂ is the most thermodynamically stable phase. Not many studies exist on brookite TiO₂ due to the difficult preparation of single phase brookite TiO₂. A few publications from this group [7-9] reported a water-based ambient condition sol (WACS) for producing predominantly brookite titania. Degussa Aerioxide TiO₂ P25 (P25) [10], consisting of 79% anatase 21% rutile, is an excellent photocatalyst under UV light.

Solvothermal synthesis was reported by Sato et al. [11] to be an excellent technique to synthesize highly crystalline fine particles. Yin et al. [12-14] explained that solvothermal titania samples prepared with ethanol or methanol showed a higher photocatalytic activity than titania samples prepared by hydrothermal reactions. The authors explained this by a higher degree of crystallinity in the solvothermal samples which meant fewer defects and thus a lower recombination rate of electrons and holes. Another study showed that nitrogen-doped titania samples prepared by a homogenous precipitation-solvothermal process in methanol or ethanol solutions possessed superior photocatalytic activity for nitrogen monoxide destruction than those prepared in a completely aqueous solution. Again, the solvothermal technique produced a greater degree of crystallinity in the structure, and yielded a higher specific surface area [15].

Our previous solvothermal titania study [16] utilized a technique developed from barium titanate treatment [17, 18]. The solvothermal post-treatment with sec-butanol as the solvent produced a lower lattice hydroxyl content in polymorphic titania nanoparticles thus enhancing the photocatalytic activity. In this paper, photocatalytic activity of titania that was prepared by solvent-based ambient condition sol (SACS) process using N-methylpyrrolidone (NMP) is reported. NMP is a nitrogen containing
high boiling point (~202°C) organic solvent. Because of its high boiling point, we will be able to apply high temperature (170°C) during the solvothermal treatment. Doping titania, especially anatase titania, with nitrogen has been widely reported to improve the photocatalytic activity under visible light irradiation by narrowing the band gap of titania [19, 20]. However, few visible light active polymorphic titania studies using a solvothermal treatment have been done. WACS and SACS with NMP solvent polymorphic titania were investigated by various physical characterization techniques and photocatalytic activities under both ultraviolet (UV) and visible light (VL) irradiation, evaluated by the degradation of methyl orange. They were also compared to a commercial reference, Degussa P25.

4.2 Experimental

The WACS process, titanium tetrachloride (TiCl₄ – Reagent grade obtained from Aldrich Chemical) in a 1:2 ratio of water-isopropanol solution with 0.3 M hydrochloric acid under refluxing conditions at 83°C for 15 hours [7-9], was used to prepare polymorphic TiO₂. A post-treatment to the WACS process, called SACS [16-18], was carried out in N-methylpyrrolidone (NMP) at 170°C for 4 hours in a sealed Teflon container. WACS samples were calcined in air at 200°C for 2 hours, and the SACS samples were calcined at various temperatures in air for 2 hours. The nomenclature to be used throughout this paper, preparation conditions, and % phase composition of titania samples are shown in Table 4.1.

An X-ray diffractometer was used to determine phase composition and crystallite size of the TiO₂ samples using an XDS 2000, Scintag PAD V with CuKα radiation at
1.5406 Å, measured with a step size of 0.020° over a range of 20 to 35° (2θ). The phase composition of titania was calculated from the following equations used by Zhang and Banfield [21]:

\[ W_A = \frac{k_A A_A}{k_A A_A + A_R + k_B A_B}, \]  
\[ W_B = \frac{k_B A_B}{k_A A_A + A_R + k_B A_B}, \]  
\[ W_R = \frac{A_R}{k_A A_A + A_R + k_B A_B}, \]

where \( W_A \), \( W_B \), and \( W_R \) represent the weight fractions of the anatase, brookite, and rutile phases, respectively; \( k_A \) is 0.886 and \( k_B \) is 2.721 [21]; \( A_A \), \( A_B \), and \( A_R \) are the integrated intensities of the anatase (101), brookite (121), and rutile (110) peaks, respectively. For pure brookite, \( I_{(121)\text{brookite}}/I_{(120)\text{brookite}} \) intensity ratio is approximately 0.9 [22, 23]. Therefore, we de-convoluted anatase (101) and brookite (120) overlap peaks by using 0.9 factor. The Scherrer equation (Equation 4) was applied to calculate titania crystallite size from the full-width half-height of the diffraction peak from the XRD patterns.

\[ t = \frac{0.9 \cdot \lambda}{\beta \cdot \cos(\theta)} \]

Where, \( \lambda \) is X-ray wavelength, 1.5418 Å for \( \text{CuK}_\alpha \), and \( \beta \) is the full-width half-height of the peak of interest: (121) for brookite, (110) for anatase and (101) for rutile [24].

The BET surface area, pore volume, and average pore diameter of the samples were determined by N\(_2\) physisorption at -196°C using a Micromeritics ASAP 2020 automated system. A sample amount of 0.3-0.5 grams was degassed at 200°C for 3 hours prior to N\(_2\) physisorption. The particle size and morphology of titania samples were
investigated by transmission electron microscopy (TEM), obtained from a Hitachi TEM H7600 with an accelerating voltage of 120.0 kV. TEM samples were prepared by dispersing titania powder, 0.01 grams, in isopropanol via ultrasonication, transferring the suspension drop-wise to copper TEM sample grids, and allowing isopropanol to evaporate.

The amount of nitrogen was determined using a CHNS analyzer (Perkin-Elmer 2400 series II). Absorbance spectra of titania samples were recorded by UV/Vis spectrophotometer using a GretagMacbeth Color i5 spectrometer across a UV/Vis range of 360 to 750 nm.

The relative concentrations of lattice hydroxyls and surface hydroxyls to a titania reference peak were calculated from FT-IR spectra based on our previous work [16, 18, 25-27]. The vibrational bands for total water and \(^\text{\textdegree}\)OH groups were observed by FT-IR, using Thermo-Nicolet Magna model 550 FT-IR spectrometer equipped with a Thermo-Spectra Tech foundation series diamond attenuated total reflection (ATR) accessory. Absorption bands were observed from 4000 cm\(^{-1}\) to 525 cm\(^{-1}\) with 32 sample scans. FT-IR spectra deconvolution was applied by using “fityk 0.7.4” curve fitting program (the GNU General Public License, version 2, as published by the Free Software Foundation) as shown in Figure 5(b). Previous research on titania in this group [16] has confirmed that the ATR is a valid technique for the semiquantitative analysis of hydroxyls since the results obtained from diffuse reflectance infrared Fourier transform (DRIFT) and ATR techniques were essentially the same. The peak ratios of the absorption bands for hydroxyls to that of titania, following the previous work for barium titanate [25-27] and titania [16], were calculated for a semiquantitative analysis of the hydroxyl content.
The photocatalytic degradation of the methyl orange (MO) by UV and VL irradiation was used to evaluate the photocatalytic activities. The minimal amount of titania to obtain a discernable difference between samples, 0.1 grams for UV measurements and 0.2 grams for VL irradiation, was added to 100 ml of 20 µM MO solution, and then stirred for 30 minutes without UV or VL exposure and continuously stirred throughout the reaction procedure. A Spectroline black light lamp (Model BIB-150B operating at 365 nm and 182 W) was used as the UV light source, which was positioned 36 cm above the MO solution. The VL source was a compact fluorescent lamp (Philips energy saver 60 soft white A19, 14 W) with wavelength of 560-612 nm. A portion of the suspension was taken at constant time increments, and titania powders were separated from the solution by vacuum filtration. The quantitative spectral results were monitored by a UNICAM UV/Vis spectrometer (Model: 5625). The methyl orange degradation percent value (D) was calculated by Equation 5.

\[
D = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\% \tag{5}
\]

Where, \(C_0\) is the initial MO concentration, \(C\) is the instantaneous MO concentration, \(A_0\) is the initial 490 nm absorbance peak intensity, and \(A\) is the instantaneous 490 nm peak intensity.
Table 4.1 Experimental Conditions utilized to produce polymorphic titania and % titania phase content.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% Content of TiO₂ Phase (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mode of Formation</th>
<th>Preparation or Post-treated Temperature (°C)</th>
<th>Preparation or Post-treated Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WACS</td>
<td>48 50 2</td>
<td>WACS</td>
<td>83</td>
<td>15</td>
</tr>
<tr>
<td>WACS-200</td>
<td>45 53 2</td>
<td>Calcination of WACS</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS</td>
<td>42 55 3</td>
<td>SACS of WACS</td>
<td>170</td>
<td>4</td>
</tr>
<tr>
<td>SACS-200</td>
<td>44 53 3</td>
<td></td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS-250</td>
<td>38 60 2</td>
<td></td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>SACS-300</td>
<td>45 51 4</td>
<td>Calcination of SACS</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>SACS-350</td>
<td>34 62 4</td>
<td></td>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>SACS-400</td>
<td>28 65 7</td>
<td></td>
<td>400</td>
<td>2</td>
</tr>
<tr>
<td>SACS-500</td>
<td>19 58 23</td>
<td>Obtained from Degussa</td>
<td>500</td>
<td>2</td>
</tr>
<tr>
<td>P25</td>
<td>79 - 21</td>
<td></td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<sup>a</sup> Obtained from XRD data by calculating from equation 1-3; An=Anatase, Br=Brookite, and Ru=Rutile.

4.3 Results and discussion

Identification of titania phases, confirmed by comparison to accepted standard peaks from JCPDS [22, 28, 29], were obtained from X-ray diffraction (XRD). XRD patterns of the TiO₂ samples are shown in Figure 4.1. The percent of TiO₂ phases contained within each sample, calculated from XRD data, are shown in Table 4.1. The phase composition of uncalcined (WACS and SACS) and calcined titania samples at 200-350°C for 2 hours (WACS-200, SACS-200, SACS-250, SACS-300, and SACS-350).
varied as follows: 50-62% brookite, 34-48% anatase, and less than 5% rutile. Increasing the calcination temperature above 350°C, a greater portion of rutile was introduced to the structure. Table 4.2 summarizes the crystallite sizes calculated from the XRD data using the Scherrer equation. The crystallite sizes of brookite and anatase phases for WACS, WACS-200, SACS, and SACS samples calcined at 200-300°C for 2 hours ranged from 5 to 8 nm which is approximately three times smaller than anatase phase crystallite size of P25. Above 300°C, the increasing calcination temperature increased the crystallite size of SACS samples.

Figure 4.1 The XRD pattern of the prepared titania samples and P25. A=anatase, B=brookite, and R=rutile.
Table 4.2 The physical properties of prepared titania and the reference P25.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallite size (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Average particle size (nm)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>BET surface area (m²/g)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Pore Volume (cm³/g)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Pore size average (Å)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
<td>Rutile</td>
<td>Anatase</td>
<td>Brookite</td>
</tr>
<tr>
<td>WACS</td>
<td>6</td>
<td>8</td>
<td>19</td>
<td>6</td>
<td>163</td>
</tr>
<tr>
<td>WACS-200</td>
<td>6</td>
<td>7</td>
<td>18</td>
<td>7</td>
<td>157</td>
</tr>
<tr>
<td>SACS</td>
<td>7</td>
<td>8</td>
<td>12</td>
<td>6</td>
<td>133</td>
</tr>
<tr>
<td>SACS-200</td>
<td>6</td>
<td>8</td>
<td>11</td>
<td>7</td>
<td>138</td>
</tr>
<tr>
<td>SACS-250</td>
<td>5</td>
<td>8</td>
<td>13</td>
<td>N/A</td>
<td>157</td>
</tr>
<tr>
<td>SACS-300</td>
<td>6</td>
<td>8</td>
<td>13</td>
<td>9</td>
<td>143</td>
</tr>
<tr>
<td>SACS-350</td>
<td>7</td>
<td>10</td>
<td>17</td>
<td>N/A</td>
<td>88</td>
</tr>
<tr>
<td>SACS-400</td>
<td>8</td>
<td>10</td>
<td>20</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td>SACS-500</td>
<td>7</td>
<td>20</td>
<td>71</td>
<td>18</td>
<td>34</td>
</tr>
<tr>
<td>P25</td>
<td>21</td>
<td>-</td>
<td>40</td>
<td>40</td>
<td>56</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from XRD data using the Scherrer equation (Equation 4). Error of measurement = ±5%.

<sup>b</sup> Determined by using TEM micrograph.

<sup>c</sup> Using N₂ physisorption at 77K. Error of measurement = ±10%.

Table 4.2 shows the results of BET surface area analysis, pore volume, and average pore diameter of titania samples. The BET surface area of prepared titania samples were three times larger than that of P25 samples. The effect of the calcination temperature of SACS samples on the BET surface area and the nitrogen content in the samples are given in Figure 4.2. The BET surface area of uncalcined titania (WACS and SACS) is equivalent to calcined samples at 200°C for 2 hours in air (WACS-200 and SACS-200), respectively, since all samples were pre-treated at 200°C for 3 hours in N₂. SACS and SACS-200 samples have approximately 15-20% smaller surface area than WACS and WACS-200 samples. This is most likely because NMP resided on the titania.
surface and could not be completely removed during the calcination at temperature below 200°C for 2h. The surface area of SACS shows an increasing trend up to 250-300°C calcination temperatures. Above 300°C, the surface area decreased with increasing the temperature. The surface area of SACS-250 and SACS-300 are similar to that of WACS samples. All NMP and nitrogen in SACS samples were likely released by calcination at the temperatures above 250°C. This assessment is supported by CHNS analysis, which shows no nitrogen in SACS-300 and SACS-400. Visible observation of the color of SACS, SACS-200, and SACS-250 is brown, which indicates nitrogen formed or NMP remaining on the surface and in the structure, on the other hand SACS-300, SACS-350, SACS-400, and SACS-500 powders are white. The surface area of SACS samples, calcined at temperatures above 350°C, rapidly decreased since the titania nanoparticles were sintered during the heat treatment. TEM micrographs are shown in Figure 4.3 and Table 4.2 shows the average particle size of TiO₂ as determined from TEM micrographs. The average particle size of as-prepared titania samples are much smaller than P25. As the calcination temperature is increased, the average particle size of the polymorphic titania slightly increased at temperatures below 300°C. Above 300°C, the average particle size increased linearly with increasing temperature by the sintering of nanoparticles during the heat treatment.

UV/Vis spectra of titania samples are shown in Figure 4.4. SACS samples exhibited visible light active potential by shifts of the absorption shoulders to the visible light region, compared with P25 and WACS-200 in the inset of Figure 4.4. The increase in absorbance at wavelengths greater than 550 nm, in increasing order is SACS ≈ SACS-200 ≈ SACS-250 > SACS-300 >> SACS-350> SACS-400 ≈ WACS-200 > SACS-500 ≈
P25. The more nitrogen found in the samples, given by CHNS analysis, the greater visible light absorption. Because of N atoms in SACS-NMP samples, a narrowing of titania band gap occurs [19, 20, 30-38]. The mechanism that N-doped TiO$_2$ responds to visible light arises from the formation of a N-induced mid-gap level slightly above the (O-2p) valence band edge was determined by Nakamura et al. [35]. The authors concluded that N ions were substituted at oxygen sites in TiO$_2$ to achieve a narrower titania band gap. In support of the evaluation for nitrogen present in SACS-NMP samples, XPS spectra of SACS-200 revealed a main N 1s peak at 398.3 eV, which indicates the anionic N$^-$ in O-Ti-N linkages [36], and some small peaks from 395.5 to 398 eV which are anionic nitride (N$_3^-$) in TiN [39-41].

Figure 4.2 The effect of calcination temperature for SACS samples on BET surface area and nitrogen content.
Figure 4.3 TEM micrographs of (a) WACS-200, (b) SACS, (c) SACS-200, (d) SACS-300, (e) SACS-400, and (f) SACS-500.
The obtained FT-IR spectra for SACS and WACS titania samples are given in Figure 4.5(a). Deconvolution of the spectra, illustrated in Figure 4.5(b), gave rise to 4 peaks at 1625 cm\(^{-1}\), 2730 cm\(^{-1}\), 3130 cm\(^{-1}\), and 3400 cm\(^{-1}\). The \(\cdot\)OH stretching vibrations of hydrogen-bonded \(\cdot\)OH groups (lattice hydroxyls), and adsorbed molecular water absorption bands (surface hydroxyls) can be found at wavenumbers around 3400-3500, and 1625 cm\(^{-1}\), respectively [16, 42-44]. Analysis of the FT-IR spectra is given in Figure 4.5(c), containing the calculated relative band intensities for surface and lattice hydroxyls. The peaks fitting result of WACS-200 by fityk 0.7.4 program is shown in the inset of Figure 4.5(c). In order to compare the amount of hydroxyls given by FT-IR spectra, the band intensities of hydroxyls were normalized with the band intensity of the Ti-O stretching band. The baseline method, as reported in the literature [16, 18, 25-27],
was applied to calculate band intensity ratios ($A_S/A_T$ and $A_L/A_T$) of the absorbance peaks of surface hydroxyls ($A_S$) at wavenumber 1625 cm$^{-1}$ and a broad band centered at approximately 3400 cm$^{-1}$, the lattice hydroxyls peak ($A_L$), to the reference peak for titania ($A_T$), the same wavenumber for all samples at 900 cm$^{-1}$. The semiquantitative comparison of band intensities indicates that WACS-200, relatively, has significantly larger lattice hydroxyls peaks than SACS, SACS-200, and SACS-400, since the solvothermal treatment extracted the lattice hydroxyls from the titania particles. The surface hydroxyls of SACS and SACS-200 are similar to WACS-200. However, SACS-400 shows significantly fewer surface hydroxyls than samples calcined at lower temperatures. The surface hydroxyl can be removed by heat treatment at temperatures above 200°C.

Figures 4.6(a) and 4.6(b) depict the photocatalytic activities of polymorphic titania samples compared to P25 samples, determined by the methyl orange degradation under UV exposure. As a time comparison to degrade methyl orange, 80% of total methyl orange degraded is arbitrarily chosen. As shown in Figure 4.6(a), the degradation by SACS and SACS-200 samples is approximately 60% faster than WACS and WACS-200 even though SACS samples have a lower surface area than WACS. Compared to the previous research [16] on SACS samples prepared in sec-butanol, the degradation by SACS prepared in NMP solvent samples is two times faster than in sec-butanol. The research on SACS in sec-butanol found that with greater lattice hydroxyl content in polymorphic titania, the lower the photocatalytic activity. Therefore, the superior photocatalytic activity of SACS samples is due to not only fewer lattice hydroxyls but also nitrogen present in SACS samples. FT-IR data supported that fewer lattice hydroxyl
are found in SACS samples than in WACS samples. The lattice hydroxyl may produce Ti-OH bonds as defects in the titania lattice structures [45]. It has been reported in the literature [46-50] that bulk defects decrease the photocatalytic activity since these defects produce sites for the recombination of electrons and holes. In order to increase the photocatalytic activity of TiO$_2$, reducing OH defects by extracting OH from the lattice is necessary. Polymorphic TiO$_2$ (SACS, SACS-200, WACS, and WACS-200), with three times larger surface area than P25, yielded a higher photocatalytic activity than P25, as expected. The effect of calcination temperature of SACS samples on MO degradation activity is shown in Figure 4.6(b). The photocatalytic activity, under UV exposure, of SACS samples, calcined at various temperatures, increased in the following order: SACS $\approx$ SACS-200 $\approx$ SACS-250 $> $ SACS-300 $>> $ SACS-350 $> $ SACS-400 $\approx$ SACS-500. The orange color of MO did not completely degrade within 120 minutes by UV irradiating SACS-400 and SACS-500. The increase of treatment temperature up to 400 and 500°C not only reduces the surface area, but also changes the phase composition, increasing rutile while sacrificing brookite and anatase. The lower surface area, elimination of nitrogen, and higher rutile content [9, 23] caused a reduction of photocatalytic activities. According to our CHNS analysis results, the more nitrogen presents in TiO$_2$, the higher the photocatalytic activity under both UV and VL exposure. This is consistent with the results of Aita et al. and Irie et al. [19, 20]. Nitrogen doped titania in SACS and SACS-200 showed a significant band gap narrowing, as found from UV/Vis spectra, which resulted in an increase in VL photocatalytic activity. The results may well agree with the observation made by Li et al. for their anatase titania with MO decolorization [51]. Preliminary results of MO degradation under VL irradiation in Figure 4.7 confirmed that
SACS-200 has a much higher VL photocatalytic activity than WACS-200 and Degussa P25. VL activated SACS-200 completely degraded MO after 1 hour. WACS-200 and P25 did not show the MO degradation after VL irradiation for 16 hours. The time to decolorize MO is relative since the visible light source is a low intensity custom-designed lamp.

**4.4 Conclusions**

Solvothermal post-treatment technique, using NMP as the solvent, is a useful method to extract lattice hydroxyls and to decorate nitrogen on the titania surface or in the structure as shown in the comparison between WACS and SACS. The greater the number of lattice hydroxyls in polymorphic titania, the lower the photocatalytic activity. The more nitrogen presents in SACS samples, the higher the photocatalytic activity. SACS-200 showed the best photocatalytic activity under both UV and VL irradiation among prepared titania samples and P25. Therefore, in this study, the optimum calcination temperature for SACS samples is 200°C for 2 hours. Moreover, other calcination variables such as time and calcination atmosphere, which can potentially influence the phase composition and structure and thus the photocatalytic activity, are being investigated.
Figure 4.5 (a) FT-IR spectra using ATR of the prepared titania samples; (b) deconvolution of the FT-IR spectra; (c) ratio (A_S/A_T) of absorbance by FI-IR spectra of surface hydroxyls (A_S) or lattice hydroxyls (A_L) to the reference peak (A_T) at wavenumber 900 cm\(^{-1}\); and inset of Figure 4.5(c) shows FT-IR fitting result of WACS-200.
Figure 4.6 Methyl orange degradation under UV light of (a) uncalcined and calcined WACS and SACS samples compared to commercial P25 and (b) SACS samples calcined at vary temperature.
Figure 4.7 Methyl orange degradation under VL irradiation of SACS-200, WACS-200 and P25.

4.5 References


[22] JCPDS #29-1276.


[28] JCPDS #29-1272.
[29] JCPDS #29-1360.


CHAPTER FIVE

STUDY OF VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY ACHIEVED BY NMP SOLVENT TREATMENT OF POLYMORPHIC BROOKITE TITANIA


Abstract

Visible light active polymorphic titania samples were prepared by post-treatment of a water-based ambient condition sol (WACS) sample using a solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent. SACS samples were calcined in either air or nitrogen atmosphere under various conditions. Nitrogen incorporation of SACS titania was investigated by CHN analysis and x-ray photoelectron spectroscopy (XPS). All samples were also characterized by x-ray diffraction, N₂ physisorption, UV-Vis absorption spectroscopy, and TEM and compared to a commercial titania powder, Degussa P25. The calcination conditions, especially the temperature and calcination atmosphere, have an influence on the BET surface area, crystallite size, titania phase content, and photocatalytic activity, evaluated by the degradation of methyl orange dye under visible light irradiation. SACS calcined in air at 200°C for 2 hours showed the best visible light activated photocatalytic performance in this study.

5.1 Introduction
It is known that titania is activated by ultraviolet (UV) light for photocatalytic reactions. However, visible light (VL), wavelengths ~400-700 nm, is the major fraction (about 45%) of solar radiation which has only 5% of UV with the remaining for infrared [1]. The band gap of titania is about 3.2 eV, which can only absorb wavelengths shorter than 388 nm, which is out of the VL region. For efficient utilization of solar energy by titania photocatalysts, narrowing its band gap to VL energy range is required. Many researchers have studied visible light active (VLA) anatase and rutile titania by doping the titanias with transition metals such as Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Os$^{5+}$, V$^{4+}$, or Rh$^{3+}$, or non-metals such as N, C, F, P, or S to narrow their band gap. Asahi et al. [2] claimed that anionic doping is superior to metal cation doping since metal cations often give localized $d$ states deep in the band gap of titania but create new recombination centers of $e^-\cdot h^+$. They reported that N-doped anatase titania showed higher photodegradation activities of methylene blue and gaseous acetaldehyde than un-doped titania under VL (wavelength < 500 nm) [2]. They accounted for the improvement by N-substitution into oxygen sites of titania. The substitutional N doping was the most effective among other non-metals doping since its $p$ states contribute to the band-gap narrowing by mixing with O $2p$ states. However, only a few papers on VLA brookite titania were found [3, 4]. Recently, many studies have been reported on preparation of nitrogen doped titania by using various techniques such as annealing under a gaseous NH$_3$ flow [5], sputtering TiO$_2$ in N$_2$ gas [2], using an aqueous ammonia solution [6], urea [7], an amine precursor solution [8], or a solvothermal treatment in N precursor solvents [3, 9, 10].

Our previous solvothermal titania study [9] reported that the solvent-based ambient condition sol (SACS) process, using N-methylpyrrolidone (NMP) as solvent,
enhanced the photocatalytic activities of polymorphic titania under VL irradiation. The nitrogen atoms contained in NMP, when incorporated with titania, narrowed the band gap of titania. The preliminary results showed that the calcination temperatures affected BET surface area, particle size, titania phase content, and photocatalytic activities. The results presented below are from further examination of the influence of calcination conditions, i.e., calcination atmosphere, temperature, and time. The physical properties with nitrogen incorporation in all titania samples are reported. The photocatalytic activities under VL exposure, evaluated by the degradation of methyl orange (MO) dye, are presented with that of a commercial reference titania, Degussa P25.

5.2 Experimental

Polymorphic titania was prepared by the water-based ambient condition sol (WACS) process, using titanium tetrachloride (TiCl$_4$) in a 1:2 ratio of water-isopropanol system with 0.3 M hydrochloric acid under a refluxing condition as described in our previous papers [11-13]. The WACS samples were calcined in air at 200°C for 2 hours. A solvothermal post-treatment, or SACS [9, 14-16], was applied to modify the WACS samples. The SACS process was carried out in N-methylpyrrolidone (NMP) at 170°C for 4 hours in a sealed Teflon container followed by calcination in either air or nitrogen at 200°C for 2, 4, or 6 hours and also at 300°C and 400°C for 2 hours. The nomenclature, preparation conditions, and percent phase composition of titania samples are given in Table 5.1.

Phase composition and crystallite size of all samples were determined, as shown in our previous reports [9, 14, 17], by X-ray diffractometry (XRD) using XDS 2000,
Scintag PAD V utilizing CuK\textsubscript{α} radiation at 1.5406 Å, measured with a step size of 0.020° over a range of 20 to 35°, and a 2θ angular region. The BET surface area, pore volume, and average pore diameter of the samples were determined by N\textsubscript{2} physisorption at -196°C using a Micromeritics ASAP 2020 automated system. The amount of nitrogen in the titania samples was determined using a CHN analyzer (Perkin-Elmer 2400 SeriesII). The chemical states of species in the TiO\textsubscript{2} samples were investigated using X-ray photoelectron spectroscopy (XPS), employing Kratos XPS with a monochromatic Al-K\textsubscript{α} X-ray source system. Light absorbance of the titania samples were recorded using a UV/Vis spectrophotometer of GretagMacbeth Color i5 across a UV/Vis range of 360 to 750 nm.

The photocatalytic activities of TiO\textsubscript{2} samples were evaluated by observing the photocatalytic degradation of the MO under VL irradiation with wavelength at 560-612 nm. The MO test experiment followed the procedure found in the literatures [9, 13, 14]. Titania samples of 0.2 grams were added to 100 ml of 20 µM MO solution, and then stirred for 30 minutes without VL exposure and continuously stirred throughout the reaction. A sample was taken every 30 minutes, then the titania particles were separated from the MO solution by vacuum filtration to prevent scattering. A compact fluorescent lamp (Philips energy saver 60 soft white A19, 14 W) was used as the VL source. The quantitative spectral results of MO were monitored by a UNICAM UV/vis spectrophotometer (Model: 5625). The MO degradation percent value, D, was calculated by Equation 1.

\[
D = \frac{A_0 - A}{A_0} \times 100\% \quad (1)
\]
Where, $A_0$ is the initial 490 nm absorbance peak intensity and $A$ is the instantaneous 490 nm peak intensity [9, 13, 14].

**Table 5.1** Experimental Conditions used to produce polymorphic titania and % content of titania phase.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% Content of TiO$_2$ Phase (wt%)*</th>
<th>Mode of Formation</th>
<th>Preparation or Post-treated Temperature (°C)</th>
<th>Preparation or Post-treated Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WACS</td>
<td>48 50 2</td>
<td>WACS</td>
<td>83</td>
<td>15</td>
</tr>
<tr>
<td>WACS-200</td>
<td>45 53 2</td>
<td>Calcination of WACS</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS</td>
<td>42 55 3</td>
<td>SACS of WACS</td>
<td>170</td>
<td>4</td>
</tr>
<tr>
<td>SACS-200/2/A</td>
<td>44 53 3</td>
<td>Calcination of SACS in air</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS-200/4/A</td>
<td>45 52 3</td>
<td>Calcination of SACS in air</td>
<td>200</td>
<td>4</td>
</tr>
<tr>
<td>SACS-200/6/A</td>
<td>46 52 2</td>
<td>Calcination of SACS in air</td>
<td>200</td>
<td>6</td>
</tr>
<tr>
<td>SACS-300/2/A</td>
<td>45 51 4</td>
<td>Calcination of SACS in air</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>SACS-400/2/A</td>
<td>28 65 7</td>
<td>Calcination of SACS in air</td>
<td>400</td>
<td>2</td>
</tr>
<tr>
<td>SACS-200/2/N</td>
<td>45 52 3</td>
<td>Calcination of SACS in air</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS-200/4/N</td>
<td>47 51 2</td>
<td>Calcination of SACS in air</td>
<td>200</td>
<td>4</td>
</tr>
<tr>
<td>SACS-200/6/N</td>
<td>42 56 2</td>
<td>Calcination of SACS in air</td>
<td>200</td>
<td>6</td>
</tr>
<tr>
<td>SACS-300/2/N</td>
<td>41 57 2</td>
<td>Calcination of SACS in air</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>SACS-400/2/N</td>
<td>34 63 3</td>
<td>Calcination of SACS in air</td>
<td>400</td>
<td>2</td>
</tr>
<tr>
<td>P25</td>
<td>79 - 21</td>
<td>High T flame oxidation</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Obtained from XRD data; An=Anatase, Br=Brookite, and Ru=Rutile.
5.3 Results and discussion

XRD patterns of all SACS samples are given in Figure 5.1. The calculated percent of TiO$_2$ phases from XRD data are shown in Table 5.1. The phase composition of uncalcined WACS and SACS and calcined SACS at 200-300°C varied as follows: 50-55% brookite, 40-48% anatase, and a small amount of rutile (less than 5%). The crystallinity of the prepared WACS and post-treatment SACS samples was relatively similar, as obtained from the XRD pattern. The proportion of brookite and rutile in the structure increased for calcined SACS at 400°C either in air or N$_2$ atmospheres. The crystallite size in Table 5.2, calculated from the XRD data using the Scherrer equation, of all prepared titania samples ranged from 5 to 10 nm, which is approximately three times smaller than that of P25. This agrees well with the size determined by TEM micrographs which was reported in our work [9]. However, the rutile phase, which is very small in proportion within the prepared titania polymorph, shows the crystallite size ~10 to 20 nm.

BET surface areas, pore volume, and average pore diameter of the titania samples are given in Table 5.2. The surface area of as-prepared titania samples is approximately three times larger than that of P25 sample. The surface area of SACS, SACS-200/2/A, and SACS-200/2/N samples were similar, approximately 15-20% less than that of WACS and WACS-200 samples. It can be explained that calcination at 200°C for 2h in either air or N$_2$ could not completely remove residual NMP on the titania surface. In Figure 5.2, the surface area of calcined SACS samples in a N$_2$ atmosphere shows a decreasing trend with increasing calcination temperature and time. This is attributable to the sintering of titania nanoparticles and the residual decomposition products of NMP by the heat treatment. On the other hand, the surface area of calcined SACS samples in air for 4 and
6 hours increased approximately 24% from those calcined for 2 hours. Unlike the calcination in nitrogen, some of NMP was oxidized and removed from the titania surface by the heating in oxidizing atmosphere. At a higher calcination temperature of 400°C in air, the surface area reduced by 50% because of the sintering.

Figure 5.1 The XRD patterns of the prepared titania samples and P25 (A=anatase, B=brookite, and R=rutile).
Table 5.2 The physical properties of as-prepared titania and the reference P25.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallite size (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BET surface area (m²/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pore Volume (cm³/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pore size average (Å)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Doped N content (wt%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
<td>Rutile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WACS</td>
<td>6</td>
<td>8</td>
<td>19</td>
<td>163</td>
<td>0.1</td>
</tr>
<tr>
<td>WACS-200</td>
<td>6</td>
<td>7</td>
<td>18</td>
<td>157</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS</td>
<td>7</td>
<td>8</td>
<td>12</td>
<td>133</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-200/2/A</td>
<td>6</td>
<td>8</td>
<td>11</td>
<td>138</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SACS-200/4/A</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>171</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-200/6/A</td>
<td>5</td>
<td>7</td>
<td>19</td>
<td>172</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SACS-300/2/A</td>
<td>6</td>
<td>8</td>
<td>13</td>
<td>143</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-400/2/A</td>
<td>8</td>
<td>10</td>
<td>20</td>
<td>68</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-200/2/N</td>
<td>5</td>
<td>8</td>
<td>14</td>
<td>139</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-200/4/N</td>
<td>5</td>
<td>7</td>
<td>14</td>
<td>128</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-200/6/N</td>
<td>5</td>
<td>9</td>
<td>19</td>
<td>118</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-300/2/N</td>
<td>5</td>
<td>9</td>
<td>13</td>
<td>114</td>
<td>0.1</td>
</tr>
<tr>
<td>SACS-400/2/N</td>
<td>9</td>
<td>10</td>
<td>21</td>
<td>82</td>
<td>0.1</td>
</tr>
<tr>
<td>P25</td>
<td>21</td>
<td>-</td>
<td>40</td>
<td>56</td>
<td>0.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from XRD data using the Scherrer equation. Error of measurement = ±5%.

<sup>b</sup> Using N<sub>2</sub> physisorption at -196°C. Error of measurement = ±10%.

<sup>c</sup> Determined by CHN analyzer.
Figure 5.2 The effect of calcination temperature and time for SACS samples on BET surface area.

Figure 5.3(a) exhibits nitrogen content and Figure 5.3(b) presents carbon and hydrogen contents, obtained from CHN analysis, of calcined SACS samples as a function of both calcination temperature and time. The nitrogen, carbon, and hydrogen contents decreased with increasing the temperature and time of calcination in either air or nitrogen. Some of N, C, and H have been volatilized, expectedly more from air calcination. SACS-200/2/N has approximately 5 times more nitrogen content than SACS-200/2/A, since nitrogen in the SACS samples was oxidized by O$_2$ gas in air atmosphere. Nitrogen was completely released when calcined at a temperature above 300$^\circ$C in air and 400$^\circ$C in nitrogen.
Figure 5.4 shows UV/Vis spectra of titania samples. SACS samples exhibited shift of the absorption shoulders to the VL region, compared with P25 and WACS-200 in the previous study [9]. The shifting of absorption shoulders of all SACS samples calcined in nitrogen is greater than the WACS-200 and P25. The SACS samples calcined in air showed less absorption since much of the doped nitrogen was released by the reoxidation [6]. In the case of SACS calcined in nitrogen, the greater shifting was observed with increasing calcination time and temperature. On the other hand, the absorption shoulders shifting of SACS calcined in air with increasing calcination time was similar, but dramatically decreased with increasing calcination temperature. In the case of calcination in air, CHN analysis results in Figure 5.3 depict that the more N in the structure with decreasing calcination temperature, the greater the VL absorption. The shifting of absorption shoulders to VL region, or a narrowing of titania band gap, occurs because of N atoms in the SACS samples [2, 5-8, 18-23]. The greater contribution, however, must come from the partially decomposed NMP remaining as charred organic.

The chemical state of nitrogen in SACS samples calcined in air and nitrogen was examined using XPS as shown in Figure 5.5(a) and (b). N 1s XPS during the oxidation process of TiN was investigated by Saha and Tompkins [24] and assigned the peaks as atomic $\beta$-N at 396 eV and molecularly chemisorbed $\gamma$-N$_2$ at 400 and 402 eV. However, the N peak at 396 eV was not always present [25]. The XPS spectrum of SACS-200/2/A in Figure 5.5(a) reveals three N 1s peak at 398.1, 399.5, and 400.7 eV. Figure 5.5(b) is the N 1s XPS peak of SACS-200/2/N revealing two peaks at binding energies of 398.1, and 399.9 eV. The main N 1s peak at 398.1 is attributed to C-N bonds, anionic azide (N$_3^-$), or NH$_3$ [26-28]. The peak at ~ 400 eV is for the N atom in the environment of O-Ti-N.
or the presence of hyponitrite which is responsible for the VLA photocatalysis [25, 29]. This N peak at ~400 eV was also attributed to the doping of the nitrogen into the TiO₂ [25, 30]. Both SACS samples contained N 1s peak at 399-401 eV; however, the value of the peak height ratios of O-Ti-N to C-N of SACS-200/2/A is greater than that of SACS-200/2/N.
Figure 5.3 The effect of calcination temperature for SACS samples on (a) nitrogen content, and (b) carbon and hydrogen content.

Figure 5.4 UV/Vis spectra of as-prepared SACS samples.
The photocatalytic activities of the as-prepared titania samples compared to the reference P25, determined by the MO degradation under VL irradiation, are given in Figure 5.6(a) and 5.6(b). For the sake of discussion and comparison of the reaction times between samples, eighty percent of MO degradation is arbitrarily set. The results exhibit that SACS samples calcined in air and nitrogen at 200°C are all VLA. The MO degradation by SACS samples calcined in both atmospheres at 200°C is 2-3 times faster than the MO degradation for the samples calcined at 300°C. SACS-200/2/A exhibits the highest photocatalytic activity among the other titania samples. SACS-400/2/A, SACS-400/2/N, WACS-200, and P25, which have no nitrogen, are not VLA as expected. The photocatalytic results of SACS calcined in air were supported by UV/Vis spectra and CHN analysis. The more nitrogen present in SACS calcined in air, the higher the photocatalytic activity. The photocatalytic activities of SACS samples, calcined in nitrogen at various temperatures as shown in Figure 5.6(b), increased in the following order: SACS-200/2/N ≅ SACS-200/4/N ≅ SACS-200/6/N > SACS > SACS-300/2/N >> SACS-400/2/N. The VL activity trend of SACS calcined in nitrogen was inconsistent with the UV/Vis absorbance in Figure 5.4. For example, according to UV/Vis absorbance, SACS-400/2/N should be the most VLA sample. These results indicate that VL photocatalytic performance is not directly related to the VL absorbance [6]. Moreover, the much lower photocatalytic activities of SACS calcined at temperatures above 200°C can be attributed to the significantly lower BET surface area. In the case of calcination at 200°C for 2 hours, MO degradation with SACS calcined in air is 2 hours faster than when calcined in nitrogen, even though SACS-200/2/A contained about 5 times less nitrogen than SACS-200/2/N. This result has two possible explanations. First,
not all states of nitrogen in titania are VLA. There is more nitrogen in the form of hyponitrite [25, 29], which is required for VL photocatalysis, in SACS-200/2/A than in SACS-200/2/N. Additionally, it has been suggested that the partial release of doped nitrogen is necessary for samples to appear to be VLA [6]. By varying the time for 200°C calcination in both air and nitrogen atmospheres, results were obtained that showed calcination time have little influence on photocatalytic activities in nitrogen atmosphere. Contrarily, when SACS samples were calcined in air for various times, the photocatalytic activity declined with increasing time after and initial period of 2 hours by reducing the content of hyponitrite.

5.4 Conclusions

A post-treatment, called SACS process with NMP solvent, of as-prepared polymorphic titania, improved the VL photocatalytic activity of the samples. The calcination conditions, i.e., temperature, time, and calcination atmosphere (either air or nitrogen) affected the photocatalytic activities. The photocatalytic activity declined with increasing calcination temperature and time. However, calcination time did not have a significant effect on VLA properties, especially in the SACS samples calcined in nitrogen. SACS-200/2/A showed the best VLA performance, since SACS-200/2/A has greater amount of VLA nitrogen in the form of hyponitrite than that in SACS-200/2/N.
Figure 5.5 N 1s XPS spectrum of (a) SACS-200/2/A, and (b) SACS-200/2/N.
Figure 5.6 MO degradation under VL irradiation of (a) SACS samples calcined in air compared to WACS-200 and commercial P25, and (b) uncalcined SACS and SACS samples calcined in nitrogen.
5.5 References


CHAPTER SIX

VISIBLE LIGHT PHOTOCATALYTIC ACTIVITIES OF POLYMORPHIC BROOKITE TITANIA

[Reproduced the paper published in *Journal of Sustainable Energy* 1 (2009) 0231011-0231017, and selected for the April 6, 2009 issue of *Virtual Journal of Nanoscale Science & Technology*, which was published by the American Institute of Physics and the American Physical Society]

Abstract

TiO$_2$ nanoparticles were prepared by water-based ambient condition sol (WACS) process followed by lattice dehydroxylation using hot N-methyl pyrrolidone (NMP) yielded a mixed crystal phases of brookite titania with anatase as the minor phase. The mixed phase titania exhibited superior photocatalytic activities for an organic dye degradation under 14 W visible light (VL) and hydrogen evolution from an aqueous solution irradiated by a 300W Xe arc lamp (Oriel) ($\lambda > 420$ nm for VL) as compared with several available reference titania samples. The superior VL photocatalytic activity is explained as the effective charge separation by the intercrystalline electron transport from brookite to anatase grains complemented by the strong VL absorption by the nitrogen species in NMP. The probable electron transport mechanism is illustrated.
6.1 Introduction

Titania is a well known photocatalyst which works well under UV. For the obvious reason, there have been great many efforts to make the photocatalyst visible light (VL) active. Among the polymorphs of titania, brookite is the least known and least investigated. We have adopted and developed a low temperature synthesis method, called “water based ambient condition sol” (WACS) process, which yielded high surface area nanoparticle titania with brookite as the predominant phase [1-6]. We have reported that our titania with brookite as the major phase is superior photocatalytically to other titania phases [6] under UV. We further refined the WACS process to enhance the visible light activity (VLA). The WACS processed titania was exposed to a hot hydrophilic organic solvent which removed some of the entrapped protons [2-4]. The post solvent treatment, called solvent-based ambient condition sol (SACS) process, improved the VLA further [2-4]. In this communication we reported various photocatalytic properties including water splitting for hydrogen evolution. This work was carried out under active international collaboration (Department of Chemical & Environmental Engineering, POSTECH, Pohang, Korea) [7].

6.2 Experimental

The procedure for producing polymorphic titania with brookite as the major phase (polymorphic brookite titania: PBT or WACS) and the post solvent treatment with N-methylpyrrolidone (NMP) to enhance VLA are described in our previous reports [1-6]. Table 6.1 lists some of notable physical properties of PBT as compared with other reference titania samples. All titania samples were characterized by X-ray diffractometry
(XRD), N\textsubscript{2} physisorption at -196°C, electron microscopy, and UV/Vis spectrophotometry [2-4, 6]. The VLA or VL photocatalytic activities (PCA) of TiO\textsubscript{2} samples were evaluated by observing the photocatalytic degradation of the methyl orange (MO) under VL irradiation with a 14W fluorescent lamp in the wavelength range of 560-612nm at the distance of 36 cm from the sample cell. The MO test procedure is found in our previous papers [2, 3].

Hydrogen generation by splitting water under VL was carried out under active international collaboration with Department of Chemical & Environmental Engineering, POSTECH, Pohang, Korea) [7]. The powder titania samples were decorated with platinum using a photo-deposition method. For the platinization a 0.5 g/L aqueous suspension of SACS in 1 M methanol (electron donor) and 10\textsuperscript{-3} M chloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6}) was exposed to UV irradiation for 30 min with a 200W mercury lamp. After the irradiation, the SACS and PBT powders were filtered and washed with distilled water. A typical Pt loading on these samples was estimated to be ca. 1 wt %. The suspension was irradiated by a 300W Xe arc lamp (Oriel) combined with a 10-cm IR water filter and a cut-off filter (\(\lambda > 420\, \text{nm}\) for VL) as the light source. The filtered light was focused onto a 57 mL reactor [total volume (30mL) + head space (27mL)]. A typical incident light intensity was measured using a power meter (Newport 1830-C) and determined to be about 100 mW/cm\textsuperscript{2} in the wavelength range of 420-550 nm. In the H\textsubscript{2} generation experiments, the aqueous solutions containing Pt/titania and 10 mM ethylenediamine tetra-acetic acid (EDTA) as electron donor at the initial pH\textsubscript{i} of 3 was deaerated by N\textsubscript{2} sparging before the irradiation. The production of H\textsubscript{2} was monitored
using a HP6890A GC equipped with a thermal conductivity detector and a 5A molecular sieve column.

**Table 6.1** Experimental Conditions utilized to produce all titania samples and % titania phase content.

| Sample ID | % Content of TiO₂ Phase (wt%)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>An</td>
</tr>
<tr>
<td>PBT</td>
<td>48</td>
</tr>
<tr>
<td>PBT-200</td>
<td>45</td>
</tr>
<tr>
<td>SACS</td>
<td>42</td>
</tr>
<tr>
<td>SACS-200</td>
<td>44</td>
</tr>
<tr>
<td>P25</td>
<td>79</td>
</tr>
<tr>
<td>POSTECH</td>
<td>100</td>
</tr>
<tr>
<td>TiOz-200</td>
<td>100</td>
</tr>
<tr>
<td>TiOz-SACS</td>
<td>100</td>
</tr>
<tr>
<td>TiOz-SACS-200</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode of Formation</th>
<th>Preparation or Post-treated Temperature (°C)</th>
<th>Preparation or Post-treated Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WACS</td>
<td>83</td>
<td>15</td>
</tr>
<tr>
<td>Calcination of PBT</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS of PBT</td>
<td>170</td>
<td>4</td>
</tr>
<tr>
<td>Calcination of SACS</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>High T flame oxidation</td>
<td>1100-1200</td>
<td>N/A</td>
</tr>
<tr>
<td>Hydrothermal in NH₄OH Calc. in air at 400°C</td>
<td>120</td>
<td>72</td>
</tr>
<tr>
<td>Acid hydrolysis of butoxide Calc. in air at 200°C</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>SACS of TiOz</td>
<td>170</td>
<td>4</td>
</tr>
<tr>
<td>Calcination of TiOz-SACS</td>
<td>200</td>
<td>2</td>
</tr>
</tbody>
</table>

*a Obtained from XRD data; An=Anatase, Br=Brookite, and Ru=Rutile.

*b SACS means the post treatment of WACS in N-methylpyrrolidone (NMP)

**6.3 Results and discussion**

Figure 6.1 shows ~8 nm of randomly oriented well-crystallized grains of the as-synthesized PBT or WACS particles [5]. Table 6.1 lists some of notable physical
properties of PBTs as compared with other reference titania. Figure 6.2 shows UV-visible spectra of as-synthesized PBT after calcination at 200°C which shows a weak absorbance of VL in the range of 400-600 nm. This means, though brookite is the predominant phase in PBT, the VL absorbance of brookite is so small that no significant VLA is expected. This is indeed shown in Figure 6.3 that PBT-200 was inactive under 14W VL.

![High resolution TEM of PBT particles showing well crystallized grains.](image)

**Figure 6.1** High resolution TEM of PBT particles showing well crystallized grains.

The proportions of the crystal phase in PBT were calculated from the XRD patterns as described in the references [2-4, 8, 9]. Table 6.2 shows relevant physical properties of all the titania samples compared in this work. The crystallite sizes of brookite and anatase phases for the as-prepared titania, calculated from the XRD data
using the Scherrer equation, ranged from 6 to 8 nm which agree well with size estimated by TEM in Figure 6.1. BET specific surface area (SSA) of solvent treated samples (SACS-200 and TiOz-SACS-200) is approximately 12%-17% smaller than untreated samples (PBT-200 and TiOz-200). It can be explained that NMP resided on the titania surface and could not be completely removed during by calcination in air at 200°C for 2 hours [3].

**Table 6.2** The physical properties of all titania samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallite size (nm)</th>
<th>BET surface area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore size average (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
<td>Rutile</td>
<td></td>
</tr>
<tr>
<td>PBT</td>
<td>6</td>
<td>8</td>
<td>19</td>
<td>163</td>
</tr>
<tr>
<td>PBT-200</td>
<td>6</td>
<td>7</td>
<td>18</td>
<td>157</td>
</tr>
<tr>
<td>SACS</td>
<td>7</td>
<td>8</td>
<td>12</td>
<td>133</td>
</tr>
<tr>
<td>SACS-200</td>
<td>6</td>
<td>8</td>
<td>11</td>
<td>138</td>
</tr>
<tr>
<td>P25</td>
<td>21</td>
<td>-</td>
<td>40</td>
<td>56</td>
</tr>
<tr>
<td>Postech</td>
<td>22</td>
<td>-</td>
<td>-</td>
<td>93</td>
</tr>
<tr>
<td>TiOz-200</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>208</td>
</tr>
<tr>
<td>TiOz-SACS-200</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>173</td>
</tr>
</tbody>
</table>

*Calculated from XRD data using the Scherrer equation. Error of measurement = ±5%.*

*Using N₂ physisorption at -196°C. Error of measurement = ±10%.*

The UV-visible spectra of SACS samples, as given in Figure 6.2, show a much stronger absorbance of VL as compared to P25 and the solvent untreated samples. The increase in the absorbance at wavelengths greater than 550 nm (VL region), in increasing order is TiOz-SACS-200 > SACS-200 >> Postech > PBT-200 > TiOz-200 ≅ P25. SACS treated with NMP provided the effect of nitrogen chromophore incorporation as well as previously reported dehydroxylation from the PBT crystal lattice [2, 3].
Figure 6.2 UV/Vis spectra of all titania samples compared.

Figure 6.3 exhibits the PCA of the titania samples, determined by the MO degradation under the 14W VL exposure. The superior PCA of PBT to anatase under UV has been reported in our previous publication [6]. SACS titania samples are active under VL irradiation as supported by UV/Vis spectra. This demonstrates that SACS post-treatment is an efficient technique to decorate titania surface with nitrogen in addition to the lattice dehydroxylation effect, in order to improve their VLA properties [2, 3]. The degradation rate by SACS-200 is approximately 2.8 times faster than TiOz-SACS-200 despite the lower SSA of SACS-200 than that of TiOz-SACS-200. This VLA superiority of SACS-200 must be due to the presence of ~53% brookite with the significant proportion of anatase. This mixed phase titania is analogous to the anatase and rutile
mixed phase in P25. The superior UV PCA of P25 has been delineated by the efficient intercrystalline electron transport and charge separation by the minor rutile phase acting as the electron ‘antenna’ [10]. Ozawa et al. [11] proposed strong coupling between anatase and brookite in their mixed phase titania.

![Graph showing Methyl orange degradation under VL irradiation of all titania samples compared.](image)

**Figure 6.3** Methyl orange degradation under VL irradiation of all titania samples compared.

The importance of charge separation via heterojunction in photosemiconductors for a more efficient PCA has been emphasized by many researchers [10-13]. A possible mechanism of this mixed phase PBT is illustrated in Figure 6.4 along with that of P25 [10] for an analogy. The incident VL excites the electrons in brookite (or anatase) and the excited electrons ($e^-$) are transferred to the other phase. It is believed that this is an effective way to transport and trap the electrons in the conduction band reducing the
recombination of electron (e$^-$) and hole (h$^+$). A question with an uncertain answer is the transfer direction of the e$^-$’s. It is reasonable to assume that e$^-$’s flow, in a mixed phase, from low band gap (E$_g$) phase to high E$_g$ phase. Nevertheless, there is a confusion with respect to the E$_g$ of brookite (E$_{g,Br}$). The value of E$_{g,Br}$ is currently unknown as some reported E$_{g,Br} > E_{g,An}$ [14], but some reported E$_{g,Br} < E_{g,An}$ [15, 16]. Mo and Ching [17] suggested that the calculated E$_{g,Br}$ is approximately 10% smaller than E$_{g,An}$. E$_{g,Br}$ was reported as either a direct band gap semiconductor [17] or an indirect band gap semiconductor [16].

**Figure 6.4** Proposed electron transport mechanism of the enhanced VLA in PTB-SACS crystals and that of P25 [7].

PBT-200, TiOz-200, and P25 did not show any MO degradation under the 14 W VL exposure, since these titanias have no nitrogen and/or no brookite phase. POSTECH sample, which is a hydrothermal nitrogen doped anatase, absorbed some VL as shown in UV/Vis spectra, but was surprisingly VLA inactive under the 14W VL source. The twice smaller SSA of POSTECH titania than SACS-200 and TiOz-SACS-200 could also contribute to the poor VLA. KRONOS® [18], a commercial high SSA 100% anatase
titania claiming VLA [19], were later received and tested for MO degradation in comparison with SACS-200. Both KRONOS samples, VLP 7000 (SSA > 225 m$^2$/g) and VLP 7001 (SSA > 225 m$^2$/g), were much inferior to SACS-200. For 50% MO degradation, when SACS-200 took ~20 min, KRONOS VLP 7000 took ~110 min, and VLP 7001 never even reached the 50% mark within the testing time period of 180 min.

The probable mechanism shown in Figure 6.4 is based on our preliminary data on phase transformation of brookite under the different experimental conditions including heat treatment. In the synthesis of PBT, the lower refluxing temperature and time favored anatase formation. The role of the trace rutile phase in PBT may not be ignored, and further study is needed [20].

The result of H$_2$ generation from aqueous EDTA solution under VL, given in Figure 6.5, shows that SACS titania is superior to other available references. HBK is a commercial anatase titania with the name Hombikat UV 100 having SSA >200 m$^2$/g. In spite of the high SSA of HBK, the hydrogen generation of HBK is similar to that of PBT which has SSA of ~160 m$^2$/g. The crystallographic difference between HBK and PBT is the phase composition. HBK is fully anatase and PBT is anatase with more than 50% brookite. This supports the positive nature of brookite presence in a mixed phase crystal. Although it is known that VLA for free radical organic decomposition is operated under different mechanism from VL water splitting, SACS with brookite as the predominant phase is shown to be promising for further investigation for VL H$_2$ generation from water.

The reason for HBK showing an appreciable hydrogen evolution under VL is the formation of VL absorbing EDTA-complex on the high SSA titania. H$_2$ production from
an undoped Pt/TiO2 has been frequently observed when EDTA was used as an electron donor. This effect becomes more noticeable for high SSA particles such as HBK. This phenomenon is the subject of a separate study and is being investigated in our collaborated laboratory (Postech, Korea). Thus, the major contributing factors for the observed superior VL-PCA from the PBT are listed as: (1) the lower lattice hydroxyl content [3, 4], (2) the residual nitrogen from NMP on the surface of PBT for enhanced VLA [2, 3], and (3) the effective charge separation and intergrain transfer of VL excited electrons from one phase to the other [10-13, 20].

6.4 Conclusions

A polar solvent treatment or SACS process of the polymorphic brookite enhanced VLA significantly. SACS-NMP was proved to have superior VLA properties for both dye degradation and H2 generation to several available reference anatase titania samples. The possible mechanism, analogous to the commercial reference titania P25, shows an effective intergrain electron transfer and charge separation. This, in turn, reduced the electron and hole recombination rate. Further study to quantify the phase relationship is warranted.
Figure 6.5 Hydrogen evolution from water by titania samples tested under VL [7].

6.5 References


CHAPTER SEVEN

DEACTIVATION AND REGENERATION OF VISIBLE LIGHT ACTIVE
PREDOMINANTLY BROOKITE TITANIA NANOPARTICLES IN THE
PHOTOCATALYTIC DEGRADATION OF ORGANIC DYE

[As submitted to Applied Catalysis B: Environmental Journal (2009)]

Abstract

This study was performed to investigate the deactivation and regeneration of predominantly brookite titania powders. Visible light active (VLA) polymorphic titania particles were prepared by a water-based ambient condition sol (WACS) process followed by a solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent. Fresh and used titania samples were characterized by x-ray diffraction, N₂ physisorption, UV-Vis absorption spectroscopy, FT-IR, thermogravimetric analysis, and x-ray photoelectron spectroscopy and compared to a commercial VLA titania powder, Kronos VLP7000. Deactivation of all samples was evaluated by the degradation of methyl orange (MO) dye under either UV or VL irradiation for four reaction cycle runs. The photocatalytic activity (PCA) under VL exposure of NMP samples calcined at 200 °C for 2 hours in air (NMP-200) was approximately 3.3 times higher than that of VLP7000, despite the much lower surface area of the NMP-200. Nonetheless, PCA of all titania samples under VL gradually decreased with an increase in testing time and number of runs. The cause of the deactivation of the titania samples in this study was identified as the deposition of the decomposed MO on the nanoparticle surface. Among the possible regeneration or
reactivation procedures for the used samples, methanol washing was shown to be the most effective up to ~80% of the PCA recovery. The used NMP-200 samples could not be completely recovered, since a regeneration process would possibly remove some of nitrogen species responsible for the VLA.

7.1 Introduction

Titanium dioxide or titania (TiO$_2$) is one of the most well-known and widely used photocatalysts under UV irradiation [1-6]. Nitrogen-doped titania has been widely studied in order to improve the photocatalytic activity (PCA) under visible light (VL) irradiation by narrowing the band gap of titania [7-17].

In our previous papers [18-20], the preparation of VL active (VLA) polymorphic titania samples was reported. It was done by post-treating a water-based ambient condition sol (WACS) polymorphic brookite titania using a solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent. SACS calcined sample in air at 200 °C for 2 hours showed superior VL photocatalytic performance, evaluated by the degradation of methyl orange (MO) dye, to WACS and commercial titania P25. It was explained in our previous papers of the solvothermal post-treatment of titania with sec-butanol [21] or NMP [18-20] that the lower lattice hydroxyl content in polymorphic titania nanoparticles enhances the PCA.

Deactivation of catalysts is a serious problem in photocatalytic reactions, especially in liquid phase, since it severely reduces PCA. Phillips and Raupp [22] reported that water and organic species adsorbed on TiO$_2$ surfaces possibly cause the reduction of PCA, i.e., the deactivation of photocatalysts. A study of deactivation and
regeneration for photocatalytic oxidation of toluene by mixed anatase and rutile TiO$_2$ was reported by Cao et al. [23]. They concluded that severe deactivation of TiO$_2$ is due to the accumulation of partially oxidized intermediates, such as benzaldehyde and benzoic acid, on active sites. For complete recovery of deactivated catalysts, the regeneration requires a calcination temperature above $420 \, ^\circ\text{C}$ in air, which may cause the phase transformation of anatase to rutile and sintering of the TiO$_2$ nanoparticles.

TiO$_2$ deactivations for only anatase and/or rutile TiO$_2$ phase have been widely studied [24-28]. Most studies [24-28] reported that the drop in PCA during organic oxidation is due to an accumulation of partial oxidation products on TiO$_2$ surface. Nevertheless, the deactivation of the VLA polymorphic brookite titania, which is significantly more photocatalytically active than commercial anatase titania samples [18-20], has never been reported.

In this chapter, we reported the deactivation of polymorphic brookite titania in the decomposition of MO dye under both UV and VL irradiation. Titania samples were reused for four reaction cycle runs without intermittent treatments. The possible regeneration procedures are reported. A commercial VLA TiO$_2$, Kronos VLP7000 [20], was used as the reference.

### 7.2 Experimental

A polymorphic brookite titania was prepared by a WACS process, as described in our previous papers [18-21, 29-32]. A SACS process, a post-treatment of the WACS sample, is presented in the references [18-21]. The as-prepared samples were calcined in air at $200 \, ^\circ\text{C}$ for 2 hours, and they were named “WACS-200” and “NMP-200”.
Phase composition and crystallite size of all samples were determined, as described in our previous reports [18, 19, 33], by X-ray diffractometry (XRD) using XDS 2000, Scintag PAD V utilizing CuKα radiation at 1.5406 Å, measured with a step size of 0.020° over a range of 20 to 35°, and a 2θ angular region. N2 physisorption at -196 °C, by the Micromeritics ASAP 2020 automated system, was used to identify the BET surface area, pore volume, and average pore diameter of the samples. Prior to the BET analysis, a sample was degassed under vacuum at 120 °C for 3 hours. Absorbance of the titania samples was recorded using a UV/Vis spectrophotometer of GretagMacbeth Color i5 across a UV/Vis range. Thermogravimetric analysis (TGA) was used to determine weight loss patterns of water and some carbonaceous deposits in the TiO2 samples performed by the TA Instruments TGA model 2950. A TiO2 sample of ca. 10-20 mg with increased temperature, from room temperature to 800 °C at the rate of 10 °C/min in air, was used in the operation. The IR vibrational bands for water, 'OH groups, methyl orange, and hydrocarbons were observed by Fourier-Infrared spectroscopy (FT-IR), using Thermo-Nicolet Magna model 550 FT-IR spectrometer equipped with a Thermo-Spectra Tech foundation series diamond attenuated total reflection (ATR) accessory. Absorption bands were observed from 4000 cm\(^{-1}\) to 525 cm\(^{-1}\) with 32 sample scans and 4.0 cm\(^{-1}\) for resolution. X-ray photoelectron spectroscopy (XPS), employing Kratos XPS with a monochromatic Al-Kα X-ray source system, was used to identify the chemical states of species in the TiO2 samples.

The deactivation of polymorphic brookite titania was evaluated by observing the photocatalytic degradation of MO under either UV with wavelength of 365 nm, or VL irradiation of 560-612 nm. The experimental MO test and the calculated MO degradation
percent value, D, were obtained by the procedure found in the literatures [18, 19, 21, 32]. NMP-200 of 0.1 grams, for VLA test, was dispersed in a 100 ml of 20 µM MO solution, and 0.5 grams of other TiO$_2$ samples were used in a 300 ml of 20 µM MO solution. A Spectroline black light lamp (Model BIB-150B operated at 365 nm and 182 Watt) and a 150W halogen lamp were utilized as the UV and VL sources, respectively. The UV lamp and the VL lamp were positioned above the MO solution 35 cm and 17 cm, respectively. The MO quantitative spectral results were monitored by a UNICAM UV/vis spectrophotometer (Model: 5625). Titania samples were reused for four reaction cycle runs without any intermittent treatments in a fresh MO solution. After each run, a used titania sample was separated from the MO solution by vacuum filtration, followed by being dried at 150 °C for 4 hours in an oven for a next run. Sample IDs of used TiO$_2$ samples are composed of the fresh TiO$_2$ sample ID, UV or VL irradiation or dark, and # of cycle runs. For example, the NMP-200 sample after the first run of MO degradation under VL irradiation was called “NMP-200-VL#1”.

After the first reaction cycle, the used sample was regenerated by several possible procedures, i.e., solvent washing or recalcination at various temperatures. The regeneration of the catalyst was investigated by reusing 0.1 grams of a regenerated titania sample in the second reaction cycle under the same condition as the first one.

**7.3 Results and discussion**

**7.3.1 Catalyst characterization**

Figure 7.1 shows XRD patterns of titania samples. The phase composition, calculated from XRD analysis, of prepared titania samples varied as follows: 50-55%
brookite, 40-48% anatase, and a small amount of rutile (less than 3%). The reference Kronos samples are 100% anatase phase and have similar crystallite size to our prepared titania. Table 7.1 gives the crystallite size, BET surface areas, pore volume, and average pore diameter of the titania samples. The surface areas of as-prepared titania samples are approximately 1.8 times smaller than that of Kronos sample.

UV/Vis spectra of titania samples are given in Figure 7.2(a). The NMP-200 sample exhibited a shift of the absorption shoulders to the VL region, compared to WACS-200 and VLP7000.

![Figure 7.1 The XRD patterns of the prepared titania samples and VLP7000 (A=anatase, B=brookite, and R=rutile).](image)
Table 7.1 The physical properties of fresh and used TiO$_2$ samples and the reference VLP7000.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallite size (nm)$^a$</th>
<th>BET surface area (m$^2$/g)$^b$</th>
<th>Pore volume (cm$^3$/g)$^b$</th>
<th>Pore size average (Å)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
<td>Rutile</td>
<td></td>
</tr>
<tr>
<td>WACS-200</td>
<td>5</td>
<td>9</td>
<td>11</td>
<td>169</td>
</tr>
<tr>
<td>WACS-200-UV#1</td>
<td>7</td>
<td>10</td>
<td>10</td>
<td>177</td>
</tr>
<tr>
<td>NMP-200</td>
<td>7</td>
<td>8</td>
<td>13</td>
<td>157</td>
</tr>
<tr>
<td>NMP-200-VL#1</td>
<td>7</td>
<td>9</td>
<td>11</td>
<td>220</td>
</tr>
<tr>
<td>NMP-200-VL#2</td>
<td>5</td>
<td>8</td>
<td>16</td>
<td>202</td>
</tr>
<tr>
<td>NMP-200-VL#3</td>
<td>6</td>
<td>7</td>
<td>12</td>
<td>175</td>
</tr>
<tr>
<td>NMP-200-VL#4</td>
<td>7</td>
<td>7</td>
<td>10</td>
<td>185</td>
</tr>
<tr>
<td>NMP-200-UV#1</td>
<td>6</td>
<td>7</td>
<td>12</td>
<td>206</td>
</tr>
<tr>
<td>VLP7000</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>290</td>
</tr>
<tr>
<td>VLP7000-VL#1</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>287</td>
</tr>
</tbody>
</table>

$^a$ Calculated from XRD data using the Scherrer equation. Error of measurement = ±5%.

$^b$ Using N$_2$ physisorption at -196 °C. Error of measurement = ±10%.
Figure 7.2 UV/Vis spectra of (a) fresh titania samples, and (b) fresh and used WACS samples.
7.3.2 Catalyst recycling and deactivation

The stabilities of WACS-200 and NMP-200, determined by the MO degradation under UV irradiation, are given in Figures 7.3(a) and 7.3(b), respectively. MO with titania samples stirred in the dark was not degraded. The MO degradation by NMP-200 was 10 minutes faster than by WACS-200, as expected, because of fewer lattice hydroxyls in NMP-200 sample [18, 19]. Both samples did not deactivate after the first reaction cycle. After the second cycle, however, PCA of both samples gradually decreased with the increase in the testing time.

The deactivation of NMP-200 and VLP7000, evaluated by MO degradation under VL irradiation, is reported in Figures 7.3(c) and 7.3(d), respectively. The MO degradation rate by NMP-200 exhibited approximately 3.3 times higher than that of VLP7000, as shown in the inset of Figure 7.3(d), despite the much lower surface area of NMP-200 than that of VLP7000. This VLA superiority of NMP-200 must be due to the presence of brookite phase with the significant proportion of anatase, as reported in our previous paper [20], compared to 100% anatase for VLP7000. It is also supported by UV/Vis spectra in Figure 7.2(a) that NMP-200 can absorb more VL than VLP7000. Nonetheless, both NMP-200 and VLP7000 gradually deactivated with the increasing number of reaction cycles. The initial rate of MO degradation of NMP-200-VL#2 was approximately 47% less than that of NMP-200-VL#1. MO degradation by VLP7000 in the second cycle was 30% slower than the first cycle. However, the same amount of NMP-200-VL#4 (the 4th cycle) presented significantly higher VLA than VLP7000-VL#1 (the 1st cycle). The catalyst deactivation is possibly attributed to the deposition of the decomposed MO. The carbonaceous deposit, called “coke” [23, 27, 34], was examined
by FT-IR (Figures 7.4(a) and 7.4(b)), TGA (Figure 7.5), and XPS (Figures 7.6(a) and 7.6(b)). FT-IR spectra of MO are given in the inset of Figure 7.4(a). The two FT-IR peaks at wavenumbers of 1150 and 1210 cm\(^{-1}\), which can be assigned for C-O stretch in –C-O-C- and –C-OH [35], were found in all used samples, and their relative intensities increased with the increasing number of reaction cycles. It can be concluded from the FT-IR spectra that the deposition of decomposed MO products was observed in all used TiO\(_2\) samples. Weight loss percentage, calculated from TGA at temperatures between 425 °C and 800 °C, is presented in Figure 7.5. The carbonaceous deposit can be removed from titania samples at a temperature of about 420 °C in air atmosphere [23]. The % weight loss, which was attributed to the amount of carbonaceous deposits, of all samples increased with increasing number of cycle runs. The results agree well with FT-IR results. Moreover, the observed color of used WACS-200 samples changed from off-white to light brown resulting from the deposition of the decomposed MO. UV/Vis absorption of used WACS-200 samples, given in Figure 7.2(b) also shifted to the VL region.

In addition, the chemical state of carbon in NMP-200 samples was examined using XPS as shown in Figures 7.6(a) and 7.6(b). The XPS spectrum of fresh NMP-200 in Figure 7.6(a) reveals three C 1s peak at 282.7, 283.4, 284.6 eV. Figure 7.6(b) is the C 1s XPS peak of NMP-200-VL#1 revealing two peaks at binding energies of 282.8, and 286.7 eV. The C peak at ~283-284 eV was assigned to the C remained in the precursor organic compound, while the peak of 286.7 eV at higher binding energy was attributed to C-O bond (either C-OH or C-O-C) [36, 37]. The XPS results suggested that there was
the C remained in the precursor organic compound in both samples, but only the used NMP-200 sample was found the oxidized carbonaceous deposits.

After any reaction cycles, the percent of titania phases, the crystallite size, and also the crystallinity of used samples did not changed, since the MO degradation was operated at room temperature. The average particle size of fresh and used titania samples, obtained from TEM images which were included in Appendix B, did not significantly differ; thus, the used titania nanoparticles did not agglomerate.

BET surface areas of used WACS-200 and VLP7000 were similar to fresh WACS-200 and VLP7000, respectively. On the other hand, the used NMP-200 samples, after the MO degradation under either UV or VL exposure, exhibited approximately 30%-40% larger BET surface area than the fresh one. In order to explain the increasing in surface area, NMP-200 was tested under a controlled experimental setup; 0.5 grams of NMP-200 were added into 300 ml of water and the mixture was kept in the dark with or without stirring for 3.5 hours. After 3.5 hours, the NMP-200 particles were separated from water and dried at 150 °C for 4 hours. The BET surface areas of those NMP-200 samples were similar to NMP-200-VL#1. This means that water itself increased the BET surface area and pore size of NMP-200 sample. However, water did not have an effect on the surface area of WACS-200. Therefore, an increase in the surface area can be explained by water possibly opening up pores in NMP-200 by removing some NMP or residual organics which block the pores of NMP-200. The increase of surface area can explain why the PCA under UV irradiation of NMP-200-UV#1 and WACS-200-UV#1 were similar to those of the second cycle. Nevertheless, the VL-PCA of NMP-200-VL#2 was lower than NMP-200-VL#1 due to the leaching of nitrogen VLA species on the TiO2
surface during the first reaction cycle. This nitrogen loss of the used NMP-200 sample is supported by the N 1s peak result from XPS which was not included here. There was 0.7 wt% of N on the fresh NMP-200 surface, while the N 1s could be not observed in the used NMP-200 sample which means that the N content of the used sample was less than the instrument detection limit (<0.5 wt%).

(a)
Figure 7.3 The stabilities, determined by the MO degradation, of (a) WACS-200 under UV irradiation, (b) NMP-200 under UV irradiation, (c) NMP-200 under VL irradiation, (d) VLP7000 under VL irradiation, and inset of (d) showing the first reaction cycle of MO degradation under VL exposure of NMP-200 and VLP7000.
Figure 7.4 FT-IR spectra of (a) fresh and used WACS-200 samples, inset of (a) showing that of MO, and (b) fresh and used NMP-200 samples.
Figure 7.5 Percent of weight loss, calculated from TGA at temperatures between 425 °C and 800 °C.

(a)
7.3.3 Catalyst regeneration

The possible regeneration procedures of used NMP-200 samples, i.e., solvent washing, or recalcination at various temperatures, were investigated. To study the catalyst regeneration by solvent washing, NMP-200-VL#1 was washed with various solvents, i.e., methanol (MeOH), ethanol (EtOH), isopropanol (IPA), or acetone. After washing, the titania powders were filtered and dried at 100 °C for 4 hours. For regeneration by recalcination, the used NMP-200 samples were recalcined at either 200 °C or 250 °C for 2 hours in air. From our previous studies [18, 19], both NMP and nitrogen, responsible for VLA properties, in NMP-200 samples can likely be released by calcination at temperatures above 250 °C for 2 hours in air. Moreover, the surface area of NMP samples, calcined at temperatures above 350 °C, rapidly decreased and their
average particle size would increase proportional to the increased temperature due to sintering [18, 19]. Figures 7.7(a) and 7.7(b) present the regeneration of NMP-200-VL#1 by washing and recalcination, respectively, evaluated by the MO degradation under VL irradiation. Among the washing procedures of the used samples, given in Figure 7.7(a), MeOH washing was shown to be the most effective up to ~80% recovery of the fresh sample. The initial rate of MO degradation of recalcined NMP-200 samples, as shown in Figure 7.7(b), was about 75% of that of NMP-200-VL#1. Therefore, NMP-200-VL#1 could not completely be recovered by the recalcination at both 200 °C and 250 °C, as expected. This can be explained by TGA analysis that the carbonaceous deposit on the used NMP-200 sample could be removed by combustion at the temperature above 420 °C [23]. The complete recovery of deactivated catalysts was limited by the sintering and nitrogen removal by high temperature heat treatment, and/or nitrogen leaching by solvent washing. Hence, further regeneration procedures by the combination of solvent washing and recalcination in vacuum at low temperatures will be worthwhile to study.
Figure 7.7 The regeneration of NMP-200-VL#1, evaluated by the MO degradation under VL irradiation, by (a) washing, and (b) recalcination.
7.4 Conclusions

The deactivation of WACS-200 and NMP-200 was evaluated by the degradation of MO under either UV or VL irradiation for 4 reaction cycle runs without intermittent treatments, and then compared to VLP7000. NMP-200 was found to be much more VLA than VLP7000, although NMP-200 has 1.8 times smaller BET surface area than VLP7000. This VLA superiority of NMP-200 is due to mixed brookite and anatase titania phases, compared to pure anatase phase of VLP7000. However, PCA under VL of both NMP-200 and VLP7000 gradually decreased with increasing the number of reaction cycles. The cause of the deactivation of the titania samples in this study was identified as the deposition of the decomposed MO or the carbonaceous deposit, called “coke”. Nevertheless, WACS-200 and NMP-200 did not show the deactivation after the first reaction cycle, because of an increase in surface area. The regeneration of the used NMP-200 samples was also investigated. NMP-200-VL#1 could not fully be recovered by recalcination at either 200 °C or 250 °C since coke would not be removed at temperatures below 420 °C. Among the solvent washing procedures for used NMP-200, MeOH washing was shown to be the most effective with up to ~80% of the PCA recovery. The NMP-200 sample could not be completely recovered since the regeneration process would possibly remove some of the nitrogen species responsible for the VLA and decrease its surface area with a high regeneration temperature. Further studies on alternative regeneration procedures by compromising solvent washing and recalcination in vacuum at low temperatures should be the next step.
7.5 References


CHAPTER EIGHT

SUMMARY AND RECOMMENDATIONS

8.1 Summary

In this research, the effect of hydroxyl content on PCAs of predominantly brookite titania nanoparticles was investigated. WACS samples were post-treated by a SACS process in sec-BuOH. It was observed by FT-IR and solid state $^1$H NMR that the SACS process is a practical technique to remove the lattice hydroxyls from the titania structure. PCA of titania samples was evaluated by methyl orange (MO) degradation under UV irradiation. By a comparison between WACS and SACS samples with similar surface areas and crystallinity, SACS samples, with reduced lattice hydroxyls, are more photocatalytically active than WACS or hydroxylated samples. An increase in the surface area of SACS samples is not the main factor for the improvement of photocatalytic activity but rather fewer lattice hydroxyls. In addition, all prepared polymorphic titania samples showed a higher photocatalytic activity under UV irradiation than a commercial P25 sample.

An alternative high boiling point polar solvent, NMP, was utilized in SACS process at a higher treatment temperature. SACS, using NMP as the solvent and being called “SACS-NMP”, was able to extract lattice hydroxyls and to decorate nitrogen on the titania surface or in the structure. The PCA of SACS-NMP was higher than that of SACS-sec-BuOH. With more nitrogen present in SACS-NMP samples, PCA under UV exposure was higher. The influence of calcination temperature in air of SACS-NMP was investigated. SACS-NMP, calcined at 200°C for 2 hours, showed the best PCA under UV irradiation among prepared titania samples and P25.
In the following study, other calcination conditions, i.e., temperature, time, and calcination atmosphere (either air or nitrogen), were investigated. It was found that SACS-NMP also improved the PCA of the titania samples under VL irradiation. The PCA declined with increasing calcination temperature and time. Nonetheless, calcination time did not have any significant effect on VLA properties, especially for the samples calcined in nitrogen. It could be concluded that the sample calcined at 200\(^\circ\)C for 2 hours in air showed the best VLA performance since the sample calcined in air had a greater amount of VLA nitrogen in form of hyponitrite than the one calcined in nitrogen.

In addition, SACS-NMP was proved to have superior VLA properties to several available reference anatase titania samples. This was explained by an improved effective charge separation by intercrystalline electron transport from brookite to anatase grains complemented by the strong VL absorption by the nitrogen species from NMP. The summary of physical and photocatalytic properties of the polymorphic titania samples compared to the available reference titania samples are given in Table 8.1.

Although SACS-NMP exhibited excellent PCA under VL irradiation, the deactivation of titania, which reduces the PCAs, could possibly occur. To compare with a commercial VLA titania powder, Kronos VLP7000, the deactivation of WACS-200 and NMP-200 was evaluated by the degradation of MO under both UV and VL irradiation for four reaction cycle runs without intermittent treatments. SACS-NMP was found to be much more VLA than VLP7000 even though SACS-NMP had 70\%–85\% smaller BET surface area than VLP7000. This VLA superiority of SACS-NMP is caused by the presence of both brookite and anatase titania phases, compared to the pure anatase phase in VLP7000. Nevertheless, PCA under VL of both SACS-NMP and VLP7000 gradually
decreased with increasing the number of reaction cycles. From FT-IR, TGA, and XPS results, the deposition of the decomposed MO or the carbonaceous deposit, called “coke”, resulted in the deactivation of the polymorphic titania. The possible regeneration procedures, recalcination and solvent washing, were studied. The used SACS-NMP could not be fully recovered by recalcination at either 200°C or 250°C since coke would only be removed at a temperature above 420°C. For the solvent washing procedures, methanol washing was the most effective for regenerating the used SACS-NMP samples up to ~80% of the as-prepared sample. It could be surmised that the SACS-NMP could not be completely regenerated because regeneration would have removed some of the nitrogen species responsible for the VLA and reduced its surface area at a high recalcination temperature.
Table 8.1 The summary of physical and photocatalytic properties of the polymorphic titania samples compared to the available reference titania samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mode of Formation</th>
<th>% Content of TiO₂ Phase (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Crystallite size (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BET surface area (m²/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Bandgap energy (eV)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Initial rate of MO degradation (mol x min⁻¹ x g⁻¹ cat⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A  B  R</td>
<td>A  B  R</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WACS</td>
<td>WACS</td>
<td>48  50  2</td>
<td>6  8  19</td>
<td>163</td>
<td>2.99</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>WACS-200</td>
<td>Calcination of WACS at 200°C2h in air</td>
<td>45  53  2</td>
<td>6  7  18</td>
<td>157</td>
<td>2.97</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>SACS1</td>
<td>SACS with see-BuOH at 100°C for 4h</td>
<td>46  51  3</td>
<td>6  6  21</td>
<td>200</td>
<td>3.03</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>SACS1-200</td>
<td>Calcination of SACS1 at 200°C2h in air</td>
<td>44  54  2</td>
<td>6  8  18</td>
<td>189</td>
<td>2.92</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>NMP</td>
<td>SACS with NMP at 170°C for 4h</td>
<td>42  55  3</td>
<td>7  8  12</td>
<td>133</td>
<td>1.76</td>
<td>2.5×10&lt;sup&gt;8&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>NMP-200</td>
<td>Calcination of NMP at 200°C2h in air</td>
<td>44  53  3</td>
<td>6  8  11</td>
<td>138</td>
<td>1.71</td>
<td>6.3×10&lt;sup&gt;8&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;, 2.6×10&lt;sup&gt;7&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>P25</td>
<td>High T flame oxidation</td>
<td>79  -  21</td>
<td>21  -  40</td>
<td>56</td>
<td>3.03</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Postech</td>
<td>Hydrothermal in NH₄OH calcn. in air at 400°C</td>
<td>100  -  -</td>
<td>22  -  -</td>
<td>93</td>
<td>2.91</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>TiOz-200</td>
<td>Acid hydrolysis of butoxide</td>
<td>100  -  -</td>
<td>7  -  -</td>
<td>208</td>
<td>3.00</td>
<td>Inactive&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>TiOz-SACS-200</td>
<td>SACS of TiOz with NMP at 170°C for 4h</td>
<td>100  -  -</td>
<td>7  -  -</td>
<td>173</td>
<td>1.69</td>
<td>3.7×10&lt;sup&gt;8&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>VLP7000</td>
<td>Refinement by either sulfate or chloride process</td>
<td>100  -  -</td>
<td>7  -  -</td>
<td>290</td>
<td>3.01</td>
<td>1.2×10&lt;sup&gt;7&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from XRD data using the Scherrer equation. Error of measurement = ±5% (A=Anatase, B=Brookite, and R=Rutile).

<sup>b</sup> Using N₂ physisorption at -196°C. Error of measurement = ±10%. N/D=not determined.

<sup>c</sup> Calculated from UV/Vis spectra.

<sup>d</sup> The MO degradation results were evaluated using 0.2g TiO₂ in 100ml of 20µM MO under VL (14W) at room temperature.

<sup>e</sup> The MO degradation results were evaluated using 0.1g TiO₂ in 100ml of 20µM MO under VL (150W) at room temperature.
8.2 Recommendations

To advance the development of VLA properties of predominantly brookite titania nanoparticles for more applications, i.e., H₂ generation, the following future studies are recommended:

- Although the SACS process was shown to be an effective method to reduce the lattice hydroxyls (resulting in much higher PCA than WACS sample and available commercial titania samples), the PCA can be improved by applying higher solvent treatment temperatures. Since higher temperatures are required for the SACS treatment, a high boiling point is imperative in the polar solvent.

- Few studies on nitrogen doped titania synthesis via solvothermal process have been reported. To achieve high VLA properties, doped precursor solvents, containing dopants such as N, C, F, or S, should be considered as dopant sources via the SACS process.

- Apparent activation energies of the MO degradation reaction of all TiO₂ samples should be calculated. The calculated apparent activation energies will be able to prove whether the photocatalytic reaction or mass transfer of MO on TiO₂ surface control kinetics.

- The calculation of C to H ratio, which is obtained from CHN analysis, will provide more information on the SACS-NMP samples. This data will identify the residual organic compounds on the SACS-NMP samples.

- By reason of the instability of the nitrogen species in the SACS-NMP samples, alternative regeneration procedures combining solvent washing and recalcination in vacuum at low temperatures should be investigated.
- It is possible that the solvent washing procedure can remove some of nitrogen species from the SACS-NMP samples. Therefore, the nitrogen content of the washed NMP samples should be investigated using either CHN analysis or XPS.
APPENDIX A

EXPERIMENTAL VARIABLES EFFECT ON PHOTOCATALYTIC ACTIVITY

Figure A.1 Effect of VL intensity on the photocatalytic activity of SACS-NMP sample calcined at 200°C for 2 hours in air (NMP-200).

Figure A.2 Effect of WACS-200 loading on the photocatalytic activity under UV exposure.
Figure A.3 Effect of NMP-200 loading on the photocatalytic activity under UV exposure.

Figure A.4 Effect of NMP-200 loading on the photocatalytic activity under VL (14 Watts) exposure.
APPENDIX B

TEM IMAGES OF TITANIA SAMPLES

(a) NMP-200-Fresh

(b) NMP-206-UV#1
Figure B.1 TEM images of (a) fresh NMP-200, (b) NMP-200-UV#1, (c) NMP-200-VL#1, and (d) WACS-200-UV#1.
APPENDIX C

VISIBLE LIGHT SPECTRUM

C.1 Light spectrum

![Figure C.1 Light spectrum of a fluorescent lamp and a halogen lamp [1]](image)

C.2 Reference